

PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE FACULTY OF PHYSICS

EFFECT OF PHONONS ON THE OPTICAL PROPERTIES OF COLOR CENTERS IN DIAMOND

by

Ariel Norambuena

A dissertation presented by Ariel Norambuena to The Faculty of Physics in partial fulfillment of the requirements for the degree of Ph.D. in Physics.

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Declaration of Authorship

I, Ariel Norambuena, declare that this thesis titled, 'EFFECT OF PHONONS ON THE OPTICAL PROPERTIES OF COLOR CENTERS IN DIAMOND' and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

III. The principle of vibration

"Nothing rest; everything moves; everything vibrates."

The Kybalion: A study of the Hermetic Philosophy of Ancient Egypt and Greece.

PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE

Abstract

Ph.D. in Physics

by Ariel Norambuena

During the last decade color centers in large bandgap materials have received great attention due to the large degree of control that is possible to achieve of their internal degrees of freedom. They are leading candidates for quantum information and quantum metrology applications. At the same time, they have allowed the scientific community to explore and understand fundamental aspects related to the interaction between a system and its environment. In particular, the interaction of an electronic spin (the system) and vibrational degrees of freedom (the environment) deserve special attention for the successful implementation of systems in optoelectronic devices. Here, in this thesis we present microscopic models to theoretically understand the effect of phonons on the electronic and optical properties of color centers in diamond. First, we consider a microscopic model to study the electron-phonon interaction between the localized electronic states of a single negatively charged silicon-vacancy center and lattice vibrations. Using the spin-boson model, the Kubo formula, and molecular dynamics simulations we numerically reproduce the observed isotopic shift of the phonon sideband in good agreement with recent experiments. Second, we develop a microscopic model for the spin-lattice relaxation dynamics of the negatively charged nitrogen-vacancy center in diamond in order to reproduce the temperature dependence of the longitudinal spin relaxation rate from temperatures ranging from 10 mK to 475 K. Next, we consider a microscopic model for the electron spin resonance (ESR) absorption spectrum of $e \otimes E \otimes SU(2)$ Jahn-Teller systems when an oscillating magnetic field is applied. This system is studied in order to understand the phononic dynamical suppression of the electron spin resonance in color centers with spin-1/2. Finally, we introduce the strain Hamiltonian of the negatively charged silicon-vacancy center in diamond. This Hamiltonian has interesting properties for optomechanical systems based on the strain-induced coupling between compression modes of a diamond cantilever and individual negatively charged silicon-vacancy centers.

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I am very grateful to realize my bachelor studies and subsequently my Ph.D. in Physics in the Pontificia Universidad Católica of Chile. The high level of teaching and research is incredibly inspiring for students with a thirst for infinite knowledge. I am very fortunate to have had the possibility to do my Ph.D. under the supervision of professor Jerónimo Maze. His experience in experimental and theoretical physics and his high impact in the international community of color centers in diamond taught me that the limits are bounded by the world and that all problems can be solved if you accept the challenge with responsibility, scientific rigor, and hard work. Furthermore, Jero is an incredible person with a high level of compromise with all students, he always had the time to teach me physics in a very inspiring way, as well as guide me in the most difficult periods of my Ph.D.

During my first theoretical project (Chapter 2), I was lucky to work with Sebastián Reyes, José Mejía, and Adam Gali. Sebastián Reyes has a high level of comprehension in solid-state physics as well as an incredible sincerity to clarify some personal doubts during my Ph.D. My first approach to understand the effect of lattice phonons on the electronic states of siliconvacancy centers in diamond was largely discussed with Jero and Sebastián. I must also thank the computational skills of José Mejía, especially, the density functional theory approach to reproduce the phonon spectrum and additional numerical calculations. These numerical simulations were crucial to finding the elastic constant of the force-constant model used to describe the emission spectrum of the silicon-vacancy center in diamond. I give special thanks to Adam Gali for fruitful discussions, comments, and clever ideas in the final part of the project. In particular, the dynamical symmetry breaking mechanism described in Chapter 2 has a strong inspiration in the Herzberg-Teller effect described in a paper led by Adam Gali and the student Elisa Londero.

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Abbreviations

\mathbf{NV}^{-}	Negatively charged Nitrogen-Vacancy $% {\bf V} = {\bf V} $
\mathbf{NV}^0	Neutral Nitrogen-Vacancy
${ m SiV}^-$	Negatively charged \mathbf{S} ilicon- \mathbf{V} acancy
\mathbf{ZPL}	\mathbf{Z} ero \mathbf{P} honon \mathbf{L} ine
\mathbf{PSB}	$\mathbf{P} \mathrm{honon} \ \mathbf{S} \mathrm{ide} \ \mathbf{B} \mathrm{and}$
\mathbf{PL}	Photo Luminescence
QME	$\mathbf{Q} \text{uantum } \mathbf{M} \text{aster } \mathbf{E} \text{quation}$
\mathbf{JT}	${f J}ahn-{f T}eller$
\mathbb{IR}	Irredible \mathbf{R} epresentation

Physical Constants

Planck Constant	\hbar	=	$1.0546 \times 10^{-34} \text{ m}^2 \text{kgs}^{-1}$
Electron charge	e	=	$1.6022 \times 10^{-19} \text{ C}$
Electron mass	m_e	=	$9.1094 \times 10^{-31} \text{ kg}$
Proton mass	m_p	=	$1.6726 \times 10^{-27} \text{ kg}$
Neutron mass	m_n	=	$1.6749 \times 10^{-27} \ \rm kg$
Bohr radius	a_B	=	$5.2918 \times 10^{-11} \ {\rm m}$
Electric constant	k_e	=	$8.987\times 10^9~{\rm m}^{-3}{\rm kg}^{-1}{\rm s}^4{\rm A}^2$
Magnetic constant	μ_0	=	$1.2566 \times 10^{-6} \text{ NA}^{-2}$
Speed of Light	c	=	$2.997~924~58\times 10^8~{\rm ms}^{-{\rm S}}$

Symbols

ω	Angular Frequency	[rad Hz]
ν	Linear Frequency	[Hz]

P Power $[Js^{-1}]$

Dedicado a mis padres, Juan y Sandra, a mis hermanas, Amanda y Lorena, y a mi compañera de vida, Valeria Bolívar.

Chapter 1

Introduction

Color centers in diamond are promising candidates for applications ranging from single photon sources [1–3], color markers for biological structures [4–6], spin-qubit quantum information processing [7], quantum sensing at the atom-resolution [8, 9], and nanomechanical resonators for cooling schemes [10–13]. All these technological applications crucially depend on the electronic properties, optical manipulation, and the spin relaxation dynamics of color centers in diamond. From several experiments, *ab initio* calculations, and theoretical models we know that the physical observables associated with the color centers are modified by the environment, *i.e.*, the diamond lattice. In addition, we know from recent experiments that the lattice effects has a non-trivial temperature dependence. Therefore, a theoretical challenge is the correct mathematical modeling of the interaction between the lattice and color centers in order to predict and understand the measured physical observables.

In particular, color centers in diamond are stable molecules at room temperature embedded in a solid-state environment composed of carbon atoms, magnetic impurities randomly located over the lattice (¹³C, ¹⁴Ni, ²⁹Si, NV-center, and SiV-center), and charge distributions in the diamond lattice. At the moment, three color centers have been studied in the community: the negatively charged nitrogen-vacancy (NV⁻) center, the neutral charged nitrogen-vacancy (NV⁰) center, and the negatively charged silicon-vacancy (SiV⁻) center in diamond. Interestingly, the ground and excited states of color centers are energetically separated from the valence and conduction band about of the order of ~ 1 eV. Even at 500 K the charge transference from the color center to the conduction band minimum is suppressed, which is crucially different from other interesting quantum systems (ion traps, single atoms, superconducting qubits). As a consequence, the internal degrees of freedom of color centers in diamond can be optically manipulated with a high control and it is possible to initialized and read-out with different experimental techniques. However, between the initialization and the and read-out, the dynamics of the orbital states and spin degrees of freedom are perturbed by the lattice degrees of freedom such as magnetic impurities, charge distributions, static strain, the stress of the lattice, and phonons.

Phonons are important when we perform experiments in solid-state systems since the effect of quantum vibrations is suppressed only at the absolute zero temperature. In consequence, for every solid-state technology, the effect of phonons is always present, and therefore, must be considered if it has an observable effect. In the case of color centers in diamond, the vibrations of the diamond lattice introduce a dynamical effect on the molecular states. Physically, every time that the lattice vibrates in some vibrational mode, the atoms of the color centers collective start to oscillate with some frequency, amplitude and spatial direction. This leads to a change in the potential seen by each atom of the color center. As a consequence, this results in a modification of the local electronic distribution of the color center due to the electron-ion Coulomb interaction. In addition, the spin-orbit interaction and the spin-spin interaction leads to a change in the spin states when the electronic distribution is modified. In consequence, phonons directly modified the electronic distributions and indirectly induces spin relaxation. Such phonon-induced effects can be experimentally observed in the photoluminescence spectrum (phonon sideband), the spin relaxation dynamics (longitudinal and transverse relaxation rates), the phononic dynamical suppression of the electron spin resonance (ESR) response, among others. Therefore, in order to understand the microscopic origin of the effect of phonons on the color centers we need to build mathematical models based on the experimental evidence.

1.1 Description of this thesis

This thesis describes several microscopic models in order to understand and reproduce the effect of phonons on the optical properties of color centers in diamond using as a starting point the experimental evidence of the community. Chapter 2 presents a microscopic model to understand the effect of phonons on the optical properties of the emission spectrum of single negatively charged silicon-vacancy centers in diamond. Chapter 3 introduces the spin-lattice relaxation dynamics induced by phonons for the ground triplet state of the negatively charged nitrogen-vacancy center in diamond. Chapter 4 develop a model to



Figure 1.1: Emission spectra of color centers in diamond. Here, we observe the PL spectrum of the nitrogen-vacancy center and the silicon-vacancy center in diamond at room temperature T = 300 K. The ZPL transition of each center is broadened by the interaction between the color center and lattice phonons. At the same temperature, the width of the PSB of the SiV⁻ center is 5 nm, while the width of the PSB of the NV⁻ center is of the order of ~ 100 nm. The symmetry of each center only differs by the additional inversion symmetry of the SiV⁻ center. Due this additional symmetry, the SiV⁻ center has a weak electron-phonon coupling with the environment, and therefore, a narrow phonon sideband associated with the PL spectrum.

understand the effect of temperature on the electron spin resonance absorption spectrum of $E \otimes e \otimes SU(2)$ Jahn-Teller systems with residual electronic spin-1/2. Chapter 5 provides a group theoretical derivation of the strain Hamiltonian of the negatively charged silicon-vacancy center in diamond. Finally, in Chapter 6 we summarize the main results of the thesis and we discuss some future projects.

1.2 Emission spectrum of color centers in diamond

A common problem in solid-state physics is how to determine the effect of vibrations on the radiative transitions associated with the electronic states. In literature, it is known that vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecular system due to the absorption or emission of a single photon with a specific energy. The problem is how to determine the intensity of each vibronic transition when you excited the system with a pumping laser. When a molecule is excited with light the resulting photoluminescence (PL) spectrum contains a zero-phonon line (ZPL) transition and the phonon sideband contribution (PSB). The ZPL is associated with a purely electronic transition where phonons are not present. On the other side, the PSB is the experimental evidence of the contribution of phonons. Phonons modified the shape of the PL spectrum and the visual effect is associated with an inhomogeneously broadened. In Fig. 1.1 we can observe the PL spectrum of the NV^- center and the SiV⁻ center in diamond. The PL spectrum of the NV^- center and SiV⁻ center in diamond are very different from each other although they differ in one atom in their molecular composition. The NV^- center has a broad emission ranging from 637 nm ZPL to 750 nm; meanwhile, the emission of the SiV⁻ has a width of few nanometers at the same room temperature [14].

In Chapter 2, we present a detailed microscopic model to study the PL spectrum of a single SiV^- center in diamond. In particular, we study the effect of the symmetry of the molecule using group theory and we solve a molecular dynamics simulation to estimate of the electron-phonon interaction of a single SiV^- center embedded in a finite size diamond structure composed by ~ 3400 atoms. Our approach takes advantage of the symmetrized description of the electronic states and the vibrational modes of the finite diamond structure. We introduce a dynamical symmetry breaking mechanism that mixes the electronic wavefunctions of the color center when ungerade (antisymmetrical) phonons are considered. This mechanism emerges as a good candidate to incorporate the observed isotopic shift associated with the sharp feature of the PSB. Our results are in good agreement with experimental data and show the observed isotopic shift of the PSB associated with three different isotopic compositions of the silicon atom of the color center. We also introduce the effect of temperature by using the Kubo formula to describe the PL spectrum of an electronic system embedded in a thermal phonon environment.

1.3 Spin-lattice relaxation dynamics of color centers

Understanding the effect of vibrations on the relaxation process of individual spins is crucial for implementing nano systems for quantum information and quantum metrology applications. Because of the lattice degrees of freedom the dynamics of a color center is modified by the presence of magnetic impurities, charge distributions and phonons. Figure. 1.2 shows the main ingredients of the color center - lattice dynamics. The effect of magnetic impurities on the spin state of a color center increases with the concentration of magnetic atoms in the lattice (¹³C and ¹⁴Ni) and the concentration of surrounding color centers (NV-centers and SiV-center). Basically, the spin flip-flop processes induced by the external magnetic impurities on the internal spin states of the center induces a relaxation dynamics. This relaxation



Figure 1.2: Color center - lattice dynamics. A single NV⁻ center in diamond embedded in a diamond lattice. The internal degrees of freedom of the color center is shown by the electronic and spin degrees of freedom. The external perturbations: electric fields and lasers (red dashed arrows), magnetic fields (blue dashed arrows), and temperature (black dashed arrows) are connected with the corresponding internal degrees of freedom of the color center depending on the nature of the interaction. The internal couplings are shown by black arrows and represent the internal dynamics of the center (between electronic and spin degrees) and the color center - lattice interaction.

dynamics is associated with two characteristic relaxation times: T_1 (longitudinal relaxation time) and T_2 (transverse relaxation time). Physically, both longitudinal and transverse relaxation times are due to fluctuating magnetic fields of the environment that induce spin rotations of the color center.

A fundamental problem is to determine the effect of phonons and its temperature dependence on the longitudinal and transverse relaxation times. We know that lattice phonons in diamond are important for the spin-lattice relaxation dynamics of the spin degree of freedom of color centers and that the temperature plays a fundamental role in the spin relaxation dynamics [15–19]. At high temperatures, 300 K < T < 500 K, the most important contribution to the longitudinal relaxation rate $1/T_1$ is due to the second-order Raman scattering [20] which leads to the observed $1/T_1 \propto T^5$ temperature dependence. Between 50 K < T < 200 K the main contribution arises from Orbach-type processes [21] which can be attributed to a strong spin-phonon interaction with a quasi-localized phonon mode with energy $\hbar\omega_{\rm loc} \approx 73$ meV [18] and leads to $1/T_1 \propto (\exp(\hbar\omega_{\rm loc}/k_BT) - 1)^{-1}$. At low temperatures (below 1 K), when one-phonon processes are more probably that two-phonon processes, recent experimental observations and *ab initio* calculations concluded that $1/T_1 = \Gamma_0 (1 + 3\bar{n}(T))$, where $\Gamma_0 = 3.14 \times 10^{-5} \text{ s}^{-1}$, and $\bar{n}(T) = (\exp(\hbar D/k_B T) - 1)^{-1}$ is the mean number of phonons at the zero-field splitting frequency $D/2\pi = 2.87$ GHz [19]. In Chapter 3, we present a theoretical microscopic model to describe the spin-lattice relaxation of individual electronic spins associated to negatively charged nitrogen-vacancy centers in diamond, although our results can be extended to other spin-boson systems. In particular, starting from a general spin-phonon Hamiltonian for a system with spin S = 1 and solving the quantum master equation we provide a detailed description of the spin-lattice relaxation dynamics of a single NV⁻ center in diamond. Our results are in good agreement with recent experimental findings and analytically describe the temperature and magnetic-field scaling of $1/T_1$.

1.4 Electron spin resonance absorption problem

Understanding the effect of temperature on the electron spin resonance (ESR) absorption spectrum is of great interest in solid-state and molecular systems for quantum metrology and information. The study of the ESR absorption spectrum is a fundamental problem from a theoretical point of view. The modeling of an ESR response is translated into the problem of modeling the linear response of out-of-equilibrium systems [22-24]. For a color center in diamond, the ESR response has interesting features, namely, the interaction between the color center with its environment. Our attention is focused on the microscopic description of the linear response of color centers in diamond with residual spin S = 1/2. In such case, the NV⁰ center and the SiV⁻ center and can be described as a $E \otimes e \otimes SU(2)$ Jahn-Teller (JT) system with an electronic spin S = 1/2. In Chapter 4, we characterize the phononic dynamical suppression of the electron spin resonance (ESR) response of $E \otimes e \otimes SU(2)$ Jahn-Teller systems. We include the effect of the linear electron-phonon coupling between the orbital and lattice degrees of freedom, the spin-orbit, and Zeeman interactions, and the linear response of the system to oscillating magnetic fields. Using the Markovian quantum master equation we characterize the spin-relaxation rate and the contrast of the ESR response as a function of temperature and several other parameters of the system.

Chapter 2

Microscopic modeling of the effect of phonons on the optical properties of solid-state emitters

In this chapter, we introduce a microscopic model to calculate the main features associated to the photoluminescence (PL) spectrum of the negatively charged silicon-vacancy (SiV^{-}) center in diamond. The model is constructed by considering the localized electronic states of a single SiV⁻ center, the lattice phonons in thermal equilibrium, and the electron-phonon interaction between them to first order in the nuclear displacement. Also, we include a molecular dynamics simulation to estimate of the electron-phonon interaction of a single SiV^{-} center embedded in a finite size diamond structure. The main purpose of this model is to microscopically understand the effect of phonons, and local symmetries, on the radiative transitions associated to the SiV⁻ when the system is relaxed from the excited to the ground state. Using the spin-boson model and the polaron transformation we obtain an analytical expression for the emission spectrum in terms of the spectral density function and the bath temperature. Using this model and the molecular dynamics simulation, we calculate the spectral density function of a single SiV⁻, and in consequence, the shape and the temperature dependence of the PL spectrum. We introduce a perturbative mechanism that mixes the defect electronic wavefunctions. This mechanism emerges as a good candidate to incorporate the observed isotopic shift associated with the sharp feature of the phonon sideband.

2.1 Introduction

Vibrations play a crucial role in nano systems by modifying their optical line shape, preventing them from being described as simple two-level systems [25]. Several works have addressed the electron-phonon coupling to model the effect of vibrations on the optical properties of molecules [26], point defects [27] and inter-band optical transitions in solids [28]. This interaction is characterized, in most cases phenomenologically, by a spectral density function [29–31] that is used to describe the dissipation dynamics due to acoustic phonons in a twolevel system [29], the absorption [32] and low temperature effects on the zero-phonon line transition [30] in quantum dots that are strongly coupled to localized vibrations. There are few works that treat the electron-phonon interaction with microscopic models [33]. The latter approach is particularly accurate for atomistic systems and highly demanded nowadays as researchers are able to engineer nanoscale devices where effectively few atoms are involved [34]. Therefore, a deep understanding of this interaction is needed for controlling and engineering the optical properties of such systems.

Here, we consider a microscopic model to study the electron-phonon interaction between the electronic states of a single SiV⁻ center in diamond and lattice vibrations. We focus on the effect of phonons on the optical properties, i.e., the zero-phonon line (ZPL) transition and the phonon sideband associated to the emission or photoluminescence spectrum. On Sec. 2.2 we introduce to the electronic states of the SiV⁻ center for which the optical emission will be calculated. Section 2.3 describes the vibrational degrees of freedom of a finite size lattice and the electron-phonon interaction between vibrations and the electronic states. Section 2.4 introduces the model used to calculate the emission spectrum taking into account the symmetries of the electronic wavefunctions and vibrations. In particular, the spectral density function and its relation to the emission spectrum is introduced. Section 2.5 discusses the role of symmetry on the defect and finally Section 2.6 takes into account these considerations to write the spectral density function for the SiV⁻ center.

2.2 Negatively charged silicon-vacancy center in diamond

In this section we present the bare ground and excited states from which the optical transitions will take place. The SiV⁻ center is a point defect composed of six carbon atoms and an interstitial silicon atom. The symmetry group associated to this defect is the C_{3v+i} group, a subgroup of the host crystal symmetry group T_d [35, 36] (an equivalent group is D_3 for which the irreducible representations a_1 and a_2 are swapped). In particular, the inversion symmetry with respect to the silicon atom leads to irreducible representations (IR) of the C_{3v+i} group to be labeled by parity: A_{1g}, A_{2g}, E_g (g = gerade or even) and A_{1u}, A_{2u}, E_u (u = ungerade or odd) representations [36]. The electronic structure of this defect can be represented by one-electron hole system with electronic spin S = 1/2. In the absence of external perturbations the relevant electronic wavefunctions associated to the electron hole representation are

$$|\Psi_{qx,qy}^{(0)}\rangle = e_{qx,qy}^{C},$$
 (2.1)

$$|\Psi_{ux,uy}^{(0)}\rangle = \frac{1}{\sqrt{1+2\mathcal{N}\beta+\beta^2}} \left(e_{ux,uy}^{\mathrm{C}} + \beta p_{x,y}^{\mathrm{Si}}\right), \qquad (2.2)$$

where $e_{gx,gy}^{C}$ (gerade) and $e_{ux,uy}^{C}$ (ungerade) are sp^{3} linear combinations of single electron orbitals associated to the carbon atoms [36], $p_{x,y}^{Si}$ are $p_{x,y}$ orbitals associated to the silicon atom (see Fig. 2.1), β is a coefficient that indicates the contribution of the latter orbitals and it is estimated to be ≈ 0.13 by ab initio calculations, and $\mathcal{N} = \langle p_{x,y}^{Si} | e_{ux,uy}^{C} \rangle$. Thanks to inversion symmetry the excited and ground state can also be labeled by parity. The degenerate ground states $|\Psi_{gx}^{(0)}\rangle$ and $|\Psi_{gy}^{(0)}\rangle$ belong to the two-fold IR $E_g = \{E_{gx}, E_{gy}\}$, respectively. Meanwhile, the degenerate excited states $|\Psi_{ux}^{(0)}\rangle$ and $|\Psi_{uy}^{(0)}\rangle$ belong to the two-fold IR $E_u = \{E_{ux}, E_{uy}\}$, respectively. These ground and excited states are energetically separated by the zero-phonon line energy $E_{ZPL} = 1.68 \text{ eV} [37]$. Therefore, the electronic structure associated to the negatively charged SiV⁻ is modeled by the following Hamiltonian

$$H_{\rm e} = \frac{1}{2} E_{\rm ZPL} \left(|\Psi_{ux}^{(0)}\rangle \langle \Psi_{ux}^{(0)}| - |\Psi_{gx}^{(0)}\rangle \langle \Psi_{gx}^{(0)}| \right).$$
(2.3)

We do not include the effect of spin-orbit interaction, neither we include the spin degree of freedom as they are not relevant for determining the broad features of the optical lineshape.

2.3 Electron-phonon Hamiltonian

In this section we derive a model for the electron-phonon interaction between a single SiV⁻ center and lattice vibrations in a finite sized crystalline structure. First, we consider a diamond lattice composed of N_{Lat} atoms including the SiV⁻ center at the origin. Atoms are arranged so that the whole structure maintains the C_{3v+i} symmetry of the point defect. We introduce the normal coordinates that describe lattice vibrations [25]

$$Q_l^{\text{Lat}} = \sum_{i=1}^{N_{\text{Lat}}} \sum_{\alpha = \{x, y, z\}} \sqrt{M_i} u_{i\alpha} h_{i\alpha, l}^{\text{Lat}}, \qquad (2.4)$$

where M_i is the mass of the *i*-th ion and $u_{i\alpha}$ is the displacement of the *i*-th ion in the α direction (x, y or z). In this notation, \mathbf{u}_i is the ion displacement vector from its equilibrium position $\mathbf{R}_i^{(0)}$, and $h_{i\alpha,l}^{\text{Lat}}$ are eigenvectors that satisfy the following eigenvalue equation [25]

$$\sum_{j=1}^{N_{\text{Lat}}} \sum_{\beta = \{x, y, z\}} D_{i\alpha, j\beta} h_{j\beta, l}^{\text{Lat}} = \omega_l^2 h_{i\alpha, l}^{\text{Lat}}, \qquad l = 1, ..., 3N_{\text{Lat}},$$
(2.5)

where $D_{i\alpha,j\beta}$ is the dynamical matrix associated with the ion-ion potential interaction and ω_l are the frequency associated with the *l*-th lattice mode. The dynamical matrix is given by [25]

$$D_{i\alpha,j\beta} = \frac{1}{\sqrt{M_i M_j}} \left(\frac{\partial^2 V_{\text{Ion-Ion}}}{\partial u_{i\alpha} \partial u_{j\beta}} \right) \Big|_{\mathbf{R}_0}, \qquad (2.6)$$

where $V_{\text{Ion-Ion}}$ is the ion-ion Coulomb interaction (see Appendix A.2 for further details). The electron-phonon interaction between the electronic states associated to this point defect and lattice vibrations can be written as

$$V_{\text{e-ph}}(\mathbf{r}, \{\mathbf{Q}\}) = \sum_{l=1}^{3N_{\text{Lat}}-6} \left[\sum_{l'=1}^{3N_{\text{D}}-6} \alpha_{l'l} \left(\frac{\partial V_{\text{e-Ion}}}{\partial Q_{l'}^{\text{SiV}}}\right)\right] Q_l^{\text{Lat}},$$
(2.7)

where $N_{\rm D}$ is the number of defect atoms ($N_{\rm D} = 7$ for the SiV⁻ center), $V_{\rm e-Ion}$ is the electronion Coulomb interaction between one electron located at **r** and the $N_{\rm Lat}$ surrounding atoms, and $Q_{l'}^{\rm SiV}$ are the local normal coordinates of the SiV⁻ center. The factor $\alpha_{l'l}$ is given by

$$\alpha_{l'l} = \langle \mathbf{H}_{l'}^{\mathrm{SiV}}, \mathbf{h}_{l}^{\mathrm{Lat}} \rangle = \sum_{i=1}^{N_{\mathrm{D}}} \sum_{\alpha = \{x, y, z\}} H_{i\alpha, l'}^{\mathrm{SiV}} h_{i\alpha, l}^{\mathrm{Lat}}, \qquad (2.8)$$
where $\mathbf{H}_{l'}^{\text{SiV}}$ center and $\mathbf{h}_{l}^{\text{Lat}}$ are the eigenvectors associated to the vibrational modes of the SiV⁻ and the finite lattice structure. We assume that the electron wavefunctions are non-zero only on the N_{D} defect atoms, therefore it is sufficient to consider the inner sum on the defect atoms only. In the Appendix A.1 we show a full derivation of the electron-phonon interaction. Next, we promote the normal coordinates and the corresponding momentum conjugate to operators as follows:

$$Q_l^{\text{Lat}} = \sqrt{\frac{\hbar}{2\omega_l}} \left(\hat{b}_l^{\dagger} + \hat{b}_l \right), \qquad P_l^{\text{Lat}} = i\sqrt{\frac{\hbar\omega_l}{2}} \left(\hat{b}_l^{\dagger} - \hat{b}_l \right), \tag{2.9}$$

where the set of $3N_{\text{Lat}} - 6$ independent boson creation \hat{b}_l^{\dagger} and annihilation \hat{b}_l operators obey the commutation relation

$$[\hat{b}_l, \hat{b}_{l'}^{\dagger}] = \delta_{ll'}.$$
 (2.10)

Note that we only quantize vibrational modes, as translational and rotational modes leave invariant the electron-phonon interaction. Finally, by expanding the electron-phonon interaction in the electronic basis $|i\rangle = \{|\Psi_{gx}^{(0)}\rangle, |\Psi_{ux}^{(0)}\rangle\}$ the following electron-phonon Hamiltonian is obtained:

$$H_{\text{e-ph}} = \sum_{i,l} \lambda_{i,l} |i\rangle \langle i| (\hat{b}_l^{\dagger} + \hat{b}_l), \qquad (2.11)$$

where the electron-phonon coupling constants are given by

$$\lambda_{i,l} = \sqrt{\frac{\hbar}{2\omega_l}} \sum_{l'=1}^{3N_{\rm D}-6} \langle \mathbf{H}_{l'}^{\rm SiV}, \mathbf{h}_l^{\rm Lat} \rangle \gamma_{i,l'}$$
(2.12)

$$\gamma_{i,l'} = \langle i | \left(\frac{\partial V_{\text{e-Ion}}}{\partial Q_{l'}^{\text{SiV}}} \right) \Big|_{\mathbf{R}_0} | i \rangle.$$
(2.13)

To evaluate $\gamma_{i,l'}$ we used symmetrized Gaussian orbitals (see Appendix A.4 for details). On Eq.(2.11) we have only kept those terms that shift the energy of the electronic states. Other terms such as

$$\sum_{i \neq j,l} \lambda_{ij,l} |i\rangle \langle j| (\hat{b}_l^{\dagger} + \hat{b}_l), \qquad (2.14)$$

are not considered. The latter terms make Hamiltonian (2.11) analytically unsolvable for a direct diagonalization calculation [30]. Nevertheless, these terms will be considered by means of dynamical symmetry breaking.

2.4 Model for the emission spectrum

The fluorescence spectrum of the emitted radiation in a thermal equilibrium state is determined by the spectral intensity radiated per unit solid angle by an oscillating dipole and it is given by [38]

$$\frac{dI}{d\Omega} = \frac{\omega_0^4}{8\pi^2 c^3} \left| (\mathbf{n} \times \mathbf{d}) \times \mathbf{n} \right|^2 E(\omega), \qquad (2.15)$$

$$E(\omega) = \int_{-\infty}^{\infty} \langle \sigma_{-}(t)\sigma_{+}(0) \rangle_{eq} e^{-i\omega t} dt, \qquad (2.16)$$

where **d** is the dipole vector and $\mathbf{n} = \mathbf{r}/|\mathbf{r}|$ is the unitary vector pointing in the direction of **r**. Therefore, we calculate the emission spectrum associated to the electronic transition from the excited $|e\rangle$ to ground state $|g\rangle$ as the Fourier transform of the current-current correlation function at thermal equilibrium by applying the Kubo formula [31, 38] Eq.(2.16), where $\sigma_{+} = |e\rangle\langle g|, \sigma_{-} = |g\rangle\langle e|, \sigma_{\pm}(t) = U^{\dagger}(t)\sigma_{\pm}(0)U(t)$ and $U(t) = e^{-iH_{\rm SB}t/\hbar}$. The Hamiltonian $H_{\rm SB}$, known as the spin-boson Hamiltonian [31], is given by

$$H_{\rm SB} = H_{\rm e} + H_{\rm e-ph} + \sum_{l} \hbar \omega_l \hat{b}_l^{\dagger} \hat{b}_l, \qquad (2.17)$$

where the first, second and third term are the Hamiltonians of the electronic states of the point defect [Eq.(2.3)], the electron-phonon interaction to first order in the ion displacements [Eq.(2.11)], and the phonon bath, respectively. The average $\langle ... \rangle_{eq}$ is taken over phonons, which are assumed to be in thermal equilibrium. The electron-phonon interaction in Eq.(2.17) describes acoustic, optical and quasi-local phonon modes coupled to the electronic states of the point defect. Physically, during the emission or absorption processes, the electronic charge changes its spatial distribution leading to a change in the potential seen by the ions close to the charge localization. Ions will seek for new equilibrium positions, resulting in a relaxation processes affect the optical properties we introduce the polaron transformation [31, 39] given by

$$H' = e^S H e^{-S}, (2.18)$$

where

$$S = \sum_{i,l} \frac{\lambda_{i,l}}{\hbar\omega_l} |i\rangle \langle i| \left(\hat{b}_l^{\dagger} - \hat{b}_l \right).$$
(2.19)

In the density operator formalism, the state of thermal equilibrium that maximizes the von Neumann entropy $S(\hat{\rho}) = -\text{Tr}(\hat{\rho} \ln \hat{\rho})$ is given by $\hat{\rho}_{eq} = e^{-\beta H_{SB}}/Z$, where $Z = \text{Tr}(e^{-\beta H_{SB}})$ is the partition function, $\beta = 1/k_{B}T$, T is the temperature, and k_{B} is the Boltzmann constant. Therefore, the expectation value can be calculated as

$$\langle \sigma_{-}(t)\sigma_{+}(0)\rangle_{\rm eq} = \frac{1}{Z} \operatorname{Tr}\left(\sigma_{-}'(t)\sigma_{+}'(0)e^{-\beta H_{\rm SB}'}\right).$$
(2.20)

Under these approximations the emission spectrum can be analytically calculated as

$$E(\omega) = \int_{-\infty}^{\infty} e^{-i(\omega - \omega_{eg} + \Delta_e - \Delta_g)t + \Phi(t)} dt, \qquad (2.21)$$

where $\omega_{eg} = \omega_e - \omega_g$ is the bare electronic frequency transition, $\Delta_i = \sum_l \lambda_{i,l}^2 / (\hbar^2 \omega_l)$ is the polaron shift and $\Phi(t)$ contains the effect of phonons on the optical line shape and is given by

$$\Phi(t) = \int_0^\infty \frac{J_0(\omega)}{(\hbar\omega)^2} \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) (\cos\omega t - 1) - i\sin\omega t \right] d\omega, \qquad (2.22)$$

and

$$J_0(\omega) = \sum_l \left(\lambda_{e,l} - \lambda_{g,l}\right)^2 \delta(\omega - \omega_l), \qquad (2.23)$$

is the spectral density function where $\lambda_{i,l}$ is the expectation value of the electron-phonon coupling between phonon modes l and the electronic wavefunction $|i\rangle$. If the electronic states interact with the same strength to phonons, both coupling constants for the ground and excited states are similar and the spectral density function is small leading to a transition involving few phonons and resulting in a fluorescent shape that closely resembles that of a phonon-free system. On the contrary, if these two couplings are substantially different, the change on electronic distribution, and therefore, on the potential seen by the ions is large and the emission spectrum is greatly modified (Fig. 2.1).

2.5 Role of inversion symmetry on the emission spectrum

The electron-phonon coupling constants depend crucially on the atomic configuration, the symmetry of the point defect and the symmetry of the host material. As an example, the fluorescent of the nitrogen-vacancy center (NV-center) and SiV^- center in diamond are very



Figure 2.1: Schematic representation of the potential energy diagram. The two parabolas represent the phononic potential of the ground e_{gx} and excited e_{ux} states of the SiV⁻ including vibrational levels. Structure of the SiV⁻ in diamond: six carbon atoms (dark gray) and the interstitial silicon atom (green) embedded in a diamond lattice (light gray). The molecular orbital representation of the electronic states e_{gx} and e_{ux} are represented by red (blue) for the positive (negative) sign of the electronic wavefunction.

different from each other although they differ in one atom in their molecular composition. The NV-center has a broad emission ranging from 637 nm zero-phonon line (ZPL) to 750 nm; meanwhile the emission of the SiV⁻ has a width of few nanometers at the same temperature [14]. The symmetry of the point defect is determined by the atomic configuration [40]. In the case of the NV-center, the nitrogen atom is substitutional and its atomic configuration does not remain the same under inversion, i.e., parity is not a good description for wavefunctions and vibrations [41]. On the contrary, in the SiV⁻, the silicon atom is interstitial between two vacancies and its configuration remains the same under inversion [35], i.e., electronic wavefunctions and vibrations can be described by parity. As the coupling constants $\lambda_{i,l}$ are the integration of three functions, its expectation value will be zero if the total product is odd. The lack of inversion symmetry in the NV-center allows in principle the contribution from all vibrational modes. Whereas the coupling constants $\lambda_{e,l}$ and $\lambda_{g,l}$ for the SiV⁻ can be very similar due to inversion symmetry. Indeed, in the SiV⁻ the ground state is a gerade (even) linear combination of dangling bond atomic orbitals meanwhile the excited state is an ungerade (odd) function of these orbitals. These wavefunctions might differ only by a phase leading to a very similar electronic distribution, a small change upon electronic transitions



Figure 2.2: Numerical phonon dispersion curves for diamond. Red lines and black circles correspond to the numerical calculations using the force-constant model to second order nearest-neighbor interactions and experimental neutron-scattering data extracted from [44]. The phonon frequencies are plotted as a function of the reduced phonon wave-vector between some symmetry points in the First Brillouin Zone.

in the trapping potential seen by the ions, and therefore a very small phonon contribution to the spectral density function $J_0(\omega)$.

2.6 Spectral density function and the emission spectrum

A quantitative analysis of the phonon modes can be performed by considering a macro molecule composed of $N \sim 10^3$ atoms where the defect is placed at its center as described in Appendix A.3. The vibrational modes are calculated using a force-constant model to second order nearest-neighbor interaction [42, 43] in order to better resemble the real phonon dispersion relation of diamond [44] (see Fig. 2.2). Using only a first order nearest-neighbor model does not give an accurate description of the high density areas for the acoustic bands from which arouses the main contribution to the spectral density function. In Appendix A.2 and A.3 we show the numerical methodology implemented to obtain the vibrational properties of the macromolecule. Vibrational modes of even parity $(a_{1g}, a_{2g} \text{ and } e_g \text{ phonons})$ contribute to the spectral density function $J_0(\omega)$ associated to the transition $|\Psi_{ux}^{(0)}\rangle \longrightarrow |\Psi_{gx}^{(0)}\rangle$ [see Fig. 2.3.(a)] with the breathing mode of symmetry a_{1g} being the strongest contribution. This peak also contains contributions from e_g phonon modes which contribute to the width of the peak. So far the motion of the silicon atom does not play a role if we consider phonon modes with even symmetry. However, recently an isotopic shift of the phonon sideband was observed for different silicon isotopes [45]: as the mass of the silicon atom increases, the distance between the ZPL and the phonon sideband decreases suggesting that a local vibrational mode primarily composed of the silicon atom is involved. Such mode is necessarily of character u (odd), and for symmetry reasons it should not contribute to the coupling constants $\lambda_{e,l}$ and $\lambda_{g,l}$ if the electronic states given in Eqs.(2.1) and (2.2) are used. This indicates that inversion symmetry is broken and it is no longer a good description of the wavefunctions. Inversion symmetry can be broken by vibrations of character u, which can dynamically mix both ground and excited states. External electric fields can also break inversion symmetry. Global strain does not mix ground and excited states as it only mix the states among each manifold [36]. In addition, *ab initio* calculations support that inversion symmetry is not broken if vibrations are not included. In this scenario, the new electronic wavefunctions can be described by

$$|\Psi_g\rangle = \sqrt{1-\epsilon^2}|\Psi_q^{(0)}\rangle - \epsilon e^{+i\theta}|\Psi_e^{(0)}\rangle, \qquad (2.24)$$

$$|\Psi_e\rangle = \sqrt{1-\epsilon^2}|\Psi_e^{(0)}\rangle + \epsilon e^{-i\theta}|\Psi_g^{(0)}\rangle, \qquad (2.25)$$

where ϵ is a mixing parameter, θ is an arbitrary phase, and $|\Psi_g^{(0)}\rangle$, $|\Psi_e^{(0)}\rangle$ are the electronic wavefunctions given in Eqs.(2.1) and (2.2). A similar argument can be given by means of the Herzberg-Teller effect which can also show a dynamical symmetry breaking [46–48]. The spectral density function $J(\omega) = \sum_l (\lambda_{\Psi_e,l} - \lambda_{\Psi_g,l})^2 \delta(\omega - \omega_l)$ can be explicitly calculated in order to incorporate the effect of the dynamical symmetry breaking given by the mixing of the ground and excited states of the SiV⁻ center. Using group theoretical arguments, averaging over the phase θ and evaluating in the small mixing limit ($|\epsilon| \ll 1$) we find that (see Appendix A.6)

$$J(\omega) = J_0(\omega) + 8\epsilon^2 J_{eg}(\omega), \qquad (2.26)$$

where $J_0(\omega)$ is given by Eq. (B.27) and

$$J_{eg} = \sum_{l} \left(\lambda_{eg,l}\right)^2 \delta(\omega - \omega_l), \quad \lambda_{eg,l} = \langle \Psi_g^{(0)} | \mathbb{H}_{e-ph}^{(l)} | \Psi_e^{(0)} \rangle, \qquad (2.27)$$

is the spectral density function that incorporates the contribution of phonon modes with odd symmetry. See Appendix A.6 for a derivation of the spectral density function $J_{eg}(\omega)$. Fig. 2.3(b) shows $J_{eg}(\omega)$ where a strong peak associated to an a_{1u} quasi-local phonon mode $(a_{2u} \text{ in } D_3 \text{ symmetry})$ is observed with a frequency of $\omega_{28} = 63.19 \text{ meV}$, $\omega_{29} = 62.66 \text{ meV}$ and $\omega_{30} = 62.16 \text{ meV}$ for isotopes ²⁸Si, ²⁹Si and ³⁰Si, respectively. The ratio between these energies is approximately $\omega_{28}/\omega_{29} \approx 1.01$ and $\omega_{28}/\omega_{30} \approx 1.02$ and has a good agreement with experimental values $(\omega_{28}/\omega_{29} = 1.016 \text{ and } \omega_{28}/\omega_{30} = 1.036 \text{ [45]})$. However, the exact value for the energy of this a_{1u} quasi-local phonon mode can be better estimated with more precise methods. The prominent sharp feature of $J_{eg}(\omega)$ has also contributions from e_u and a_{2u} modes where e_u modes contribute approximately twice as much as the a_{2u} modes. The frequency of the quasi-local phonon mode a_{1u} has a strong dependence on the silicon mass. In this mode, the silicon atom moves along the symmetry axis. In addition, we observe that $J_{eg}(\omega)$ is considerably larger that $J_0(\omega)$ and strongly depends on the silicon contribution to the electronic wavefunction (see Eq.(2.2)). Only a small mixing parameter is sufficient to make $J_{eg}(\omega)$ the largest contribution to the spectral density function given in Eq.(2.26).

This microscopic procedure allows to numerically calculate the contribution of acoustic, optical and quasi-local phonon modes to the spectral density function. However, a large number of atoms is required to have a better estimate of the mode density and of the emission spectrum. Alternatively, known models of the spectral density function can be fitted to simplify the effect of phonons. Bulk phonons have been modelled with a spectral density function of the form [29] $J_{\text{Bulk}}(\omega) = 2\alpha\omega_c^{1-s}\omega^s e^{-\omega/\omega_c}$, where α is the dissipation strength, ω_c is a cut-off frequency and s is a dimensionless parameter characterizing the regimes: subohmic (s < 1), ohmic (s = 1) and super-ohmic (s > 1). At low frequencies the contribution from acoustic phonon modes to the SiV⁻ can be modeled as $J(\omega) \propto \omega^3$ which implies a super-ohmic regime (s = 3) [33]. For quasi-local phonons $J_{\text{Loc1}}(\omega) = \frac{J_0}{\pi} \frac{\frac{1}{2}\Gamma}{(\omega - \omega_b)^2 + (\frac{1}{2}\Gamma)^2}$ [49], where J_0 is the coupling strength, Γ is a characteristic width and ω_b is the frequency of the phonon. In the numerical estimation at least two localized contributions $J_{\text{Loc1}}(\omega)$ and $J_{\rm Loc2}(\omega)$ are recognised at 63.19 meV and around 45.5 meV, respectively. We fit $J_{eg}(\omega)$ to a spectral density function of the form $J_{eq}(\omega) = J_{\text{Bulk}}(\omega) + J_{\text{Loc1}}(\omega) + J_{\text{Loc2}}(\omega)$ [50]. We found, however, that $J_{\text{Loc2}}(\omega)$ is best fit to a Gaussian function as it is probably composed of multiple quasi-local phonon modes. The emission spectrum associated with $J_{eg}(\omega)$ is shown on Fig. 2.4 and has good agreement with the observed isotopic shift [45]. The largest contribution to the phonon sideband at 766 nm is due to the main peak in $J_{eg}(\omega)$ at 63.19 meV and it is associated to an a_{1u} quasi-local mode as previously discussed (see Fig. 2.3(b)). Changing the isotopic mass indeed shifts the distance between the ZPL and this feature on the phonon sideband confirming previous observations [45]. A second contribution to the sideband is observed at 755 nm and is associated with a peak in $J_{eq}(\omega)$ at 45.5 meV and



Figure 2.3: Numerical spectral functions $J_0(\omega)$ and $J_{eg}(\omega)$ for the SiV⁻ in diamond. (a) Spectral function $J_0(\omega)$, where the blue bar graph and the green line are the numerical estimation and the fit spectral function obtained from simulations. The strongest contribution is given by an a_{1g} phonon mode (breathing mode) at around $\omega_0 = 37$ meV. (b) Spectral function $J_{eg}(\omega)$, where the blue bar graph and the green line are the numerical estimation and the fit spectral function, respectively. The strongest contribution is given by an a_{1u} quasi-local phonon mode at around $\omega_1 = 63.19$ meV. A second contribution of the $J_{eg}(\omega)$ spectral function is given at around $\omega_2 = 45.5$ meV.

does not have a dependence on the silicon mass. Other peaks in the observed experimental phonon sideband [51] can be associated to other features in the spectral density function $J_0(\omega)$ and $J_{eg}(\omega)$. A peak at 796 nm (with no dependence on the silicon mass) [45] might correspond to the highest phonon frequency of the acoustic band of highest sound speed, close to the L symmetry point of the measured dispersion relation [43, 52].

Our second nearest-neighbor model over estimate mode frequencies at higher frequencies and locates this points at 136.5 meV, frequency at which there seems to be a contribution on the spectral function $J_{eg}(\omega)$ (see Fig. 2.3(b)). A similar argument applies for a contribution at 87 meV in the observed phonon sideband corresponding to a 103.4 meV feature in $J_{eg}(\omega)$.



Figure 2.4: Numerical emission spectra of the SiV⁻ in diamond. The blue and red curves represent the numerical emission spectrum obtained for T = 4 K and T = 296 K, respectively. The ZPL at 736 nm and the prominent sharp feature of the phonon sideband at 766 nm are reproduced. The peak at 766 nm its associated with the a_{1u} quasi-local phonon mode.

The model also allows to calculate temperature effects. As an example, we have plot the emission spectrum at 4K and 297 K (see Fig. 2.4). Finally, we remark that the isotopic shift is not possible to explain with phonons that transform evenly under inversion. Therefore, a dynamical symmetry breaking is needed, which can be caused by non-inversion preserving perturbations such as external electric fields or odd vibrational modes.

Further improvements of the current numerical estimations can be performed by increasing the number of atoms around the defect for which the defect electronic wavefunctions are non-zero.

2.7 Conclusions

In summary we have presented a microscopic model for estimating the emission spectrum of the SiV^- using the Kubo formula and the spin-boson model. In addition we have considered effects to second-order on the spectral density function via dynamical symmetry breaking.

This spectral density function is estimated using a force-constant model for describing the vibrational modes and symmetrized electronic wavefunctions constructed using group theoretical arguments. This approach allows us to gain detailed insight on the microscopic origin and the role of symmetries on the emission spectra and the spectral density function, approach which is crucially different from, but validates, phenomenological models presented in previous works [29–31]. These results might be useful for understanding and engineering the optical properties of colour centers in solids by extending the analysis to other deep and shallow centers coupled to phonons and subject to instabilities such as dynamic Jahn-Teller effects and external perturbations such as electric fields or strain.

Chapter 3

Spin-lattice relaxation of individual solid-state spins

In this chapter, we present a theoretical microscopic model to describe the spin-lattice relaxation of individual electronic spins associated to negatively charged nitrogen-vacancy centers in diamond, although our results can be extended to other spin-boson systems. Starting from a general spin-lattice interaction Hamiltonian, we provide a detailed description and solution of the quantum master equation of an electronic spin-one system coupled to a phononic bath in thermal equilibrium. Special attention is given to the dynamics of one-phonon processes below 1 K where our results agree with recent experimental findings and analytically describe the temperature and magnetic-field scaling. At higher temperatures, linear and second-order terms in the interaction Hamiltonian are considered and the temperature scaling is discussed for acoustic and quasi-localized phonons when appropriate. Our results, in addition to confirming a T^5 temperature dependence of the longitudinal relaxation rate at higher temperatures, in agreement with experimental observations, provide a theoretical background for modeling the spin-lattice relaxation at a wide range of temperatures where different temperature scalings might be expected.

3.1 Introduction

The negatively charged nitrogen-vacancy (NV^{-}) center in diamond is a promising solid-state system with remarkable applications in quantum sensing with atomic-scale spatial resolution [8, 9], fluorescent marking of biological structures [4–6], single photon sources [53], and quantum communications [7]. However, most of these quantum-based applications crucially depend on the longitudinal $(1/T_1)$ and transverse $(1/T_2)$ spin relaxation rates associated with the ground state spin degree of freedom [18].

From experiments and theory, we know that lattice phonons in diamond are important for the spin-lattice relaxation dynamics of the spin degree of freedom of the NV⁻ center, and that the temperature plays a fundamental role in this relaxation process [15–19]. Phonons can be understood as collective quantum vibrational excitations that propagate through the lattice and directly interact with the orbital states of the point defect. The intensity of this interaction depends on the electron-phonon coupling between the defect and all possible phonon modes in the lattice (acoustic, optical and quasi-localized phonon modes) [48, 54, 55]. Theoretical and numerical studies show that the strain field of the diamond lattice and perturbative corrections given by the spin-orbit and spin-spin interactions introduce interesting spin-phonon dynamics between the ground state spin degree of freedom of the NV^- center and lattice phonons [56, 57].

Several theoretical works have addressed the problem of finding the relaxation rate by considering the interaction between the spin degree of freedom with two-phonon Raman [20, 58] and Orbach-type [21] processes. In general, the problem of estimating the thermal dependence of each relaxation process is translated into the problem of calculating the transition rates predicted by the Fermi golden rule for different phonon processes [19–21, 58, 59]. Using this reasoning, it is reported that the second-order Raman process induced by a linear spinphonon interaction leads to $1/T_1 \propto T^5$ [20], while the first-order Raman process induced by a quadratic spin-phonon interaction leads to $1/T_1 \propto T^7$ [58], where T is the environment temperature.

The ground triplet state of the NV⁻ center in diamond has a natural zero-field splitting $D/2\pi = 2.87$ GHz originated from the dipole-dipole interaction between electronic spins [60, 61]. This energy gap is low compared to typical optical phonon energies $\omega_{\rm ph}/2\pi \sim 15$ -40 THz and sets a characteristic thermal gap associated with the spin system $T_{\rm gap} = \hbar D/k_B \approx 0.14$ K. Experimental observations at high temperatures, from 300 K to 475 K, have shown that different samples with different NV⁻ center concentrations present a dominant two-phonon Raman process that leads to $(1/T_1)_{\rm Raman} \propto T^5$ [17, 18]. At low temperatures, between 4 K and 100 K, the relaxation rate is dominated by Orbach and spin-bath interactions. The former is associated with a quasi-localized phonon mode with

energy $\omega_{\text{loc}} \approx 73 \text{ meV} [18, 62]$ and contributes with a temperature dependence relaxation rate $(1/T_1)_{\text{Orbach}} \propto (\exp(\hbar\omega_{\text{loc}}/k_BT) - 1)^{-1}$. This, closely matches the numerical vibrational resonance predicted by *ab initio* studies [54]. Meanwhile, it is observed that dipoledipole interactions between neighboring spins lead to a constant sample-dependent relaxation rate which dominates at this temperature range [18]. In contrast, at lower temperatures (below 1 K) recent experimental observations and *ab initio* calculations concluded that the longitudinal relaxation rate is dominated by single-phonon processes, and is given by $(1/T_1) \propto \Gamma_0 (1 + 3\bar{n}(T))$, where $\Gamma_0 = 3.14 \times 10^{-5} \text{ s}^{-1}$, and $\bar{n}(T) = (\exp(\hbar D/k_BT) - 1)^{-1}$ is the mean number of phonons at the zero-field splitting frequency [19]. However, a microscopic model that predicts the temperature dependence of the longitudinal relaxation rate for a wide range of temperatures, to the best of our knowledge, is still missing.

Here, we present a microscopic model for the spin-lattice relaxation dynamics associated with the ground state of the NV⁻ center in diamond. In our model, we introduce a general spin-phonon Hamiltonian to describe the spin relaxation dynamics using the quantum master equation associated with the electronic spin degree of freedom under the effect of a phononic bath. We focus on the estimation of the longitudinal relaxation rate by evaluating the rate of the Fermi golden rule transitions to first and second-order considering the effect of acoustic and quasi-localized phonons. In Sec. 3.2, we give the Hamiltonian of the whole system and introduce the spin-phonon interaction between the triplet state of the spin degree of freedom and lattice vibrations, by considering one-phonon and two-phonon interactions. Section 3.3 introduces the phonon relaxation rates for one-phonon and two-phonon processes, by using the Fermi golden rule, the Debye approximation, and a model for strong interactions with quasi-localized phonon modes. In Sec. 3.4 we introduce the quantum master equation associated with the spin-lattice relaxation dynamics of the ground state and include the role of a stochastic magnetic noise. Finally, in Section 3.5 we discuss the longitudinal relaxation rate at low and high-temperature regimes and the role of a static magnetic field on the relaxation rate for low temperatures.

3.2 Spin degree of freedom and phonons

We consider a system composed of a single NV⁻ center in diamond interacting with lattice phonons. In this scenario, local vibrations induce a mixing between orbital states of the defect by means of the electron-phonon interaction. This phonon-induced mixing effect generates an effective interaction between the spin degree of freedom and lattice phonons. In order to model the spin-phonon relaxation dynamics, we use the following Hamiltonian

$$\hat{H} = \hat{H}_{\rm NV} + \hat{H}_{\rm s-ph} + \hat{H}_{\rm ph},\tag{3.1}$$

where the first, second and third terms represent the ground state spin Hamiltonian of the NV^- center, the interaction Hamiltonian between the spin state and lattice phonons, and the phonon bath, respectively.

The NV⁻ center is composed of a substitutional nitrogen atom next to a vacancy in a diamond lattice. The symmetry of the center is captured by including the three carbon atoms adjacent to the vacancy [63]. The atomic configuration of this point defect is associated with the C_{3v} symmetry group. The electronic structure of this point defect is modeled as a two electron-hole system with electronic spin S = 1. In this representation, the electronic wavefunctions of the excited and ground state are linear combinations of two-electron wave functions [64], where the single-electron orbitals of the NV⁻ center can be written in terms of the carbon and nitrogen dangling bonds [35, 65]. In the absence of external perturbations, such as lattice distortions or electromagnetic fields, the orbital excited states $|X\rangle$ and $|Y\rangle$ are degenerate due to the C_{3v} symmetry and belong to the irreducible representation A_2 .

In the presence of a static magnetic field B_0 along the z axis, the spin Hamiltonian of the NV⁻ center is given by ($\hbar = 1$)

$$\hat{H}_{\rm NV} = DS_z^2 + \gamma_s B_0 S_z, \tag{3.2}$$

where $\mathbf{S} = (S_x, S_y, S_z)$ are the Pauli matrices for S = 1 (dimensionless), $D/2\pi = 2.87$ GHz is the zero-field splitting constant, and $\gamma_s/2\pi \approx 2.8$ MHz/G is the gyromagnetic ratio. Figure. 3.1 shows the energy diagram of the system, including the orbital states, spin degrees of freedom and the atomic configuration of the NV⁻ center.

Quantum systems with spin S = 1 are traditionally called non-Kramers systems [66, 67]. Interestingly, there is a non-trivial connection between the spin number and the temperature dependence of the relaxation rate [20, 21, 65]. Therefore, in order to obtain the correct temperature dependence of the spin relaxation rate of the ground triplet state of the NV⁻ center we consider the most general spin-phonon interaction Hamiltonian for spin S = 1



Figure 3.1: The energy levels and the atomic structure of the NV⁻ center are shown. Here, $|X\rangle$ and $|Y\rangle$ are the orbital degenerate excited states, and $|A_2\rangle$ is the orbital ground state. The zerophonon line energy is given by $E_0 = 1.945$ eV. The spin triplet states are represented by $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$. Such spin states are separated by the zero-field splitting constant $D/2\pi = 2.87$ GHz and the static magnetic field which we have assumed is aligned along the symmetry axis of the center. Phonons are represented by a continuous band that interacts with the ground state and its transitions are represented by the labels (1), (2), and (3).

systems given by [66]

$$\hat{H}_{s-ph} = E_z S_z^2 + E_x \left(S_x^2 - S_y^2 \right) + E_y \left(S_x S_y + S_y S_x \right) + E_{x'} \left(S_x S_z + S_z S_x \right) + E_{y'} \left(S_y S_z + S_z S_y \right),$$
(3.3)

where the operators E_z , E_x , E_y , $E_{x'}$ and $E_{y'}$ have units of energy. In addition, the operators E_x , E_x , E_y , and $E_{y'}$ belong to the irreducible representation E, while the operator E_z is characterized by the irreducible representation A_1 [66]. Physically, the E_i operators can be derived from perturbative corrections of the spin-spin and spin-orbit interactions due to the effect of the strain field [57]. These operators are proportional to the nuclear displacements, and therefore, can be quantized using phonon modes [57]. In order to introduce these quantized vibrations, we expand the E_i operators in terms of lattice phonon-mode operators classified by each symmetry, including the linear and the quadratic terms, as the following

$$E_i = \sum_{k \in E} \lambda_{k,i} \hat{x}_k + \sum_{k \otimes k' \in E} \lambda_{kk',i} \hat{x}_k \hat{x}_{k'}, \quad i \neq z$$
(3.4)

$$E_z = \sum_{k \in A_1} \lambda_{k,z} \hat{x}_k + \sum_{k \otimes k' \in A_1} \lambda_{kk',z} \hat{x}_k \hat{x}_{k'}.$$
(3.5)

Here, $\lambda_{k,i}$ and $\lambda_{kk',i}$ are the linear and quadratic spin-phonon coupling constants, respectively. The operator \hat{x}_k is given by $\hat{x}_k = \hat{b}_k + \hat{b}_k^{\dagger}$ where \hat{b}_k and \hat{b}_k^{\dagger} are the boson annihilation and creation operators, respectively satisfying $[\hat{b}_k, \hat{b}_{k'}^{\dagger}] = \delta_{k,k'}$. The linear term given in Eqs. (3.4) and (3.5) has the same symmetry as the corresponding E_i operators, and phonons with these symmetry are considered in the summation. In the quadratic term we are considering combinations of phonons such that the product belongs to the irreducible representation Eor A_1 . As a consequence of the multiplication rules $A_2 \otimes A_2 = A_1$ and $A_2 \otimes E = E$, phonon modes with A_2 symmetry only contribute to the quadratic term. Therefore, the most general spin-phonon Hamiltonian for a system with spin S = 1, is given by

$$\hat{H}_{\text{s-ph}} = \sum_{i} \left[\sum_{k \in \Gamma_{i}} \lambda_{k,i} \hat{x}_{k} + \sum_{k \otimes k' \in \Gamma_{i}} \lambda_{kk',i} \hat{x}_{k} \hat{x}_{k'} \right] \hat{F}_{i}(\mathbf{S}),$$
(3.6)

where i = x, y, x', y', z is the spin label, $\Gamma_{x,y,x',y'} = E$ and $\Gamma_z = A_1$ are the irreducible representations of the C_{3v} point group. The spin functions are given by $\hat{F}_x(\mathbf{S}) = S_x^2 - S_y^2, \hat{F}_y(\mathbf{S}) = S_x S_y + S_y S_x, \hat{F}_{x'}(\mathbf{S}) = S_x S_z + S_z S_x, \hat{F}_{y'}(\mathbf{S}) = S_y S_z + S_z S_y$, and $\hat{F}_z(\mathbf{S}) = S_z^2$.

Using the spin basis that diagonalizes the spin Hamiltonian given in Eq. (3.2), i.e., $|m_s = 1\rangle = (1, 0, 0), |m_s = 0\rangle = (0, 1, 0), \text{ and } |m_s = -1\rangle = (0, 0, 1)$ we explicitly obtain

$$\hat{F}_{x}(\mathbf{S}) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \hat{F}_{x'}(\mathbf{S}) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \quad (3.7)$$

$$\hat{F}_{y}(\mathbf{S}) = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \quad \hat{F}_{y'}(\mathbf{S}) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & i \\ 0 & -i & 0 \end{pmatrix}, \quad (3.8)$$

$$\hat{F}_{z}(\mathbf{S}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$
(3.9)

We observe that only the terms $\hat{F}_x(\mathbf{S})$ and $\hat{F}_y(\mathbf{S})$ induce spin transitions between the states $m_s = \pm 1$ and $m_s = -1$, where the selection rule is $\Delta m_s = \pm 2$. On the other hand, the terms $\hat{F}_{x'}(\mathbf{S})$ and $\hat{F}_{y'}(\mathbf{S})$ induce spin transitions between $m_s = \pm 1$ and $m_s = 0$, in this case the selection rule is $\Delta m_s = \pm 1$.

Finally, the phonon Hamiltonian can be written as

$$\hat{H}_{\rm ph} = \sum_{k} \hbar \omega_k \hat{b}_k^{\dagger} \hat{b}_k, \qquad (3.10)$$

where ω_k is the frequency of each vibrational mode of the lattice (including the color center), and the summation takes into account the contribution of all phonon modes of the diamond lattice. In the next section, we will introduce the phonon-induced spin relaxation rates and the temperature dependence associated to the spin-phonon Hamiltonian given in Eq. (3.6) by considering the effect of acoustic and quasi-localized phonons in thermal equilibrium. We will show that the dimension and the symmetry of the lattice play a fundamental role in the temperature dependence of the longitudinal relaxation rate for two-phonon processes.

3.3 Fermi Golden rule and phonon-induced spin relaxation rates

In order to formally introduce the phonon-induced relaxation rates, we use the Fermi golden rule to first and second order by using the spin-phonon Hamiltonian given in Eq. (3.6). Using this procedure, it is possible to model first and second-order Raman-like processes, as well as direct absorption and emission associated with one-phonon processes. In particular, the energies associated with the spin transitions in the ground state of the NV⁻ center are given by $\omega_1 = 2\gamma_s B_0$, $\omega_2 = D + \gamma_s B_0$, and $\omega_3 = D - \gamma_s B_0$. For typical magnitudes of the static magnetic field $B_0 \sim 0 - 2000$ G and taking into account the zero field splitting constant $D/2\pi = 2.87$ GHz, we obtain that $\omega_1 \sim 0 - 11.2$ GHz, $\omega_{2,3} \sim 2.87 - 8.47$ GHz. These are the typical energies of acoustic phonons which belong to the linear branch of the phonon dispersion relation for diamond [44]. Acoustic phonons in diamond have energies of the order of $\omega_{acous} \sim 0 - 10$ THz. Therefore, the main fraction of acoustic phonons satisfy the frequency condition $\omega_{acous} \gg \omega_i$.

For the case of Raman-like processes the frequency condition is $\omega_{\rm ph,1} - \omega_{\rm ph,2} = \omega_i$ (i = 1, 2, 3). Due to the condition $\omega_{\rm acous} \gg \omega_i$ we assume in our model that the most significant contribution to two-phonon processes comes from acoustic phonons that satisfy $\omega_{\rm ph,1} \gg \omega_i$ and $\omega_{\rm ph,2} \gg \omega_i$. On the other hand, high energy phonons in diamond, with frequencies of the order of $\omega_{\rm ph} \sim 15 - 40$ THz, can be included by considering the strong interaction

with quasi-localized phonons. Therefore, in what follows we will consider the contribution of acoustic and quasi-localized phonons.

3.3.1 One-phonon processes: acoustic phonons

In the case of one-phonon processes, we need to distinguish between the absorption and the emission of a particular phonon mode with frequency ω_k , which must be resonant with a transition between the spin energy levels of the NV⁻ center in diamond. In order to introduce the temperature, we assume a phonon environment in thermal equilibrium, i.e., phonons that satisfy the Bose-Einstein distribution. Thus, we have $\langle \hat{b}_k^{\dagger} \hat{b}_k \rangle = n(\omega_k)$ and $\langle \hat{b}_k \hat{b}_k^{\dagger} \rangle = 1 + n(\omega_k)$, where $n(\omega_k) = [\exp(\hbar\omega_k/k_B T) - 1]^{-1}$ is the mean number of phonons at thermal equilibrium with k_B and \hbar being the Boltzmann and Planck constant, respectively.

For one-phonon processes the absorption and emission transition rates associated with the spin transition $|m_s\rangle \rightarrow |m'_s\rangle$ are given by the first order Fermi golden rule as

$$\Gamma_{\rm abs}^{m_s \to m'_s} = \frac{2\pi}{\hbar^2} \sum_k \left| \langle m'_s, n_k - 1 \left| \hat{H}_{\rm s-ph}, \left| m_s, n_k \right\rangle \right|^2 \delta(\omega_{m'_s, m_s} - \omega_k), \tag{3.11}$$

$$\Gamma_{\rm em}^{m_s \to m'_s} = \frac{2\pi}{\hbar^2} \sum_k \left| \langle m'_s, n_k + 1 \left| \hat{H}_{\rm s-ph} \right| m_s, n_k \rangle \right|^2 \delta(\omega_{m'_s, m_s} - \omega_k), \qquad (3.12)$$

where $\omega_{m'_s,m_s} = \omega_{m'_s} - \omega_{m_s}$ is the frequency difference between the spin sub-levels, and $|n_k\rangle$ is the number of phonons in the mode k (Fock state). Using the spin-phonon Hamiltonian given in Eq. (3.6), the spin relaxation rates associated with one-phonon processes are given by

$$\Gamma_{\rm abs}^{1,1\text{-ph}} = \frac{2\pi}{\hbar^2} n(\omega_1) J_1(\omega_1), \quad \Gamma_{\rm em}^{1,1\text{-ph}} = \frac{2\pi}{\hbar^2} (n(\omega_1) + 1) J_1(\omega_1), \quad (3.13)$$

$$\Gamma_{\rm abs}^{2,1\text{-ph}} = \frac{\pi}{\hbar^2} n(\omega_2) J_2(\omega_2), \quad \Gamma_{\rm em}^{2,1\text{-ph}} = \frac{\pi}{\hbar^2} \left(n(\omega_2) + 1 \right) J_2(\omega_2), \quad (3.14)$$

where the superscript "1" and "2" represent the spin transitions $|m_s = -1\rangle \leftrightarrow |m_s = 1\rangle$ and $|m_s = 0\rangle \leftrightarrow |m_s = +1\rangle$, respectively. Here, $J_1(\omega)$ and $J_2(\omega)$ are the spectral density functions

$$J_1(\omega) = \sum_{k \in E} \left(\lambda_{k,x}^2 + \lambda_{k,y}^2 \right) \delta(\omega - \omega_k), \qquad (3.15)$$

$$J_2(\omega) = \sum_{k \in E} \left(\lambda_{k,x'}^2 + \lambda_{k,y'}^2 \right) \delta(\omega - \omega_k), \qquad (3.16)$$

where $\lambda_{k,i}$ are the linear spin-phonon coupling constants, ω_k are the phonon frequencies, and both summations consider the contribution of E phonons. For the transition $|m_s = 0\rangle \leftrightarrow$ $|m_s = -1\rangle$ the gap frequency $\omega_3 = D - \gamma_s B_0$ can be positive or negative depending on the strength of the external magnetic field B_0 . For $\omega_3 > 0$ the absorption and emission relaxation rates are given by

$$\Gamma_{\rm abs}^{3,1\text{-ph}} = \frac{\pi}{\hbar^2} n(\omega_3) J_2(\omega_3), \qquad (3.17)$$

$$\Gamma_{\rm em}^{3,1-\rm ph} = \frac{\pi}{\hbar^2} (n(\omega_3) + 1) J_2(\omega_3), \qquad (3.18)$$

where the superscript "3" represents the spin transition $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$. In this case, the spin state $|m_s = 0\rangle$ is the lowest spin energy level and the absorption is defined by the transition $|m_s = 0\rangle \rightarrow |m_s = -1\rangle$. In the opposite case, i.e., when $\omega_3 < 0$, the relaxation rates can be written as the following

$$\Gamma_{\rm abs}^{3,1\text{-ph}} = \frac{\pi}{\hbar^2} n(|\omega_3|) J_2(|\omega_3|), \qquad (3.19)$$

$$\Gamma_{\rm em}^{3,1-\rm ph} = \frac{\pi}{\hbar^2} (n(|\omega_3|) + 1) J_2(|\omega_3|).$$
(3.20)

In this case the spin state $|m_s = -1\rangle$ is the lowest spin energy level, and the absorption is defined by the transition $|m_s = -1\rangle \rightarrow |m_s = 0\rangle$. Figure 3.2 shows the phonon-induced spin relaxation rates associated with the ground triplet state of the NV⁻ center as a function of the external magnetic field B_0 . The absorption and emission relaxation rates associated with the transitions $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$ are shown only for the case $\omega_3 < 0$. The total phonon-induced spin relaxation rate associated with one-phonon processes is defined as the sum of the absorption and emission transition rates of each process, and is given by

$$\Gamma_{1-\mathrm{ph}} = \sum_{i=1}^{3} \left(\Gamma_{\mathrm{abs}}^{i,1-\mathrm{ph}} + \Gamma_{\mathrm{em}}^{i,1-\mathrm{ph}} \right) = \sum_{i=1}^{3} A_i \operatorname{coth} \left(\frac{\hbar \omega_i}{2k_B T} \right).$$
(3.21)

This total phonon-induced spin relaxation rate will be relevant for the general solution associated with the populations of the spin states and the observable $\langle S_z(t) \rangle$ (see Section 3.5 and Eqs. (3.72) and (3.75)). In addition, this transition rate, i.e., the sum of absorption and emission of all the transitions, is the rate that limits the coherence time T_2 [68]. The parameters A_i depend on the value of the spectral density function at the resonant frequencies, i.e., $A_1 = 2\pi J_1(\omega_1), A_2 = \pi J_2(\omega_2)$, and $A_3 = \pi J_2(|\omega_3|)$. In the limit of continuous frequency, i.e., $\omega_k \to \omega$, we can introduce the following scaling for the linear spin-phonon coupling constants [69]:

$$\lambda_{k,i} \rightarrow \lambda_i(\omega) = \lambda_{0i} \left(\frac{\omega}{\omega_D}\right)^{\nu}, \qquad 0 \le \omega \le \omega_D,$$
(3.22)

where $\lambda_i(\omega)$ is the one-phonon coupling constant for acoustic phonons, $\lambda_{0i} = \lambda_i(\omega_D)$ is the strength of the one-phonon coupling constant at the Debye frequency $\omega_D = (3/(4\pi n))^{1/3} v_s$, where *n* is the atom density, and v_s is the speed of sound. For the diamond lattice the Debye frequency is given by $\omega_D/2\pi = 38.76$ THz [70]. The parameter ν is a phenomenological parameter that models the strength of the coupling for acoustic phonons and depends on the symmetry of the lattice. In the absence or presence of cubic symmetry we have $\nu = 1/2$ or $\nu = 3/2$, respectively [69]. For the NV⁻ center in diamond we use the value $\nu = 1/2$, because of the presence of the color center with $C_{3\nu}$ symmetry that breaks the symmetry of the whole system (lattice and point defect).

We introduce the density of states for acoustic phonons with E symmetry in a threedimensional lattice, with a dispersion $\omega_k = v_s |\mathbf{k}|$ in the Debye approximation ($\omega \leq \omega_D = v_s k_D$):

$$\mathcal{F}(\omega) = \sum_{k \in E} \delta(\omega - \omega_k) \to \Omega \int \frac{d^3k}{(2\pi)^3} \delta(\omega - v_s k)$$

$$= \frac{\Omega}{(2\pi)^3} \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta \int_0^{k_D} dk \, k^2 \delta(\omega - v_s k)$$

$$= \frac{\Omega \omega^2}{2\pi^2 v_s^3} \Theta(\omega_D - \omega), \qquad (3.23)$$

where we have taken the continuum limit of the sum, Ω is the volume of a unit cell, $v_s = 1.2 \times 10^4$ m/s is the speed of sound in a diamond lattice, and $\omega_D = v_s k_D$ is the Debye frequency for the diamond lattice. The frequency domain is truncated in the upper limit to the Debye frequency by the Heaviside function $\Theta(\omega_D - \omega)$. In the limit of continuous

frequency, the spectral density functions can be written as

$$J_{1}(\omega) = \sum_{k \in E} \left[\lambda_{x}^{2}(\omega_{k}) + \lambda_{y}^{2}(\omega_{k}) \right] \delta(\omega - \omega_{k})$$

$$\rightarrow \Omega \int \frac{d^{3}k}{(2\pi)^{3}} \left[\lambda_{x}^{2}(\omega_{k}) + \lambda_{y}^{2}(\omega_{k}) \right] \delta(\omega - \omega_{k})$$

$$= \left[\lambda_{x}^{2}(\omega) + \lambda_{y}^{2}(\omega) \right] \Omega \int \frac{d^{3}k}{(2\pi)^{3}} \delta(\omega - \omega_{k})$$

$$= \left[\lambda_{x}^{2}(\omega) + \lambda_{y}^{2}(\omega) \right] \mathcal{F}(\omega). \qquad (3.24)$$

Similar manipulations lead to $J_2(\omega) = [\lambda_{x'}^2(\omega) + \lambda_{y'}^2(\omega)]\mathcal{F}(\omega)$. As a result, the parameters A_i are given by

$$A_1 = \frac{\Omega\left(\lambda_{0x}^2 + \lambda_{0y}^2\right)}{\pi v_s^3 \omega_D} \left(2\gamma_s B_0\right)^3, \qquad (3.25)$$

$$A_{2} = \frac{\Omega\left(\lambda_{0x'}^{2} + \lambda_{0y'}^{2}\right)}{2\pi v_{s}^{3}\omega_{D}} \left(D + \gamma_{s}B_{0}\right)^{3}, \qquad (3.26)$$

$$A_{3} = \frac{\Omega\left(\lambda_{0x'}^{2} + \lambda_{0y'}^{2}\right)}{2\pi v_{s}^{3}\omega_{D}} \left(D - \gamma_{s}B_{0}\right)^{3}.$$
(3.27)

Therefore, the available number of phonons in the lattice, the density of phonon states, and the spin-phonon coupling constants will determine the intensity of each transition rate. In this context, the temperature is the control parameter in the laboratory that, at a quantum level, introduces available phonons that collectively act as a source of relaxation. At zero magnetic field, we have $A_1 = 0$ and $A_2 = A_3$. In the high-temperature regime, $k_B T \gg \hbar \omega_i$, the one-phonon spin relaxation rates scales linearly with the temperature, i.e., $\Gamma^{i,1-\text{ph}} \propto T$. In the opposite case, when $k_B T \ll \hbar \omega_i$, the one-phonon spin relaxation rates scales as a constant.

In the next section we introduce the second-order corrections to the Fermi golden rule using both linear and bi-linear terms in the spin-phonon interaction Hamiltonian.



Figure 3.2: The solid black lines are the energy levels of the ground triplet state of the NV⁻ center in diamond as a function of the external magnetic field along the z axis. For a given absorption and emission transition between two spin states $|m_s\rangle$, we observe three different spin relaxation processes represented by colored arrows (1=red, 2=green and 3=blue). The one-phonon relaxation rates $\Gamma_{\rm abs}^{i,1-\rm ph}$ and $\Gamma_{\rm em}^{i,1-\rm ph}$ are the absorption and emission spin relaxation rates for one-phonon phonon processes.

3.3.2 Two-phonon processes: acoustic phonons

The second-order transition rate associated with the spin transition $|m_s\rangle \rightarrow |m'_s\rangle$ is defined as

$$\Gamma_{m_s \to m'_s} = \sum_{k,k'} \sum_{l,l'} \Gamma_{m_s,n_k,n_{k'}}^{m'_s,n_l,n_{l'}}, \quad m_s, m'_s = 0, \pm 1,$$
(3.28)

where the sum is over all possible initial and final two-phonon modes, with $|i\rangle = |m_s, n_k, n_{k'}\rangle$ and $|f\rangle = |m'_s, n_l, n_{l'}\rangle$ being the initial and final states, respectively. The transition rate inside the sum in Eq. (3.28) is given by the Fermi golden rule formula to second-order

$$\Gamma_{m_{s},n_{k},n_{k'}}^{m'_{s},n_{l},n_{l'}} = \frac{2\pi}{\hbar^{2}} \left| V_{m_{s},n_{k},n_{k'}}^{m'_{s},n_{l},n_{l'}} + \sum_{m''_{s}=0,\pm 1} \sum_{p,p'} \frac{V_{m'_{s},n_{l},n_{l'}}^{m''_{s},n_{p},n_{p'}} V_{m''_{s},n_{p},n_{p'}}^{m_{s},n_{k},n_{k'}} - E_{m''_{s},n_{p},n_{p'}}}{E_{m_{s},n_{k},n_{k'}} - E_{m''_{s},n_{p},n_{p'}}} \right|^{2} \times \delta(\omega_{m'_{s},m_{s}} + n_{l}\omega_{l} + n_{l'}\omega_{l'} - n_{k}\omega_{k} - n_{k'}\omega_{k'}),$$

$$(3.29)$$

where $V_i^j = \langle i | \hat{H}_{s-ph} | j \rangle$, $|m_s'' \rangle$ is the spin state of the intermediate state, and $|n_p\rangle$, $|n_p'\rangle$ are the intermediate phonon states. The resonant frequencies of the system, i.e., $\omega_1 \sim 0 - 11.2$ GHz and $\omega_{2,3} \sim 2.87 - 8.47$ GHz are very low compared to the frequency of the acoustic phonons in diamond $\omega_{acous} \sim 0 - 10$ THz. Therefore, to second-order we assume that the most significant contribution comes from phonons that satisfy the frequency condition $\omega_{k,k'} \gg \omega_{m_s,m_s''}$.

We introduce four different types of two-phonon processes: two-phonon direct transition (Direct), Stokes transition (Stokes), anti-Stokes transition (anti-Stokes), and spontaneous emission followed by absorption (Spont), see Fig. 3.3. The direct two-phonon transition is characterized by the frequency condition $\omega_k + \omega_{k'} = \omega_{m'_s,m_s}$ and its absorption and emission relaxation rates are given by

$$\Gamma_{m_s \to m'_s}^{\text{abs, Direct}} = \sum_{k,k'} \Gamma_{m_s,n_k,n_{k'}}^{m'_s,n_k-1,n_{k'}-1}, \qquad (3.30)$$

$$\Gamma_{m'_{s} \to m_{s}}^{\text{em, Direct}} = \sum_{k,k'} \Gamma_{m'_{s},n_{k},n_{k'}}^{m_{s},n_{k}+1,n_{k'}+1}.$$
(3.31)

On the other hand, we have the Stokes and Anti-Stokes transitions which are characterized by the frequency condition $\omega_k - \omega_{k'} = \omega_{m'_s,m_s}$ and are given by

$$\Gamma_{m_s \to m'_s}^{\text{Stokes}} = \sum_{k,k'} \Gamma_{m_s,n_k,n_{k'}}^{m'_s,n_k-1,n_{k'}+1}, \qquad (3.32)$$

$$\Gamma_{m'_{s} \to m_{s}}^{\text{Anti-Stokes}} = \sum_{k,k'} \Gamma_{m'_{s},n_{k},n_{k'}}^{m_{s},n_{k}-1,n_{k'}+1}.$$
(3.33)

For the spontaneous emission followed by absorption process we define

$$\Gamma_{m_s \to m'_s}^{\text{abs, Spont}} = \sum_{k,k'} \Gamma_{m_s,n_k,n_{k'}}^{m'_s,n_k+1,n_{k'}-1}, \qquad (3.34)$$

$$\Gamma_{m'_{s} \to m_{s}}^{\text{em, Spont}} = \sum_{k,k'} \Gamma_{m'_{s},n_{k},n_{k'}}^{m_{s},n_{k}+1,n_{k'}-1}.$$
(3.35)

For acoustic phonon modes, i.e., phonons with a linear dispersion relation $\omega_k = v |\mathbf{k}|$, we can use the Debye model in order to represent two-phonon processes. In order to study the spin-relaxation rate as a function of the dimension of the system, we introduce the density

of phonon states for a d-dimensional lattice generalizing Eq. (3.23)

$$\mathcal{F}^{(d)}(\omega) = \Omega \int \frac{d^d k}{(2\pi)^d} \delta(\omega - v_s |\mathbf{k}|) = \frac{\Omega}{(2\pi)^d} \int d\hat{\Omega}_d \int_0^{k_D} dk \, k^{d-1} \delta(\omega - v_s k) = D_0 \left(\frac{\omega}{\omega_D}\right)^{d-1} \Theta(\omega_D - \omega).$$
(3.36)

Here, we have used d-dimensional spherical coordinates with measure $d^d k = d\hat{\Omega}_d dk k^{d-1}$, with $\hat{\Omega}_d$ the solid angle in d-dimensions and $\omega_D = v_s k_D$ the Debye frequency for the diamond lattice. In the last line, we defined the positive normalization constant $D_0 =$ $\Omega \hat{\Omega}_d \omega_D^{d-1} / ((2\pi)^d v_s^d) > 0$, for d = 1, 2, 3 the dimension of the lattice. We can introduce the following scaling for the quadratic spin-phonon coupling constant for the acoustic phonon modes in the limit of continuous frequency [69]

$$\lambda_{kk',i} \rightarrow \lambda_i(\omega, \omega') = \lambda_{00i} \left(\frac{\omega}{\omega_D}\right)^{\nu} \left(\frac{\omega'}{\omega_D}\right)^{\nu},$$
(3.37)

where $\lambda_i(\omega, \omega')$ is the two-phonon coupling constant for acoustic phonons, $\lambda_{00i} = \lambda_i(\omega_D, \omega_D)$ is the strength of the two-phonon coupling constant at the Debye frequency ω_D , and $\nu > 0$ is a phenomenological factor that models the spin-phonon coupling in the acoustic regime.

Using the second-order Fermi golden rule given in Eq. (B.1) and only considering acoustic phonons, we obtain the following absorption and emission transition rates

$$\Gamma_{m_s \to m'_s}^{\text{abs}} = \Gamma_{m_s \to m'_s}^{\text{abs, Direct}} + \Gamma_{m_s \to m'_s}^{\text{Stokes}} + \Gamma_{m_s \to m'_s}^{\text{abs, Spont}}, \qquad (3.38)$$

$$\Gamma_{m_s \to m'_s}^{\text{em}} = \Gamma_{m_s \to m'_s}^{\text{em, Direct}} + \Gamma_{m_s \to m'_s}^{\text{Anti-Stokes}} + \Gamma_{m_s \to m'_s}^{\text{em,Spont}}, \qquad (3.39)$$

where each transition rate is defined as

$$\Gamma_{m_s \to m'_s}^{\text{process}} = a_{m_s,m'_s}^{\text{process}}(x_D) T^{4\nu+2d-3} + b_{m_s,m'_s}^{\text{process}}(x_D) T^{4\nu+2d-2}
+ c_{m_s,m'_s}^{\text{process}}(x_D) T^{4\nu+2d-1},$$
(3.40)

where process = {Direct, Stokes, Anti-Stokes, Spont}, $x_D = \hbar \omega_D / k_B T$ is a dimensionless parameter, T is the temperature, and the coefficients $a_{m_s,m'_s}^{\text{process}}$, $b_{m_s,m'_s}^{\text{process}}$, and $c_{m_s,m'_s}^{\text{process}}$ are given in Appendix B.1. Using $\nu = 1/2$ and d = 3, we obtain the following total two-phonon spin



Figure 3.3: The red arrows represent the absorption and emission of two phonons between two different spin states $|m_s\rangle$ and $|m'_s\rangle$. The direct two-phonon process is associated to the energy condition $\omega_k + \omega_{k'} = \omega_{m'_s,m_s}$, where $\omega_{m'_s,m_s} = \omega_{m'_s} - \omega_{m_s}$ is the frequency gap. The Stokes scattering is associated to the energy condition $\omega_k - \omega_{k'} = \omega_{m'_s,m_s}$.

relaxation rate

$$\Gamma_{2-\text{ph}} = \sum_{m_s \neq m'_s} \left(\Gamma^{\text{abs}}_{m_s \to m'_s} + \Gamma^{\text{em}}_{m_s \to m'_s} \right) \\
= A_5 T^5 + A_6 T^6 + A_7 T^7.$$
(3.41)

This total spin relaxation rate will be relevant for the general solution associated with the physical observable $\langle S_z(t) \rangle$ (see Section 3.5 and Eq. (3.75)). In Table 3.1, we have shown the different temperature dependence of the spin relaxation rate associated with two-phonon processes in the acoustic limit. We observe that the symmetry of the lattice ν and the dimension of the system d determine the temperature response of the spin-lattice relaxation dynamics of the system at high temperatures.

In summary, by only considering the contribution of acoustic phonons to first and secondorder, we see three different temperature scalings of the form (T^s, T^{s+1}, T^{s+2}) , where $s = 4\nu + 2d - 3$. We observe $1/T_1 \propto T^s$ for a linear second-order Raman-like scattering, $1/T_1 \propto T^{s+2}$ for a quadratic first-order Raman-like scattering, and $1/T_1 \propto T^{s+1}$ for the mixed term between the linear and quadratic contributions to second order.

Table 3.1: The table shows the expected temperature dependence of linear and bi-linear spinphonon interactions considered to first and second order. The bi-linear term to second order is zero. When both linear and bi-linear terms are considered a mixed term appears only to secondorder. Last column indicates the temperature scaling for a three-dimensional, non-cubic lattice.

Hamiltonian	First-order	Second-order	d = 3 u = 1/2
$\hat{H} = \sum \lambda_{ki} \hat{x}_k$	$\operatorname{coth}\left(\frac{\hbar\omega}{k_{\mathrm{p}}T}\right)$	$T^{4\nu+2d-3}$	$\frac{\nu - 1/2}{T^5}$
$\hat{H} = \sum_{k,i} \lambda_{kk',i} \hat{x}_k \hat{x}_{k'}$	$\frac{(\kappa_B T)}{T^{4\nu+2d-1}}$	0	T^7
$\frac{k,k',i}{\text{Mixed term}}$	0	$T^{4\nu+2d-2}$	T^6

3.3.3 Two-phonon processes: quasi-localized phonons

Quasi-localized phonons, or vibrational resonances between a single-color-center and lattice vibrations, are good candidates for dissipative processes due to the strong electron-phonon coupling. The NV⁻ center has a strong electron-phonon coupling associated with vibrational resonances, with a continuum of vibrational modes centered at $\omega_{\rm res} = 65$ meV, and a full width at half-maximum of about $\Delta = 32$ meV as regularly observed in the phonon-sideband of the NV fluorescence spectrum under optical excitation [54]. Because of the small zerofield splitting constant induced by spin-spin interaction $(D/2\pi = 2.87 \text{ GHz or } \hbar D = 0.012 \text{ meV})$, we have $\omega_{\rm res} \gg D$, and therefore, these high-energy phonons can only be present in a two-phonon process associated with the condition $\omega_k - \omega_{k'} = \omega_i$ ($\omega_k \approx \omega_{k'}$). Strong interactions with high energy phonons can be introduced in Orbach-type processes [15]. It is shown experimentally that different NV⁻ center samples have an activation energy of 73 meV [18], which is close to the vibrational resonance frequency $\omega_{\rm res} = 65$ meV. In our formalism, quasi-localized phonons can be phenomenologically modeled by a Lorentzian spectral density function of the form [49, 55]

$$J_{\rm Loc}(\omega) = \frac{J_{\rm Loc}}{\pi} \frac{\frac{1}{2}\Delta}{\left(\omega - \omega_{\rm loc}\right)^2 + \left(\frac{1}{2}\Delta\right)^2}, \quad 0 < \omega < \omega_{\rm max}.$$
 (3.42)

In this equation, J_{Loc} is the coupling strength, Δ is a characteristic bandwidth, $\hbar\omega_{\text{max}} = 168$ meV is the maximum phonon energy in a diamond lattice [71], and ω_{loc} is the frequency of the localized phonon mode. As a simpler model we can consider the interaction with only one quasi-localized phonon mode ($\Delta \rightarrow 0$)

$$\lambda_{k,i} = \lambda_{i,\text{loc}} \delta(\omega - \omega_{\text{loc}}), \qquad (3.43)$$

where $\lambda_{i,\text{loc}}$ is the coupling strength. Using the above equation and calculating the secondorder transition rate induced by the linear spin-phonon interaction, we can obtain the following relaxation rate associated with quasi-localized phonons

$$\Gamma_{\rm loc} = A_4 \left(1 + n(\omega_{\rm loc}) \right) n(\omega_{\rm loc}) \approx \frac{A_4}{e^{\hbar \omega_{\rm loc}/k_B T} - 1}, \qquad (3.44)$$

where A_4 is a constant of units of frequency. The approximation $(1 + n(\omega_{\text{loc}})) n(\omega_{\text{loc}}) \approx n(\omega_{\text{loc}})$ is valid for temperatures below T = 300 K. For such temperatures, the mean number of phonons is low, $n(\omega_{\text{loc}}) \approx 0.1$, therefore we can write $(1 + n)n \approx n + \mathcal{O}(n^2)$.

In the next section we derive the spin-lattice relaxation dynamics using the quantum master equation.

3.4 Spin-lattice relaxation dynamics

In this section, we present the general equation associated with the spin-lattice relaxation dynamics of the ground triplet state of the NV⁻ center. We use the Markovian quantum master equation [38] for the reduced density operator $\hat{\rho}(t) = \text{Tr}_{\text{ph}}(\hat{\rho}_{\text{NV+ph}})$. We assume that the initial state at time t_0 is given by the uncorrelated state $\hat{\rho}_{\text{NV+ph}}(t_0) = \hat{\rho}_{\text{NV}}(t_0) \otimes \hat{\rho}_{\text{ph}}(t_0)$ (Born approximation), and that the phonon bath is in thermal equilibrium. In the weakcoupling limit, and using the spin-phonon Hamiltonian given in Eq. (3.6), we obtain

$$\dot{\hat{\rho}} = \frac{1}{i\hbar} [\hat{H}_{\rm NV}, \hat{\rho}] + \mathcal{L}_{1-\rm ph}\hat{\rho} + \mathcal{L}_{2-\rm ph}\hat{\rho} + \mathcal{L}_{\rm mag}\hat{\rho}, \qquad (3.45)$$

where the first term in Eq. (3.45) describes the free dynamics induced by the NV⁻ center Hamiltonian [Eq. (3.2)]. The second and third terms are given by

$$\mathcal{L}_{1-\mathrm{ph}}\hat{\rho} = \sum_{i=1}^{3} \left[\Gamma_{\mathrm{abs}}^{i,1-\mathrm{ph}} \mathcal{D}[L_{+}^{i}]\hat{\rho} + \Gamma_{\mathrm{em}}^{i,1-\mathrm{ph}} \mathcal{D}[L_{-}^{i}]\hat{\rho} \right], \qquad (3.46)$$

$$\mathcal{L}_{2-\mathrm{ph}}\hat{\rho} = \sum_{i=1}^{3} \left[\Gamma_{\mathrm{abs}}^{i,2-\mathrm{ph}} \mathcal{D}[L_{+}^{i}]\hat{\rho} + \Gamma_{\mathrm{em}}^{i,2-\mathrm{ph}} \mathcal{D}[L_{-}^{i}]\hat{\rho} \right], \qquad (3.47)$$

which describe the dissipative spin-lattice dynamics induced by one-phonon and two-phonon processes, with the index i = 1, 2, 3 representing the spin transitions of the system (see

Fig. 3.1). In Eqs. (3.46) and (3.47) we have defined the Lindblad super-operator $\mathcal{D}[\hat{O}]\hat{\rho} = \hat{O}\hat{\rho}\hat{O}^{\dagger} - \frac{1}{2}\{\hat{O}^{\dagger}\hat{O},\hat{\rho}\}$ and the spin operators

$$L^{1}_{+} = |m_{s} = 1\rangle \langle m_{s} = -1| = (L^{1}_{-})^{\dagger},$$
 (3.48)

$$L_{+}^{2} = |m_{s} = 1\rangle \langle m_{s} = 0| = (L_{-}^{2})^{\dagger}, \qquad (3.49)$$

$$L_{+}^{3} = |m_{s} = -1\rangle \langle m_{s} = 0| = (L_{-}^{3})^{\dagger}.$$
 (3.50)

The last term in Eq. (3.45) is an extra term that describes a phenomenological dynamics induced by magnetic impurities, and is given by

$$\mathcal{L}_{\mathrm{mag}}\hat{\rho} = -\frac{1}{4}\Gamma_{\mathrm{mag}}\sum_{i=x,y,z} \left[S_i, \left[S_i, \hat{\rho}(t)\right]\right],\tag{3.51}$$

where Γ_{mag} is the magnetic relaxation rate induced by an isotropic magnetic noise [72], and S_i are the Pauli matrices for S = 1. From previous works, it is expected that the parameter Γ_{mag} will proportionally depend on the concentration of neighboring NV⁻ centers [18] and temperature. Therefore, Γ_{mag} is a sample-dependent parameter that models magnetic impurities. The exact temperature dependence of Γ_{mag} is beyond the scope of this work, but we expect it to change as temperature reaches $T_{\text{gap}} = \hbar D/k_B \approx 0.14$ K. In addition, in this work we neglect the effect of electric field fluctuations (see Apeendix B.3 for further details). This is relevant for experiments that involve optical illumination and read-out of the electronic states [68].

Now, we study the longitudinal relaxation rate at low and high temperatures. In the lowtemperature limit we also investigate the effect of magnetic field on the longitudinal relaxation rate.

3.5 Discussion

3.5.1 Low-temperature limit

In this section we discuss the low-temperature limit (below 1 K) associated to the spin-lattice relaxation dynamics of the ground state of the NV⁻ center in diamond. For low temperatures, only one-phonon processes contribute to the transition rates. Therefore, we can deduce the spin-lattice dynamics from the quantum master equation by setting $\mathcal{L}_{2-\text{ph}}\hat{\rho} = 0$. From Eq. (3.45) we can find the dynamics of the spin populations $p_1 = \langle m_s = 1 | \hat{\rho} | m_s = 1 \rangle$, $p_2 = \langle m_s = 0 | \hat{\rho} | m_s = 0 \rangle$, and $p_3 = \langle m_s = -1 | \hat{\rho} | m_s = -1 \rangle$. For an arbitrary magnetic field B_0 along the z axis, using $\Gamma_{\text{mag}} = 0$, and considering only one-phonon processes, the equations at low temperatures are given by

$$\frac{\mathrm{d}p_1}{\mathrm{d}t} = -(\gamma_{+-} + \Omega_{+0}) p_1 + \Omega_{0+} p_2 + \gamma_{-+} p_3, \qquad (3.52)$$

$$\frac{\mathrm{d}p_2}{\mathrm{d}t} = -(\Omega_{0+} + \Omega_{0-}) p_2 + \Omega_{+0} p_1 + \Omega_{-0} p_3, \qquad (3.53)$$

$$\frac{\mathrm{d}p_3}{\mathrm{d}t} = -(\Omega_{0-} + \gamma_{-+}) p_3 + \gamma_{+-} p_1 + \Omega_{0-} p_2, \qquad (3.54)$$

where the direct relaxation rates between the spin states are given by $\gamma_{+-} = A_1(1 + n_1)$, $\gamma_{-+} = A_1n_1$, $\Omega_{+0} = A_2(1 + n_2)$, $\Omega_{0+} = A_2n_2$, $\Omega_{-0} = A_3(1 + n_3)$, and $\Omega_{0-} = A_3n_3$ (see Fig. 3.4), where $n_i = [\exp(\hbar\omega_i/k_BT) - 1]^{-1}$ the mean number of phonons at thermal equilibrium. Here, $\omega_1 = 2\gamma_s B_0$, $\omega_2 = D + \gamma_s B_0$, and $\omega_3 = D - \gamma_s B_0$ are the resonant frequencies associated with the spin energy levels. The A_i parameters are defined in Eqs. (3.25)-(3.27) and are estimated as a function of the magnetic field B_0 in the next section [see Eqs. (3.64)-(3.66)]. For experiments in quantum information processing and magnetometry these direct relaxation rates plays a fundamental role.

In the following we obtain the longitudinal relaxation rate for the physical observables $\langle S_z^2(t) \rangle$ and $\langle S_z(t) \rangle$ at different magnetic field regimes. However, this model can be used to determine any other physical observable, for instance, direct relaxation rates between spin states and their magnetic field and temperature dependence.

3.5.1.1 Zero magnetic field

At zero magnetic field $(B_0 = 0)$ and neglecting the effect of strain, the spin states $|m_s = 1\rangle$ and $|m_s = -1\rangle$ are degenerate (see Fig. 3.1). As a consequence, the emission and absorption rates associated with the spin transitions $|m_s = 0\rangle \leftrightarrow |m_s = 1\rangle$ and $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$ are equal.

Therefore, the system can be modeled as a simple two-level system with the degenerate excited states described by $|m_s = \pm 1\rangle$. In addition, the transition rate between $|m_s = \pm 1\rangle$ vanishes if we neglect the effect of electric field fluctuations [68]. In such scenario, the absorption and emission rates are given by $\Gamma_{\rm abs} = \Gamma_0 \bar{n}$ and $\Gamma_{\rm em} = \Gamma_0(\bar{n} + 1)$, respectively, where $\bar{n} = \left[\exp(\hbar D/k_B T) - 1\right]^{-1}$ is the mean number of phonons at the zero-field splitting



Figure 3.4: Direct relaxation rates induced by one-phonon processes. The spin populations associated with the spin states $|m_s = 0, \pm 1\rangle$ are modified by the absorption $(\gamma_{-+}, \Omega_{0-}, \Omega_{0+})$ and emission rates $(\gamma_{+-}, \Omega_{-0}, \Omega_{+0})$. For magnetic fields $\gamma_s B_0 > D$ ($B_0 > 1000$ G), the state $|m_s = -1\rangle$ is the lowest energy state and the role of Ω_{0-} and Ω_{-0} are exchanged.

frequency $D/2\pi = 2.87$ GHz. The parameter Γ_0 is obtained from Eqs. (3.26) and (3.27) for $B_0 = 0$ and is given by

$$\Gamma_0 = \frac{\Omega D^3 (\lambda_{0x'}^2 + \lambda_{0y'}^2)}{2\pi v_s^3 \omega_D}.$$
(3.55)

From Eqs. (3.52)-(3.54), we obtain

$$\frac{\mathrm{d}p_1}{\mathrm{d}t} = \Gamma_0(1+\bar{n})p_1 + \Gamma_0\bar{n}p_2, \qquad (3.56)$$

$$\frac{\mathrm{d}p_2}{\mathrm{d}t} = -2\Gamma_0 \bar{n}p_2 + \Gamma_0 (1+\bar{n})p_1 + \Gamma_0 (1+\bar{n})p_3, \qquad (3.57)$$

$$\frac{\mathrm{d}p_3}{\mathrm{d}t} = \Gamma_0(1+\bar{n})p_1 + \Gamma_0\bar{n}p_3.$$
(3.58)

Using $\langle S_z^2(t) \rangle = p_1(t) + p_3(t)$ and $p_1(t) + p_2(t) + p_3(t) = 1$ we obtain

$$\frac{\mathrm{d}\langle S_z^2(t)\rangle}{\mathrm{d}t} = -\Gamma_0(1+3\bar{n})\langle S_z^2(t)\rangle + 2\Gamma_0\bar{n}, \qquad (3.59)$$

$$\frac{\mathrm{d}p_2}{\mathrm{d}t} = -\Gamma_0(1+3\bar{n})p_2(t) + \Gamma_0(1+\bar{n}).$$
(3.60)

Using arbitrary initial conditions $p_i(0) = p_{i0}$ (i = 1, 2, 3), we have

$$\langle S_z^2(t) \rangle = \langle S_z^2(T) \rangle_{\text{st}} - (\langle S_z^2(T) \rangle_{\text{st}} - p_{10} - p_{30}) e^{-\Gamma_0(1+3\bar{n})t}, p_2(t) = (p_2(T))_{\text{st}} - ((p_2(T))_{\text{st}} - p_{20}) e^{-\Gamma_0(1+3\bar{n})t},$$
(3.61)

where the steady states are given by

$$\langle S_z^2(T) \rangle_{\text{st}} = \frac{2}{e^{\hbar D/k_B T} + 2}, \qquad (3.62)$$

$$(p_2(T))_{\rm st} = \frac{e^{\hbar D/k_B T}}{e^{\hbar D/k_B T} + 2}.$$
 (3.63)

Therefore, the phonon-induced spin relaxation rate associated with $\langle S_z^2(t) \rangle$ and $p_2(t)$ (ground state population) are given by $\Gamma_0(1+3\bar{n})$, where $\Gamma_0 = 3.14 \times 10^{-5} \text{ s}^{-1}$ [19]. This is consistent with the longitudinal relaxation rate recently measured and estimated by *ab initio* methods in Ref. [19] (see Fig. 3.2(a)). Using Eq. (3.55) and assuming $\lambda_{0x'} \approx \lambda_{0y'} \approx \lambda_{0x} \approx \lambda_{0y}$, we estimate $\lambda_{0x'}$ to be approximately 3.97 meV. With this approximation for the λ_0 factors and combining Eqs. (3.25)-(3.27) with Eq. (3.55), we can estimate the following magnetic field dependence for the one-phonon spin relaxation rates

$$A_1 \approx 2\Gamma_0 \left(\frac{2\gamma_s B_0}{D}\right)^3,$$
 (3.64)

$$A_2 \approx \Gamma_0 \left[\frac{(D + \gamma_s B_0)}{D} \right]^3, \qquad (3.65)$$

$$A_3 \approx \Gamma_0 \left[\frac{(D-\gamma_s B_0)}{D}\right]^3.$$
 (3.66)

Note that $\langle S_z(t) \rangle$ is zero as the states $|m_s = +1 \rangle$ and $|m_s = -1 \rangle$ are degenerate at zero magnetic field. In the next section we introduce the effect of low magnetic field on the longitudinal relaxation rate associated with $\langle S_z(t) \rangle$.



Figure 3.5: (a) Relaxation rate of $\langle S_z^2(t) \rangle$ at zero magnetic field. The symbols represent experimental spin relaxation rates measured at low temperatures (below 1 K) for different NV-samples [19]. The dotted lines represent the theoretical fit given by $1/T_1 = \Gamma_0(1 + 3\bar{n}) + \Gamma_{\text{mag}}$. We observe that at low temperatures, the relevant contribution comes from the emission of a phonon and the magnetic noise induced by the environment. (b) Two-dimensional parameter plot of the longitudinal relaxation rate of $\langle S_z(t) \rangle$ in logarithm scale at magnetic fields ranging from 0 to 1500 G, temperature ranging from 10 mK to 1 K, and $\Gamma_{\text{mag}} = 0$.

3.5.1.2 Low magnetic field

We define the limit of low magnetic fields when $\gamma_s B_0 \ll D$ so that $n(D + \gamma_s B_0) \approx n(D - \gamma_s B_0) \approx \bar{n}$. By considering one-phonon processes, we obtain the following set of equations

$$\frac{\mathrm{d}\langle S_{z}^{2}(t)\rangle}{\mathrm{d}t} = -\Gamma_{0}(1+3\bar{n})\langle S_{z}^{2}(t)\rangle + 3\epsilon\Gamma_{0}(1+\bar{n})\langle S_{z}(t)\rangle
+2\Gamma_{0}\bar{n}, \qquad (3.67)$$

$$\frac{\mathrm{d}\langle S_{z}(t)\rangle}{\mathrm{d}t} = -\left[\Gamma_{B}n_{B} + 3\epsilon\Gamma_{0}(1+3\bar{n})\right]\langle S_{z}^{2}(t)\rangle + 6\epsilon\Gamma_{0}\bar{n}
-\left[\Gamma_{B}(1+2n_{B}) + \Gamma_{0}(1+\bar{n})\right]\langle S_{z}(t)\rangle, \qquad (3.68)$$

where $\epsilon = \gamma_s B_0 / D \ll 1$ is a pertubative dimensionless parameter, $\Gamma_B \approx \Gamma_0 (2\gamma_s B_0 / D)^3$, and $n_B = [\exp(2\hbar\gamma_s B_0 / k_B T) - 1]^{-1}$ is the mean number of phonons at the resonant frequency $\omega_1 = 2\gamma_s B_0$. In addition, the mean number of phonons satisfies $n_B \gg \bar{n}$ due to the condition $\gamma_s B_0 \ll D$.

At low magnetic fields, the longitudinal relaxation rate associated with $\langle S_z(t) \rangle$ is given by

$$\frac{1}{T_1} \approx 2\Gamma_0(1+2\bar{n}) + \Gamma_B(1+2n_B).$$
(3.69)

The steady states satisfy the relation

$$\frac{\langle S_z^2(T) \rangle_{\text{st}}}{\langle S_z(T) \rangle_{\text{st}}} = \frac{\Gamma_0(1+\bar{n}) + \Gamma_B(1+2n_B)}{n_B \Gamma_B}.$$
(3.70)

In the next section we obtain the longitudinal relaxation rate associated with $\langle S_z(t) \rangle$ for arbitrary values of the magnetic field B_0 .

3.5.1.3 Arbitrary magnetic field values

At non-zero magnetic fields, the spin states $|m_s = -1\rangle$ and $|m_s = 1\rangle$ are split due to the Zeeman interaction (see Fig. 3.1). This implies that the system can be modeled as a dissipative three-level system consisting of the spin states $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$. From Eqs. (B.40)-(B.41), the dynamics for the longitudinal spin component is given by

$$\frac{\mathrm{d}^2 \langle S_z(t) \rangle}{\mathrm{d}t^2} + \frac{1}{T_1} \frac{\mathrm{d} \langle S_z(t) \rangle}{\mathrm{d}t} + \omega^2 \langle S_z(t) \rangle = A_0, \qquad (3.71)$$

where the parameters are given by

$$\frac{1}{T_1} = A_1(1+2n_1) + A_2(1+2n_2) + A_3(1+2n_3),$$
(3.72)

$$\omega^2 = \frac{1}{2} \left\{ A_1[A_3(1+n_3) - A_2(1+n_2)] - A_2^2 n_2(3+n_2) - A_3^2 n_3(3+n_3) + A_2 A_3(2+n_2+n_3+4n_2n_3) \right\},$$
(3.72)

$$A_0 = \frac{1}{2} \left[2A_1(A_2+A_3) + A_2^2(1+n_2)^2 + 2A_2 A_3(n_2-n_3) - A_3^2(1+n_3)^2 \right].$$
(3.73)

We observe that the relaxation rate $1/T_1$ is given by the total one-phonon spin relaxation rate given in Eq. (3.21). The general solution is that of a driven damped harmonic oscillator, where the longitudinal relaxation rate is given by

$$\frac{1}{T_1} \approx \frac{\Gamma_0}{D^3} \omega_1^3 (1+2n_1) + \frac{\Gamma_0}{D^3} \left[\omega_2^3 (1+2n_2) + \omega_3^3 (1+2n_3) \right], \qquad (3.74)$$

where $\omega_1 = 2\gamma_s B_0$, $\omega_2 = D + \gamma_s B_0$, and $\omega_3 = D - \gamma_s B_0$. In this approximation we have assumed that $\lambda_{0x'}^2 + \lambda_{0y'}^2 \approx \lambda_{0x}^2 + \lambda_{0y}^2$ (see Eqs. (3.25)-(3.27)). At low magnetic fields, $\gamma_s B_0 \ll D$, we recover the previous result given in Eq. (3.69). Figure. 3.5(b) shows the expected longitudinal relaxation rate at low temperatures for magnetic fields ranging from 0 to 1500 G. As the magnetic field increases, the longitudinal relaxation rate increases as well.

3.5.2 High-temperature limit

In this section, we consider higher temperatures for which the relaxation rate is dominated by quasi-localized phonons and two-phonon processes, usually for temperatures higher than 100 K. By solving the quantum master equation we obtain that the longitudinal spin relaxation rate of $\langle S_z(t) \rangle$ is approximately given by (see Appendix B.2)

$$\frac{1}{T_1} \approx \Gamma_{\text{mag}} + \Gamma_{1-\text{ph}} + \Gamma_{\text{loc}} + \Gamma_{2-\text{ph}},$$

$$= \Gamma_{\text{mag}} + \sum_{i=1}^{3} A_i \operatorname{coth}\left(\frac{\hbar\omega_i}{k_B T}\right) + \frac{A_4}{e^{\hbar\omega_{\text{loc}}/k_B T} - 1} + A_5 T^5 + A_6 T^6 + A_7 T^7. \quad (3.75)$$

In the above equation, $\omega_1 = 2\gamma_s B_0$, $\omega_2 = D + \gamma_s B_0$, and $\omega_3 = D - \gamma_s B_0$ are the resonant frequencies of the ground triplet states of the NV⁻ center in diamond in the presence of the static magnetic field B_0 along the z axis, and T is the temperature. Similar formulas for the longitudinal relaxation rate were obtained phenomenologically in order to fit the experimental data for different NV⁻ center samples [15, 18]. However, our work formally incorporates the phonon-induced spin relaxation rates by including the contribution of stochastic magnetic noise, direct one-phonon processes, strong interactions with quasi-localized phonon modes, and the effect of the acoustic phonons to first and second order. This is crucially different from previous works [15, 17–19], but validates, both high and low-temperature experimental observations in which electric field fluctuations is not present (see Fig 3.6). Our model can be useful to understand the temperature dependence of the longitudinal spin relaxation rate of other color centers in diamond. For instance, the observed T^7 temperature dependence of the neutral silicon-vacancy color center in diamond at high temperatures [73].

Using experimental data from Refs. [18, 19], we can fit our free parameter Γ_{mag} in order to model the magnetic noise induced by magnetic impurities in samples with different NV⁻ concentrations. On the other hand, we consider that the A_i parameters, which are related to the spin-phonon coupling constants, are not sample-dependent. The A_1 , A_2 , and A_3 parameters can be found by fitting to the experimental data at low temperature (below 1 K) [19] as described in Section 3.5.1 The parameters A_4 , A_5 , A_6 , A_7 , and ω_{loc} can be found by fitting to the experimental data for temperatures ranging from 4 K to 475 K [18].

Figure 3.6 shows the temperature dependence of the longitudinal relaxation rate for different samples at high temperatures. For the two-phonon processes we obtain $A_4 = 1.96(5) \times 10^{-3}$ s⁻¹, $A_5 = 2.06(5) \times 10^{-11}$ s⁻¹ K⁻⁵, $A_6 = 9.11(2) \times 10^{-16}$ s⁻¹ K⁻⁶, $A_7 = 2.55(3) \times 10^{-20}$ s⁻¹



Figure 3.6: The symbols represent experimental spin relaxation rates measured for different NV⁻ samples in the temperature regime 4-475 K [15, 17, 18]. The dotted lines are the theoretical fit of the longitudinal spin relaxation rate $1/T_1$ given in Eq. (3.75) for different values of the magnetic noise Γ_{mag} . The temperature at which the contribution from quasi-localized phonons and second-order phonon processes dominates is sample dependent.

 K^{-7} , and $\omega_{loc} = 73(5)$ meV. We observe a good agreement of our results with the experiments performed at high temperatures [15, 17, 18]. The largest contribution at high temperatures, 300 K < T < 500 K, is due to the second-order scattering (see Table I and Fig. 4.3) usually known as the second-order Raman scattering [20] which leads to the observed $1/T_1 \propto T^5$ temperature dependence [15, 17, 18] due to the linear spin-phonon coupling to second-order. Between 50 K < T < 200 K the main contribution arises from Orbach-type processes [21] which can be attributed to a strong spin-phonon interaction with a quasi-localized phonon mode with energy \approx 73 meV [18]. On the other hand, the magnetic noise rate Γ_{mag} is dominant in samples with a high NV concentration (red, green and black dashed curves in Fig. 3.6). Therefore, the effect of one-phonon processes (emission and absorption) can be neglected if the magnetic noise is larger than the one-phonon spin relaxation rates. We note that we are not considering other sources of relaxation such as fluctuating electric fields, in which case a relaxation with an inverse magnetic field dependence is expected [68].

3.6 Conclusions

In summary, we have presented a microscopic model for estimating the effect of temperature on the longitudinal relaxation rate $1/T_1$ of NV⁻ centers in diamond. In this model, we introduced a general spin-phonon interaction between the ground-state spin degree of freedom and lattice vibrations. We estimated the value of the phonon-induced spin relaxation rates by applying the Fermi golden rule to first and second order. The microscopic spin-lattice relaxation dynamics was derived from the quantum master equation for the reduced spin density operator. In the relaxation dynamics, we included the effect of a phononic bath in thermal equilibrium and dilute magnetic impurities phenomenologically modeled. Acoustic and quasi-localized phonons were included in the phonon processes in order to model a more general temperature dependence of the longitudinal relaxation rate.

At low temperatures, we provided a set of microscopic equations in order to study the spinlattice relaxation dynamics induced by one-phonon processes. In this limit and considering zero magnetic fields, $B_0 = 0$, we analytically obtained the relaxation rate $1/T_1 = \Gamma_0(1 + 3\bar{n})$ associated with $\langle S_z^2(t) \rangle$, where Γ_0 depends on microscopic constants. This relaxation rate is in agreement with recent experiments and *ab initio* calculations [18], as well as theoretical calculations [74]. In addition, for low magnetic fields, $\gamma_s B_0 \ll D$, we obtained the relaxation rate $1/T_1 = 2\Gamma_0(1 + 2\bar{n}) + \Gamma_B(1 + 2n_B)$ associated with $\langle S_z(t) \rangle$, where Γ_B scales as B_0^3 .

At high temperatures, we have modeled multiple two-phonon processes where the fitted relaxation rate associated to $\langle S_z(t) \rangle$ is in agreement with experimental observations [15, 17, 18]. We included both linear and bi-linear lattice interactions that lead to several different temperature scaling in a spin-boson model. In particular, for NV-centers in diamond the dominant temperature scaling is T^5 for temperatures larger than 200 K. Moreover, our model will be useful to evaluate the contribution of second-order phonon processes that give different temperature scaling (T^s, T^{s+1}, T^{s+2}) for other spin-boson systems. The power of the temperature $s = 4\nu + 2d - 3$ depends on the dimension of the system and the symmetry of the lattice, where d = 3 and $\nu = 1/2$ for the NV⁻ center.
Chapter 4

Phononic dynamical suppression of the electron spin resonance of $E \otimes e \otimes SU(2)$ Jahn-Teller systems

In this chapter, we characterize the phononic dynamical suppression of the electron spin resonance (ESR) response of $E \otimes e \otimes SU(2)$ Jahn-Teller systems with residual electronic spin-1/2. We take into account the linear electron-phonon coupling between the orbital and lattice degrees of freedom, the spin-orbit, and Zeeman interactions, and the linear response of the system to oscillating magnetic fields. Using the Markovian quantum master equation we characterize the spin-relaxation rate and the contrast of the ESR response as a function of temperature and several other parameters of the system. The presented model provides an analytical explanation for the absence of ESR contrast on spin-1/2 systems at high temperatures such as the neutral nitrogen-vacancy and negatively charged silicon-vacancy color centers in diamond, as well as for characterizing new systems.

4.1 Introduction

Since its discovery [75] and for more than seventy years, electron paramagnetic resonance (EPR) or electron spin resonance (ESR) has been extensively used to study molecular systems [76], quantum dots [77], metal complexes [78], organic radicals [79] or defects in solid-state systems [80]. Commonly, ESR consists of applying a constant frequency microwave

field and a magnetic field is swept across spin-flip resonance transitions. Crucial information has been obtained in several biochemical problems [81], on Hyperfine interactions with high resolution [82], on magnetic ions in metals [83], to name a few. The ESR absorption spectrum and the dispersion lines contain important information about the system and effects such as anisotropy of gyromagnetic factors [84], Ham reduction factors [85, 86], spin relaxation rates [87] can be obtained from the analysis of the ESR absorption spectrum.

Unfortunately, in many systems were a paramagnetic behaviour is expected, no ESR absorption is detected. Specially on those systems that are strongly coupled to vibrations, the ESR response is not observed for a wide range of temperatures. Although many works have been devoted to phenomenologically describe the ESR response, still few of them deal with microscopic aspects of the electron-phonon coupling. Several authors have addressed the problem of modeling the ESR linear response out-of-equilibrium systems [22–24]. Historically, the linear response theory associated with irreversible processes was introduced in order to give a more satisfactory description of the magnetic resonance phenomenon [24]. However, temperature effects on the linear response are still an open problem in complex solid-state systems. In particular, the thermal activation of environment-assisted dissipative processes due to electron-phonon, spin-spin, and spin-orbit interactions.

In this work we focus on a theoretical description for spin 1/2 systems that present degenerate orbital states that can couple to vibrations. Such system can be, for example, the neutral nitrogen-vacancy centre and the negatively charged silicon-vacancy centre in diamond. In both cases, the ground state configuration consists of a double degenerate orbital state with a single electron, therefore having an electronic spin 1/2. In addition, both systems can vibrate in two degenerate modes. In this scenario, and given a non-zero electron-phonon coupling, the electron and the lattice can exchange orbital angular momentum. From a theoretical point of view, these systems belong to a class of systems that can be described as a $E \otimes e$ Jahn-Teller (JT) system with an electronic spin S = 1/2. Therefore, as a first theoretical step, it is instructive to model the linear response of a $E \otimes e \otimes SU(2)$ JT system, i.e., a system composed by two orbital degenerates E-states, two degenerate e-phonon modes, and an internal electronic spin S = 1/2.

We consider the Zeeman effect induced by an arbitrary static magnetic field, the spin-orbit coupling, and the electron-phonon interaction between the orbital states and the lattice phonons. Using this model we obtain an analytical solution for the ESR absorption spectrum when an oscillating magnetic field along the x axis is applied. We focus the attention on

the derivation of the linear response function by solving the Markovian dynamics associated to physical observables. In addition, we include the effect of acoustic phonons in order to model temperature effects on the ESR absorption spectrum by means of the one-phonon processes. In Sec. 4.2, we introduce the Hamiltonian associated to the $E \otimes e \otimes SU(2)$ JT system. Section 4.3 introduces the eigenstates associated with the spin and orbital degrees of freedom. In that section, we introduce the quantization of *e*-phonons. In Section 4.4 we use the linear response theory and the Markovian quantum master equation for physical observables in order to find the ESR absorption spectrum. In Section 4.6 we discuss the limit of high spin-orbit coupling and the effect of temperature on the ESR absorption spectrum.

4.2 Hamiltonian of the system

Consider a $E \otimes e \otimes SU(2)$ system with a doubly degenerate orbital *E*-states $|X\rangle$ and $|Y\rangle$ coupled to *e*-phonon modes and a residual electronic spin S = 1/2 with states $|\uparrow\rangle = |m_s = 1/2\rangle$ and $|\downarrow\rangle = |m_s = -1/2\rangle$. We take into account that orbital and spin degrees of freedom are coupled via spin-orbit interaction, and a linear electron-phonon interaction between the orbital states and *e*-phonon modes. Including a strong static magnetic field \vec{B} in an arbitrary direction and a weak oscillating magnetic field $\vec{B}(t)$ aligned with the *x*-axis, the Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{\rm ph} + \hat{H}_{\rm e-ph} + \hat{V}(t),$$
(4.1)

where

$$\hat{H}_0 = \hat{H}_e + \hat{H}_{\rm so} + \hat{H}_{\rm z},\tag{4.2}$$

is the Hamiltonian associated with the orbital and spin degrees of freedom. The first term in Eq. (4.2) is the electronic Hamiltonian ($\hbar = 1$)

$$\hat{H}_e = E_0 \left(\mathbb{1}_e \otimes \mathbb{1}_s \right), \tag{4.3}$$

where E_0 is the energy of the degenerate states $|X\rangle$ and $|Y\rangle$. Here, $\mathbb{1}_e = |X\rangle \langle X| + |Y\rangle \langle Y|$ and $\mathbb{1}_s = |\uparrow\rangle \langle\uparrow| + |\downarrow\rangle \langle\downarrow|$ are the identity operators for the orbital and spin sub-spaces, respectively. The second term in Eq. (4.2) describes the spin-orbit interaction ($\hbar = 1$)

$$\hat{H}_{\rm so} = -\lambda(\vec{L}\cdot\vec{S}) = -\frac{1}{2}\lambda\left(\hat{\sigma}_y\otimes\hat{s}_z\right),\tag{4.4}$$

where $\lambda > 0$ is the spin-orbit coupling, \vec{L} is the orbital angular momentum operator, and $\vec{S} = \frac{1}{2}(\hat{s}_x, \hat{s}_y, \hat{s}_z)$ is the spin vector operator for S = 1/2 ($\hbar = 1$). The spin Pauli matrices are defined as

$$\hat{s}_x = |\uparrow\rangle \langle \downarrow| + |\downarrow\rangle \langle \uparrow|, \qquad (4.5)$$

$$\hat{s}_y = -i |\uparrow\rangle \langle \downarrow| + i |\downarrow\rangle \langle\uparrow|, \qquad (4.6)$$

$$\hat{s}_z = |\uparrow\rangle \langle\uparrow| - |\downarrow\rangle \langle\downarrow|, \qquad (4.7)$$

and satisfy the commutation relation $[\hat{s}_i, \hat{s}_j] = 2i\epsilon_{ijk}\hat{s}_k$. On the other hand, the operators for the orbital states are given by

$$\hat{\sigma}_x = |X\rangle \langle Y| + |Y\rangle \langle X|, \qquad (4.8)$$

$$\hat{\sigma}_{y} = -i |X\rangle \langle Y| + i |Y\rangle \langle X|, \qquad (4.9)$$

$$\hat{\sigma}_{z} = |X\rangle \langle X| - |Y\rangle \langle Y|, \qquad (4.10)$$

which satisfy the relation $[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\epsilon_{ijk}\hat{\sigma}_k$. The third term in Eq. (4.2) is the Zeeman Hamiltonian associated with the static magnetic field $\vec{B} = (B_x, B_y, B_z)$

$$\hat{H}_{z} = \left(\gamma_{s}\vec{S} + \gamma_{L}\vec{L}\right) \cdot \vec{B}$$

$$= \frac{1}{2} \left[\gamma_{s} \sum_{i=x,y,z} \left(\mathbb{1}_{e} \otimes \hat{s}_{i}\right) + \gamma_{L} \left(\hat{\sigma}_{y} \otimes \mathbb{1}_{s}\right)\right], \qquad (4.11)$$

where $\gamma_s = \mu_B g_s/\hbar$ and $\gamma_L = \mu_B g_L/\hbar$ are the spin and orbital gyromagnetic constants, respectively, being μ_B the Bohr magneton and \hbar the Planck constant. Here, $g_s \approx 2$ and $g_L = 1$ are the Landé g-factors. The second term in Eq. (4.1) is the phonon Hamiltonian associated with the e-phonon modes, and is given by [88]

$$\hat{H}_{\rm ph} = \sum_{k} \left[\frac{1}{2\mu} \left(\hat{P}_{k,x}^2 + \hat{P}_{k,y}^2 \right) + \frac{1}{2} \omega_k^2 \left(\hat{Q}_{k,x}^2 + \hat{Q}_{k,y}^2 \right) \right], \tag{4.12}$$

where μ is the reduced mass and ω_k is the phonon frequencies of the k phonon mode. The linear momentum and position operators satisfy the fundamental commutation relation $[Q_{k,i}, P_{k',j}] = i\hbar \delta_{ij} \delta_{k,k'}$. The linear electron-phonon interaction between the orbital states



Figure 4.1: Schematic representation for our $E \otimes e \otimes SU(2)$ JT system perturbed by an oscillating magnetic field. The dashed box enclosed the usual $E \otimes e$ JT system which is coupled with the spin states via the spin-orbit coupling constant λ . The static magnetic field interacts with the orbital and spin degrees of freedom, while the oscillating magnetic field perturbs the spin states.

and e-phonon modes is given by [88, 89]

$$\hat{H}_{\text{e-ph}} = \sum_{k} \left[F_k (\hat{Q}_{k,x} \hat{\sigma}_z - \hat{Q}_{k,y} \hat{\sigma}_x) \right] \otimes \mathbb{1}_s, \qquad (4.13)$$

where

$$F_{k} = \langle X | \left(\frac{\partial V(\{\mathbf{Q}\}, \mathbf{r})}{\partial Q_{k,x}} \right) \Big|_{\{\mathbf{Q}_{0}\}} | X \rangle, \qquad (4.14)$$

is the linear vibronic coupling constant for each phonon mode k [88]. Here, $V({\mathbf{Q}}, \mathbf{r})$ is the Coulomb interaction between the electronic distribution and the nuclei located at the set of coordinates ${\mathbf{Q}}$, and ${\mathbf{Q}}_0$ determines the nuclear equilibrium positions of the system.

Finally, the perturbation associated with the weak oscillating magnetic field $\vec{B}(t) = B_1 \cos \omega t$ is given by the following Hamiltonian

$$\hat{V}(t) = \frac{1}{2} B_1 \gamma_s \left(\mathbb{1}_e \otimes \hat{s}_x \right) \cos \omega t.$$
(4.15)

In our model, the condition of weak oscillating magnetic field means that $|B_1| \ll \|\vec{B}\|$, and therefore, we solve the dynamics of the system in this particular limit. Figure 4.1 shows an

schematic representation for our $E \otimes e \otimes SU(2)$ JT system including the *e*-phonon modes, the orbital *E*-states, the spin degree of freedom, the static and the oscillating magnetic fields.

4.3 Electron-spin states and quantization of phonons

In this section we introduce the eigenvalues and eigenstates of Hamiltonian \hat{H}_0 given in Eq. (4.2). Furthermore, we formally introduce the quantized form of the electron-phonon Hamiltonian given in Eq. (4.13) using the eigenstates of \hat{H}_0 and the quantization of *e*-phonons. Writing the magnetic field in spherical coordinates, i.e., $\vec{B} = (B \cos \phi \sin \theta, B \sin \phi \sin \theta, B \cos \theta)$, we find that the eigenvalues of \hat{H}_0 are

$$E_1 = E_0 - \frac{1}{2} (\gamma_L B \cos \theta + \sqrt{\gamma_s^2 B^2 + 2\gamma_s \lambda B \cos \theta + \lambda^2}), \qquad (4.16)$$

$$E_2 = E_0 + \frac{1}{2} (\gamma_L B \cos \theta - \sqrt{\gamma_s^2 B^2 - 2\gamma_s \lambda B \cos \theta + \lambda^2}), \qquad (4.17)$$

$$E_3 = E_0 + \frac{1}{2} (\gamma_L B \cos \theta + \sqrt{\gamma_s^2 B^2 - 2\gamma_s \lambda B \cos \theta + \lambda^2}), \qquad (4.18)$$

$$E_4 = E_0 - \frac{1}{2} (\gamma_L B \cos \theta - \sqrt{\gamma_s^2 B^2 + 2\gamma_s \lambda B \cos \theta + \lambda^2}).$$
(4.19)

where $B = \|\vec{B}\|$ is the magnitude of the static magnetic field, $\theta = \cos^{-1} (B_z/B)$ is the polar angle, being B_z the z component of the magnetic field along the symmetry axis of the system. The eigenstates of \hat{H}_0 can be written as

$$|i\rangle = \sum_{j=1}^{4} M_{ij} |\varphi_j\rangle, \qquad i = 1, 2, 3, 4,$$
 (4.20)

where $|\varphi_1\rangle = |X,\uparrow\rangle$, $|\varphi_2\rangle = |X,\downarrow\rangle$, $|\varphi_3\rangle = |Y,\uparrow\rangle$, and $|\varphi_4\rangle = |Y,\downarrow\rangle$ are product states that describes the orbital and spin states of the system when the interaction between them in not present. Because of Zeeman effect and spin-orbit coupling the matrix elements M_{ij} given in Eq. (4.20) depend on the magnetic field components and the spin-orbit coupling constant λ . The matrix representation of M_{ij} is given by

$$M = \begin{pmatrix} i\alpha_{+}/N_{+} & i/N_{+} & \alpha_{+}/N_{+} & 1/N_{+} \\ i\beta_{+}/M_{+} & i/M_{+} & \beta_{+}/M_{+} & 1/M_{+} \\ i\beta_{-}/M_{-} & -i/M_{-} & -\beta_{-}/M_{-} & 1/M_{-} \\ i\alpha_{-}/N_{-} & -i/N_{-} & -\alpha_{-}/N_{-} & 1/N_{-} \end{pmatrix},$$
(4.21)



Figure 4.2: Energy diagram of the eigenstates of \hat{H}_0 as a function of the polar angle θ and the magnitude of the magnetic field $\vec{B} = (B \cos \phi \sin \theta, B \sin \phi \sin \theta, B \cos \theta)$. The filled coloured areas represent the possible values of the energies E_i for a range of the polar angle θ . The energies are plotted for (a) values between $0 \le \theta \le \pi/2$ and (b) values between $\pi/2 \le \theta \le \pi$. The transitions between the states $|i\rangle$ induced by phonons and the oscillating magnetic field are illustrated with black arrows and the capital letters A, B, C, D, E, and F.

where $\alpha_{\pm} = e^{-i\phi} (\lambda \pm \gamma_s B \cos \theta - \Delta_{\pm})/(\gamma_s B \sin \theta)$, $\beta \pm = e^{-i\phi} (\lambda \pm \gamma_s B \cos \theta + \Delta_{\pm})/(\gamma_s B \sin \theta)$, $N_{\pm} = \sqrt{2 + 2|\alpha_{\pm}|^2}$, $M_{\pm} = \sqrt{2 + 2|\beta_{\pm}|^2}$, and $\Delta_{\pm} = \sqrt{\gamma_s^2 B^2 \pm 2\gamma_s \lambda B \cos \theta + \lambda^2}$). The exact solution for the eigenstates $|i\rangle$ given in Eq. (4.20) is valid for arbitrary magnetic fields, except at the singularity point B = 0.

At zero magnetic field, $\vec{B} = \vec{0}$, we have that $\{|1\rangle, |2\rangle\}$ is the ground state with energy $E_0 - \lambda/2$, while $\{|3\rangle, |4\rangle\}$ is the excited state with energy $E_0 + \lambda/2$. At non-zero magnetic fields, $\vec{B} \neq \vec{0}$, the ground and excited states are splitted according to Eqs. (4.16)-(4.19). Interestingly, we can observe that the energy levels E_i of the Hamiltonian \hat{H}_0 only depends on the magnitude B and the polar angle θ . Figure 4.2 shows the eigenvalues E_i as a function of the magnitude of the external magnetic field and the polar angle.

Now, we introduce the quantization of the *e*-phonon modes as follow

$$\hat{Q}_{k,x} = q_{0,k} \left(\hat{a}_k + \hat{a}_k^{\dagger} \right), \quad \hat{Q}_{k,y} = q_{0,k} \left(\hat{b}_k + \hat{b}_k^{\dagger} \right),$$
(4.22)

where $q_{0,k} = \sqrt{\hbar/2\mu\omega_k}$ is the mechanical size of the zero-point oscillation, \hbar is the Planck constant. Here, \hat{a}_k (b_k) and \hat{a}_k^{\dagger} (\hat{b}_k^{\dagger}) are the boson annihilation and creation operators, respectively satisfying $[\hat{a}_k, \hat{a}_{k'}^{\dagger}] = \delta_{k,k'}$ and $[\hat{b}_k, \hat{b}_{k'}^{\dagger}] = \delta_{k,k'}$. The boson operators \hat{a} and \hat{b} commutes between them because they are associated with independent coordinates. Using the eigenstates of \hat{H}_0 the linear electron-phonon Hamiltonian can be written as

$$\hat{H}_{\text{e-ph}} = \sum_{i,j,k} \left[\lambda^a_{ij,k} (\hat{a}_k + \hat{a}^{\dagger}_k) - \lambda^b_{ij,k} (\hat{b}_k + \hat{b}^{\dagger}_k) \right] |i\rangle \langle j|, \qquad (4.23)$$

where $|i\rangle$, $|j\rangle$ are the eigenstates of \hat{H}_0 (i, j = 1, 2, 3, 4), $\lambda^a_{ij,k}$ and $\lambda^b_{ij,k}$ are the electronphonon coupling constants given by

$$\lambda_{ij,k}^{a} = F_{k} \sqrt{\frac{\hbar}{2\mu\omega_{k}}} \alpha_{ij}^{a}, \quad \lambda_{ij,k}^{b} = F_{k} \sqrt{\frac{\hbar}{2\mu\omega_{k}}} \alpha_{ij}^{b}, \qquad (4.24)$$

where $\alpha_{ij}^a = (A_i A_j^* + B_i B_j^* + C_i C_j^* + D_i D_j^*)$ and $\alpha_{ij}^b = (A_i C_j^* + A_j^* C_i + B_i D_j^* + B_j^* D_i)$ are the mixing parameters, F_k is the vibronic coupling constant given in Eq. (4.14), μ is the reduced mass, ω_k are the phonon frequencies, and $A_i = (M^{-1})_{1,i}$, $B_i = (M^{-1})_{2,i}$, $C_i = (M^{-1})_{3,i}$, $D_i = (M^{-1})_{4,i}$ are the column elements of the inverse of the matrix M defined in Eq. (4.21).

Similarly, in the basis spawned by the eigenstates of \hat{H}_0 the perturbation associated with the oscillating magnetic field can be written as

$$\hat{V}(t) = \sum_{i,j} g_{ij} |i\rangle \langle j| \cos \omega t = \hat{A} \cos \omega t, \quad i, j = 1, 2, 3, 4,$$
(4.25)

where $|i\rangle$ are the eigenstates of \hat{H}_0 , ω is the frequency of the external perturbation, and

$$\hat{A} = \sum_{i,j} g_{ij} |i\rangle \langle j|, \quad i, j = 1, 2, 3, 4,$$
(4.26)

is the perturbed observable when the oscillating magnetic field aligned with the x axis is applied. The coupling constants associated with the oscillating magnetic field are given by

$$g_{ij} = \frac{1}{2} \gamma_s B_1 \left(A_i B_j^* + A_j^* B_i + C_i D_j^* + C_j^* D_i \right).$$
(4.27)

The couplings constants g_{ij} physically describe the probability amplitudes associated with the transitions $|i\rangle \rightarrow |j\rangle$ when the perturbation is activated, i.e., $g_{ij} = \langle i | \hat{A} | j \rangle$. From Eq. (4.27) we can observe that $g_{ji} = g_{ij}^*$ and $g_{ii} \in \mathbb{R}$. In addition, these coupling constants depends on the matrix elements of M (Eq. (4.21)), and therefore, has a non-trivial dependence in terms of the magnitude of the static magnetic field B and its orientation θ , as well as, of the value of the spin-orbit coupling constant λ .

For static magnetic fields aligned with the z axis the eigenstates of the system are given by $|1\rangle = |e_-, \downarrow\rangle, |2\rangle = |e_+, \uparrow\rangle, |3\rangle = |e_+, \downarrow\rangle, \text{ and } |4\rangle = |e_-, \uparrow\rangle, \text{ where } |e_{\pm}\rangle = (|X\rangle \pm i |Y\rangle)/\sqrt{2}$ are the eigenvectors of the angular momentum operator $\hat{L}_z = \hbar \hat{\sigma}_y$. In this basis, the perturbation can be written as $\hat{V}(t) = (B_1 \gamma_s)/2(\hat{S}_+ + \hat{S}_-) \cos \omega t$, where $\hat{S}_+ = |2\rangle \langle 3| + |4\rangle \langle 1|$ and $\hat{S}_- = |3\rangle \langle 2| + |1\rangle \langle 4|$ are the spin raising and lowering operators, respectively. Therefore, for magnetic fields of the form $\hat{B} = B_z \hat{z}$ the allowed transitions induced by the oscillating magnetic field are $|1\rangle \leftrightarrow |4\rangle$ and $|2\rangle \leftrightarrow |3\rangle$ only. If the static magnetic field has an arbitrary direction we can induce all possible transitions between the eigenstates $|i\rangle$ of the system when the oscillating magnetic field is applied. This is crucially different from the allowed transitions for static magnetic fields aligned with the z axis.

In the next Section we introduce to the ESR absorption spectrum by calculating the dynamical susceptibility of the system. In addition, we introduce to the Markovian quantum master equation in order to analytically solve the linear response of our $e \otimes E \otimes SU(2)$ JT system.

4.4 Linear response theory and lattice effects

Now, we evaluate the ESR absorption spectrum using the linear response theory. Physically, the oscillating magnetic field drives the system from its equilibrium state. The response of the system can be theoretically described using the linear response theory [31, 90]. In particular, we use the Kubo formula in the weak coupling limit, i.e., when $|B_1| \ll \|\vec{B}\|$. First, we introduce the dynamical susceptibility $\chi(\omega)$ as follow [90]

$$\chi(\omega) = \int_0^\infty e^{i\omega\tau} R(t) \, dt = \chi'(\omega) + i\chi''(\omega), \qquad (4.28)$$

where $\chi'(\omega)$ and $\chi''(\omega)$ are the real and imaginary parts of the dynamical susceptibility. The function $R(\tau)$ is known as the linear response function and is defined as [90]

$$R(t) = i\Theta(t) \left\langle \left[\hat{A}(t), \hat{A}(0) \right] \right\rangle, \qquad (4.29)$$

where $\Theta(t)$ is the Heaviside function and the operator $\hat{A}(\tau)$ is $(\hbar = 1)$

$$\hat{A}(t) = e^{-i\hat{H}_{\text{tot}}t}\hat{A}e^{i\hat{H}_{\text{tot}}t}, \quad \hat{A} = \sum_{i,j} g_{ij} \left|i\right\rangle \left\langle j\right|, \qquad (4.30)$$

where $\hat{H}_{\text{tot}} = \hat{H}_0 + \hat{H}_{\text{ph}} + \hat{H}_{\text{e-ph}}$ is the total Hamiltonian of our $e \otimes E \otimes \text{SU}(2)$ JT system. The average given in Eq. (4.29) is a thermal average given by $\langle \hat{O} \rangle = \text{Tr}(\hat{O}e^{-\beta\hat{H}_{\text{tot}}})/Z$, where $Z = \text{Tr}(e^{-\beta\hat{H}_{\text{tot}}})$ is the partition function, $\beta = 1/(k_B T)$, k_B is the Boltzmann constant and T is the temperature. Temperature plays a fundamental role in solid-state system because of the activation of different dissipative processes. In our case, the presence of *e*-phonons and its interaction with the orbital states introduces a relaxation dynamics between the eigenstates of the system. Such phonon-induced relaxation rates will be described in the next section by means of the Fermi golden rule transitions.

During the relaxation dynamics of the orbital and spin states, phonons and magnetic impurities are important. In the first case, the phonon-induced relaxation dynamics can be formally introduced using the quantized version of the electron-phonon Hamiltonian given in Eq. (4.23). On the other hand, we phenomenologically introduce the effect of magnetic impurities. A more detailed description of the effect of magnetic impurities needs to consider the interaction between the spin degree of freedom and a spin bath. In this work, we introduce the spin bath as a dissipatice term in the quantum master equation by considering an stochastic noise. Using these approximations, the time evolution of the perturbed physical observable $\hat{A}(t)$ can be found by solving the following Markovian quantum master equation $(\hbar = 1)$ [91]

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{A}(t) = i[\hat{H}_0, \hat{A}(t)] + \mathcal{L}_{\mathrm{ph}}\hat{A}(t) + \mathcal{L}_{\mathrm{mag}}\hat{A}(t), \qquad (4.31)$$

where the first term describes the free dynamics induced by Hamiltonian \hat{H}_0 [Eq. (4.2)], while the last two terms describes the dissipative dynamics induced by phonons and magnetic impurities. The Lindblad superoperator associated with phonons is given by

$$\mathcal{L}_{\rm ph}\hat{A}(t) = \sum_{i \neq j} \Gamma_{ij} \mathcal{D}[\hat{\pi}_{ij}] \hat{A}(t), \quad i, j = 1, 2, 3, 4,$$
(4.32)

where $\hat{\pi}_{ij} = |i\rangle \langle j|$ is an operator, being $|i\rangle$ and $|j\rangle$ the eigenstates of \hat{H}_0 . Here, Γ_{ij} is the onephonon relaxation rate associated with the transition $|i\rangle \rightarrow |j\rangle$ (with $i \neq j$). The operator $\mathcal{D}[\hat{O}]\hat{A}$ is defined as

$$\mathcal{D}[\hat{O}]\hat{A} = 2\hat{O}\hat{A}\hat{O}^{\dagger} - \frac{1}{2}\{\hat{O}^{\dagger}\hat{O}, \hat{A}\},$$
(4.33)

where $\{\hat{B}, \hat{C}\} = \hat{B}\hat{C} + \hat{C}\hat{B}$ is the anti-commutator. The phenomenological dynamics induced by magnetic impurities is modeled using the the following Lindblad superoperator [72]

$$\mathcal{L}_{\text{mag}}\hat{A}(t) = -\frac{1}{4}\Gamma_{\text{mag}}\left[3\hat{A}(t) - \sum_{i=x,y,z} \left(\mathbb{1}_e \otimes \hat{s}_i\right)\hat{A}(t)\right],\tag{4.34}$$

where Γ_{mag} is the magnetic relaxation rate induced by an isotropic white magnetic noise, $\mathbb{1}_e = |X\rangle \langle X| + |Y\rangle \langle Y|$ is the identity operator for the orbital states, and \hat{s}_i are the spin operators given in Eqs. (4.5)-(4.7).

Now, we define the ESR absorption spectrum $I(\omega)$ as follow

$$I(\omega) \equiv \chi''(\omega) = \operatorname{Im}\left(\int_0^\infty e^{i\omega t} R(t) \, dt\right),\tag{4.35}$$

where R(t) is the linear response function of the system given in Eq. (4.29). By solving Eq. (4.31) for the operator $\hat{A}(t) = \sum_{ij} g_{ij} |i\rangle \langle j|$ and using this result to calculate the linear response function R(t) we can obtain the following absorption spectrum

$$I(\omega) = \sum_{i \neq j} |g_{ij}|^2 f(\omega, \omega_{ij}, \Gamma_{ij}^{\text{tot}}), \qquad (4.36)$$

where i, j = 1, 2, 3, 4, and the parameters are given by

$$\Gamma_{ij}^{\text{tot}} = \sum_{k \neq i,j} \left(\Gamma_{ki} + \Gamma_{kj} \right), \quad \omega_{ij} = E_i - E_j, \qquad (4.37)$$

where Γ_{ij} are the one-phonon relaxation rates associated with the transitions $|i\rangle \rightarrow |j\rangle$, and E_i are the energy levels of Hamiltonian \hat{H}_0 (see Eqs (4.16)-(4.19)). The function $f(\omega, \omega_0, \Gamma)$ is given by

$$f(\omega, \omega_0, \Gamma) = \left[\frac{\Gamma/2}{(\omega - \omega_0)^2 + (\Gamma/2)^2} - \frac{\Gamma/2}{(\omega + \omega_0)^2 + (\Gamma/2)^2}\right],$$
(4.38)

and consists of two Lorentzian functions centered at the resonant frequencies $\omega = \pm \omega_0$ with a full width at high maximum equal to Γ . In Appendix C.1 we carefully derive the analytic expression for the absorption spectrum $I(\omega)$.



Figure 4.3: (a) A single $E \otimes SU(2)$ system embedded in a lattice and interacting with a static magnetic field $\vec{B} = (B \cos \phi \sin \theta, B \sin \phi \sin \theta, B \cos \theta)$ and perturbed by an oscillating magnetic field $\vec{B}_1(t) = B_1 \sin(\omega t)\hat{x}$. (b) Lattice effects represented by propagating phonons in the lattice and magnetic impurities randomly located. (c) Emission and absorption relaxation rates induced by phonons between two arbitrary eigenstates $|i\rangle$ and $|j\rangle$ of the Hamiltonian \hat{H}_0 . (d) Energy levels of our $E \otimes SU(2)$ systems and all possible transitions.

4.5 Phonon relaxation rates

In this section, we introduce to the temperature dependence of the one-phonon relaxation rates Γ_{ij} introduced in Eq. (4.32). From the absorption spectrum obtained in Eq. (4.36) we know that the phonon relaxation rates determines to great extent the shape of the spectrum. In fact, the peaks of the absorption spectrum at the resonant frequencies of the system are broadened and reduced if the phonon relaxation rates increase, and conversely. Therefore, the temperature dependence of the phonon relaxation rates Γ_{ij} is crucial for understanding the effect of temperature on the ESR absorption spectrum.

Using the Fermi golden rule to first-order in the interaction Hamiltonian \hat{H}_{e-ph} given in Eq. (4.23) we can find the absorption and emission relaxation rates associated with the transition $|i\rangle \rightarrow |j\rangle$. When $E_i < E_j$, the transition $|i\rangle \rightarrow |j\rangle$ is associated with the following

absorption relaxation rate

$$\Gamma_{ij}^{\text{abs}} = \frac{2\pi}{\hbar^2} \sum_{k} \left| \langle j, n_k - 1 | \hat{H}_{\text{e-ph}} | i, n_k \rangle \right|^2 \delta(\omega_{ji} - \omega_k), \qquad (4.39)$$

where $\omega_{ji} = (E_j - E_i)/\hbar > 0$ is the resonant frequency and $|n_k\rangle$ is number of phonons in mode k (Fock state) and E_i is the energy of state $|i\rangle$. When $E_i > E_j$, the transition $|i\rangle \to |j\rangle$ is associated with the following emission relaxation rate

$$\Gamma_{ij}^{\rm em} = \frac{2\pi}{\hbar^2} \sum_{k} \left| \langle j, n_k + 1 | \hat{H}_{\rm e-ph} | i, n_k \rangle \right|^2 \delta(\omega_{ij} - \omega_k), \tag{4.40}$$

where $\omega_{ij} = (E_i - E_j)/\hbar > 0$. By solving the expectation values $\langle j, n_k - 1 | \hat{H}_{e-ph} | i, n_k \rangle$ and $\langle j, n_k + 1 | \hat{H}_{e-ph} | i, n_k \rangle$ using the quantized electron-phonon Hamiltonian and assuming phonons in thermal equilibrium, we obtain

$$\Gamma_{ij}^{\text{abs}} = \frac{2\pi}{\hbar^2} J_{ij}(\omega_{ji}) n(\omega_{ji}), \quad \omega_i < \omega_j, \qquad (4.41)$$

$$\Gamma_{ij}^{\text{em}} = \frac{2\pi}{\hbar^2} J_{ij}(\omega_{ij})[n(\omega_{ij})+1], \quad \omega_i > \omega_j, \qquad (4.42)$$

where $\omega_{ij} = (\omega_i - \omega_j)/\hbar$, $n(\omega) = (\exp(\hbar\omega/k_B T) - 1)^{-1}$ is the mean number of phonons at thermal equilibrium. The function $J_{ij}(\omega)$ is know as the phonon spectral density function, and is given by

$$J_{ij}(\omega) = \sum_{k} \left[\left(\lambda_{ij,k}^{a} \right)^{2} + \left(\lambda_{ij,k}^{b} \right)^{2} \right] \delta(\omega - \omega_{k}), \quad \omega > 0,$$
(4.43)

where $\lambda_{ij,k}^{a,b}$ are the electron-phonon coupling constants introduced in Eq. (4.24). The phonon spectral density function plays a fundamental role in system interacting with a phonon bath. In the limit of continuous phonon modes, the frequency of each vibrational mode can be mapped into a continuous frequency, i.e., $\omega_k \longrightarrow \omega$. In this limit and considering the effect of acoustic phonons we can introduce the following representation of the electron-phonon coupling constants given in Eq. (4.24)

$$\lambda_{ij,k}^{a,b} \longrightarrow \lambda_{ij}^{a,b}(\omega) = \lambda_{ij,0}^{a,b} \left(\frac{\omega}{\omega_D}\right)^{1/2}, \quad 0 \le \omega \le \omega_D, \tag{4.44}$$

where ω_D is the Debye frequency and $\lambda_{ij,0}^{a,b}$ is the value of the electron-phonon coupling constants at the Debye frequency, i.e., $\lambda_{ij,0}^{a,b} = \lambda_{ij}^{a,b}(\omega_D)$. We introduce the density of phonon

states $D(\omega)$ for acoustic phonons as follow

$$D(\omega) = \frac{\Omega \omega_D^2}{2\pi^2 v_s^3} \left(\frac{\omega}{\omega_D}\right)^2, \quad 0 \le \omega \le \omega_D, \tag{4.45}$$

where Ω is the volume of the unit cell and v_s is the speed of sound. Using Eq. (4.44) and (4.45) into Eqs. (4.41) and (4.42) we have

$$\Gamma_{ij}^{\text{abs}} = \frac{\Omega}{\pi \hbar^2 v_s^3 \omega_D} \left[\left(\lambda_{ij,0}^a \right)^2 + \left(\lambda_{ij,0}^b \right)^2 \right] \omega_{ji}^3 n(\omega_{ji}), \tag{4.46}$$

$$\Gamma_{ij}^{\text{em}} = \frac{\Omega}{\pi \hbar^2 v_s^3 \omega_D} \left[\left(\lambda_{ij,0}^a \right)^2 + \left(\lambda_{ij,0}^b \right)^2 \right] \omega_{ij}^3 [n(\omega_{ij}) + 1].$$
(4.47)

The value of the coupling constants $\lambda_{ij,0}^a$ can be obtained or estimated using Eq. (4.24). We define $F(\omega_{\rm ph})$ as the linear vibronic coupling constant at the phonon frequency $\omega_{\rm ph}$. Here, $\omega_{\rm ph}$ is an acoustic phonon frequency. Following this argument, in the continuous limit we have $\lambda_{ij}^{a,b}(\omega_{\rm ph}) = F(\omega_{\rm ph})\sqrt{\hbar/(2\mu\omega_{\rm ph})}\alpha_{ij}^{a,b}$ (see Eq. (4.24)). From the relation $\lambda_{ij}^{a,b}(\omega_{\rm ph}) = \lambda_{ij,0}^{a,b}(\omega_{\rm ph}/\omega_D)^{1/2} = F(\omega_{\rm ph})\sqrt{\hbar/(2\mu\omega_{\rm ph})}\alpha_{ij}^{a,b}$ we finally deduce the following expressions

$$\Gamma_{ij}^{\text{abs}} = \frac{E_{\text{JT}}\Omega}{\pi\hbar v_s^3} \left(\left| \alpha_{ij}^a \right|^2 + \left| \alpha_{ij}^b \right|^2 \right) \omega_{ji}^3 n(\omega_{ji}), \tag{4.48}$$

$$\Gamma_{ij}^{\rm em} = \frac{E_{\rm JT}\Omega}{\pi\hbar v_s^3} \left(\left| \alpha_{ij}^a \right|^2 + \left| \alpha_{ij}^b \right|^2 \right) \omega_{ji}^3 \left(n(\omega_{ij}) + 1 \right), \tag{4.49}$$

where $E_{\rm JT} = (F/\omega_{\rm ph})^2/(2\mu)$ is the JT energy of the system when the quadratic electronphonon interaction is neglected [89]. The phonon absorption and emission relaxation rates given in Eqs. (4.48) and (4.49) include all the relevant physical parameters of the system. First, the JT energy $E_{\rm JT}$ depend on the value of the linear vibronic coupling constant and the reduced mass of the system. Second, the mixing parameters $\alpha_{ij}^{a,b}$ introduced in Eq. (4.24) depend on the overlap between the spin and orbital states induced by the external magnetic field and the spin-orbit coupling. Third, the resonant frequencies of the system $\omega_{ij} = (E_i - E_j)/\hbar$ depend on the eigenstates E_i of Hamiltonian \hat{H}_0 , and therefore, depend on the magnitude of the static magnetic field, the polar angle and the value of the spinorbit coupling constant. Finally, the value of the mean number of phonons at the resonant frequencies, $n(\omega_{ij}) = (\exp(\hbar\omega_{ij}/k_BT) - 1)^{-1}$, introduce the temperature dependence of the phonon relaxation rates. Finally, the parameters Ω and v_s depends on the volume of the unit cell and the bulk properties of the lattice, respectively.

In the next section, we describe the main features of the ESR absorption spectrum. We note

that this model can be used to describe the colour centres SiV^- and NV^0 in diamond. These colour centres are particular cases of $E \otimes e \otimes \text{SU}(2)$ Jahn-Teller systems.

4.6 Discussion

In this section we analyse two important features of the ESR absorption spectrum associated with our $E \otimes e \otimes SU(2)$ JT system (SiV⁻ center): the maximum intensity I_{max} and the full width at half maximum (FWHM) for the transition $|1\rangle \rightarrow |4\rangle$, although our results can be used to analyse an arbitrary transition $|i\rangle \rightarrow |j\rangle$ (for i, j = 1, 2, 3, 4). Here, the eigenstates $|i\rangle$ are defined in Eq. (4.20) and its eigenvalues are given by Eqs. (4.16)-(4.19). We introduce the effect of temperature T, the magnitude of the static magnetic field B, the polar angle θ , and the spin-orbit coupling constant λ using of the phonon relaxation rates Γ_{ij} defined in Eqs. (4.48) and (4.49).

We use the values $\Omega = a^3$ with $a = 3.57 \times 10^{-10}$ m and $v_s = 1.2 \times 10^4$ m/s in what follows [89]. In addition, from *ab initio* calculations of the dynamic JT effect in NV⁻ centers in diamond we know that the linear vibronic coupling is approximately F = -0.74 eV/Å for the phonon energy $\hbar \omega_{\rm ph} = 71$ meV and that the JT energy is $E_{\rm JT} = 25$ meV [89]. We use these value as a reference to estimate the linear vibronic coupling constant of SiV⁻ centers in diamond [92]. The spin-orbit coupling constant for individual SiV⁻ centers in diamond is approximately given by $\lambda \approx 50$ GHz [33, 36].

4.6.1 Absorption spectrum

Figure. 4.4 shows the ESR absorption spectrum $I(\delta)$ as a function of detuning frequency $\delta = \omega - \omega_{ij}$, where $\omega_{ij} = (E_i - E_j)/\hbar$ is the resonant frequency of the transition $|i\rangle \rightarrow |j\rangle$, and ω is the frequency of the oscillating magnetic field. We can observe the ESR response for the transition $|1\rangle \rightarrow |4\rangle$ (Fig. 4.4(a)) for $\Gamma_{mag} = 3$ MHz, B = 50 G, $\theta = \pi/4$, and $\phi = \pi/4$. When temperature increases from 10 mK to 10 K the ESR absorption spectrum is broadened and suppressed by the presence of phonons (Fig. 4.4(b)). We call this phenomenon as the phononic dynamical suppression of the ESR response. Phonons are the responsible of this effect due to the phonon-induced relaxation processes described in the quantum master equation Eq. (4.31) and the phonon relaxation rates given in Eqs. (4.48) and (4.49).



Figure 4.4: Theoretical absorption spectrum. The ESR signal $I(\delta)$ is plotted as a function of the detuning $\delta = \omega - \omega_{ij}$ for the transition $|1\rangle \rightarrow |4\rangle$. We use the values B = 50 G, $\lambda = 50$ GHz, $\theta = \pi/4$, $\phi = \pi/4$. The full width at high maximum is given by the relaxation rate $\Gamma_{14}^{\text{tot}} =$ $\Gamma_{\text{mag}} + \sum_{k \neq 1,4} (\Gamma_{k1} + \Gamma_{k4})$, where $\Gamma_{\text{mag}} = 3$ MHz is the magnetic relaxation rate phenomenologically introduced in Eq. (4.34). The inset plot in (b) shows the maximum value of the ESR absorption spectrum in comparison with its value at zero temperature $I_{\text{max}}(\omega)/I_{\text{max}}(T = 0)$.

The phononic dynamical suppression of the ESR response depends on the FWHM and the maximum intensity of the signal. The observed FWHM is given by the relaxation rates $\Gamma_{14}^{\text{tot}} = \Gamma_{\text{mag}} + \sum_{k \neq 1,4} (\Gamma_{k1} + \Gamma_{k4})$. The contribution of the magnetic noise introduce a constant FWHM, while phonon introduces the temperature dependence due to the absorption and emission processes. On the other hand, we compare the maximum value of the ESR response I_{max} respect its value at zero temperature $I_{\text{max}}(T = 0)$. From the inset of Fig. 4.4(b) we observe that the ratio $I_{\text{max}}(\omega)/I_{\text{max}}(T = 0)$ decreases when the temperature increases. This effect is due to the dynamic Jahn-Teller effect induced by linear electron-phonon coupling. At higher temperatures the mean number of phonons increases, as a result, the phonon-induced relaxation rates also increases (see Eqs. (4.48) and (4.49)). At very low temperatures (T < 100 mK), when phonons are frozen, the effect of the magnetic noise Γ_{mag} plays a fundamental role since determines the FWHM. Therefore, when the temperature increases the absorption signal is broadened and reduced by relaxation processes induced by the dynamic Jahn-Teller effect leading to a suppression of the ESR signal.

4.6.2 Phonon relaxation rate

The relevant phonon relaxation rates for the absorption spectrum are given by the parameters Γ_{ij}^{tot} introduced in Eq. (4.37) which determines the FWHM and the maximum value of



Figure 4.5: Two dimensional plot of the expected relaxation rate Γ_2 for the transition $|1\rangle \rightarrow |2\rangle$.(a) Two-dimensional parameter plot of the relaxation rate Γ_2 in logarithm scale at temperatures ranging from 1 mK to 10 K, magnetic fields ranging from 10^{-2} G to $2\lambda/\gamma_s$ G, where $\lambda = 50$ GHz. (b) Two-dimensional parameter plot of the relaxation rate Γ_2 in logarithm scale at temperature ranging from 1 mK to 10 K and linear vibronic coupling parameter F ranging from $10^{-1} \times F^*$ to $10 \times F^*$, where $F^* = -0.74$ eV/Å is the reference value extracted from the NV⁻ center [89].

the observed signal at the resonant frequencies ω_{ij} . For the transition $|1\rangle \rightarrow |2\rangle$ the rate Γ_{ij}^{tot} it is experimentally defined as $\Gamma_2 = \Gamma_1/2 + \Gamma_{\text{mag}}$. In our case Γ_1 is determined by the phonon relaxation rates. Figure. 4.5(a) shows the expected relaxation rate Γ_2 at temperatures ranging from 1 mK to 10 K and linear vibronic coupling constant ranging from $10^{-1} \times F^*$ to $10 \times F^*$, where $F^* = -0.74 \text{ eV/Å}$ is the reference value extracted from the NV⁻ center [89]. We observe a qualitative change in Γ_2 for temperatures above 0.1K. In addition, if we increase the value of the linear vibronic coupling constant F the intensity of Γ_2 also increases. In Fig. 4.5(b) shows the expected relaxation rate Γ_2 at temperatures ranging from 1 mK to 10 K and magnetic fields from 10^{-2} G to $2\lambda/\gamma_s \approx 5679$ G. As the magnetic field increases, the longitudinal relaxation rate increases as well. Interestingly, we observe a magnetic field resonance near $B \sim 10^3$ G.

4.7 Conclusions

We have presented a model to describe the dynamic Jahn-Teller effect on doubly degenerated orbital systems with a single electron and its effect on the electronic spin resonance response as a function of temperature. An analytical explanation for the absence of contrast in the ESR response at high temperatures is presented confirming qualitative expectations for this effect [93, 94]. Interestingly, and confirmed by recent experiments [95, 96], the contrast of ESR is recovered at temperatures of the order of tens-hundreds of mK where the relaxation due to phonons is suppressed. The contrast of the ESR response and the relaxation rate is analyzed as a function of temperature and of several system parameters such as spin-orbit, electron-phonon coupling and strength and orientation of the magnetic field relative to the symmetry axis of the system. The model can be used to characterize new spin-1/2 systems at low temperatures for metrology and quantum information applications.

Chapter 5

Optomechanical systems with color centers in diamond

In this chapter, we introduce the strain-induced Hamiltonian of a single SiV⁻ center embedded at the end of a diamond cantilever. This system is very interesting for optomechanical applications related to cooling schemes of the low-frequency mode associated with the bending motion of a cantilever. The theoretical approach used to derive the strain Hamiltonian takes advantage of the symmetrized molecular orbitals of the system and the symmetry decomposition of the strain tensor into the symmetries of the color center. This is required in order to understand how the local distortions of the lattice induce transitions between the orbital and spin states of color centers. We introduce the ground and excited states associated with the orbital degree of freedom of the SiV⁻ center in the electron-hole representation. In addition, we include the spin degree of freedom associated with the spin S = 1/2 associated with the SiV⁻ center in diamond. The interaction between the orbital and spin states is introduced via the spin-orbit coupling Hamiltonian of the system. Finally, we use the basis spawned by the eigenstates of the spin-orbit Hamiltonian in order to mathematically describe the strain-induced Hamiltonian of the system.

5.1 Introduction

Cooling a mechanical resonator mode close to the ground states is a difficult task in quantum mechanical systems. Interestingly, several theoretical ideas based on the strain-induced





Figure 5.1: Optomechanical system with a single color center. Single SiV⁻ center at the end of a diamond cantilever with a large l, width w, and thickness t. The catilever has a characteristic bending mode with frequency ω_b which is approximately given by $\omega_b \approx \sqrt{Et^2/(12\rho(1.88/l)^2} \approx 2\pi \times 480$ kHz for $l \approx 25 \ \mu m$ [12], where E and ρ are the Young modulus and the density of the diamond lattice. The compression modes of the diamond cantilever directly interacts with the SiV⁻ center in diamond via the strain-induced Hamiltonian.

interaction between color centers and nano-mechanical resonators has been explored in the last years [10–13]. The physical principle is simple, the vibrational mode of the resonator can be coupled to the internal degrees of freedom of the color center by means of some interaction (spin-phonon or electron-phonon interactions). The excitation of the internal states of the color center is accompanied by the absorption or emission of particular vibrational quanta. This extra energy is then dissipated at some rate Γ into the phonon bath. By using controlled microwave fields is possible to engineering the absorption of the vibrational mode of the resonator. This processes can be iterate several times in order to remove more and more vibrational quanta. As a result, the mechanical resonator is cooled to the ground state.

Figure. 5.1 shows a single SiV^- center embedded at the end of a diamond cantilever. A relevant question in this optomechanical system is how to model the coupling between the color center and the compression modes. The compression modes are important since they are related distortions of the molecular structure of the color center. In order to answer this question, we will introduce the microscopic derivation of the strain Hamiltonian for the silicon-vacancy center. In the next section, we carefully introduced to the strain-induced Hamiltonian for color centers in diamond. In particular, we develop a group theoretical approach that takes advantage of the symmetries associated with the molecular structure of the color center.

5.2 Microscopic strain Hamiltonian

In this section we introduce the strain Hamiltonian of a single SiV⁻ center in diamond using elements of elasticity and group theory. We introduce the mechanical distortions of the diamond lattice when ions are displacements around its equilibrium positions. For a finite lattice composed by N ions we can define $R_{ni}^{(0)}$ as the equilibrium position associated with the "i" cartesian coordinate of the *n*-th ion. If ion are displacement in a small quantity given by δR_{ni} , we obtain that ion positions can be written as

$$R_{ni} = R_{ni}^{(0)} + \delta R_{ni}, \tag{5.1}$$

where n = 1, ..., N and i = x, y, z are the atom and coordinates labels, respectively. The validity of small displacements is considered in terms of the lattice constant for the Diamond lattice a = 3.57 Å at 300 K, i.e., $|\delta R_{ni}| \ll a$ for all ions. The SiV⁻ center in diamond can be modeled as a one-electron hole system [36]. We define $V_{\text{e-ion}}(\mathbf{r}, {\mathbf{R}})$ as the electron-ion potential energy consistent with this one-electron description. If the electron is located at the position \mathbf{r} and the positions of the ions are given by ${\mathbf{R}} = \mathbf{R}_1, ..., \mathbf{R}_N$, to first order in the ion displacements we obtain

$$V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\}) = V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}_{n}^{(0)}\}) + \sum_{n=1}^{N} \sum_{i=x,y,z} \left. \frac{\partial V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\})}{\partial R_{ni}} \right|_{0} \delta R_{ni} + \mathcal{O}\left(\delta R_{ni}\right)^{2}.$$
(5.2)

The first term in the above expansion is related with the constant energy when all ions are in equilibrium. The second terms in Eq. (5.2) is the first correction due to small displacements of ions. The constant term can be neglected if we are interested in the electronic transitions of the system. Using the chain rule is possible to write

$$\frac{\partial V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\})}{\partial R_{ni}} \bigg|_{0} = \sum_{j=x,y,z} \left. \frac{\partial V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\})}{\partial (\delta R_{nj})} \right|_{0} \left. \frac{\partial (\delta R_{nj})}{\partial (R_{ni})} \right|_{0}.$$
(5.3)

Now, we assume that $\partial (\delta R_{nj}) / \partial (R_{ni})|_0$ doesn't depend on the index *n*. Using the last approximation we can write

$$V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\}) \approx \sum_{i,j=x,y,z} \left| \sum_{n=1}^{N} \frac{\partial V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\})}{\partial (\delta R_{nj})} \right|_{0} \delta R_{ni} \left| \frac{\partial (\delta R_{j})}{\partial R_{i}} \right|_{0}$$
$$= \sum_{i,j=x,y,z} V_{ij} \gamma_{ij}, \qquad (5.4)$$

where $\gamma_{ij} = \partial (\delta R_j) / \partial R_i$ defines a relative change of the shape of the system, which is usually known as the strain. In what follows we use $\hat{\gamma}_{ij}$ as a short notation for the strain tensor, where i, j = x, y, z or 1, 2, 3. The tensor $\hat{\gamma}_{ij}$ can be decomposed as follow

$$\hat{\gamma}_{ij} = \frac{1}{2} \left(\hat{\gamma}_{ij} + \hat{\gamma}_{ji} \right) + \frac{1}{2} \left(\hat{\gamma}_{ij} - \hat{\gamma}_{ji} \right) = \hat{\epsilon}_{ij} + \hat{a}_{ij}.$$
(5.5)

The first and second terms in the above equation are the symmetric and antisymmetric parts of the strain tensor. The antisymmetric part, \hat{a}_{ij} , describes rotations of the whole system, and therefore leave invariant the electron-ion potential $V_{\text{e-ion}}(\mathbf{r}, \delta\{\mathbf{R}\})$. In order to describe the effect of strain on the electronic structure of the SiV⁻ center in diamond we only consider the symmetric part given by $\hat{\epsilon}_{ij}$. Therefore, $\hat{\gamma}_{ij}$ can be considered as a symmetric tensor. Using the symmetric part the strain tensor into Eq. (5.4) we obtain

$$V_{\text{e-ion}}(\mathbf{r}, \{\mathbf{R}\}) = \sum_{i,j=x,y,z} V_{ij} \hat{\gamma}_{ij}, \qquad \hat{\gamma}_{ij} = \hat{\gamma}_{ji}, \qquad (5.6)$$

where $\hat{\gamma}_{ij}$ is the symmetric strain tensor and has the following matrix representation

$$\hat{\gamma} = \begin{pmatrix} \gamma_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \gamma_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \gamma_{zz} \end{pmatrix}.$$
(5.7)

In order to find the strain Hamiltonian, we expand the symmetric part of the strain given in Eq. (5.6) in some complete and orthonormal electronic basis $|\alpha\rangle$, and we obtain the following strain Hamiltonian

$$\hat{H}_{\text{strain}} = \sum_{i,j,\alpha,\beta} \langle \alpha \mid V_{ij} \mid \beta \rangle \hat{\gamma}_{ij} \mid \alpha \rangle \langle \beta \mid .$$
(5.8)

In the next section we introduce the electronic ground and excited excites of the SiV^- center in diamond.

5.3 Strain-induced Hamiltonian for the SiV⁻ center in diamond

For the SiV^- center in diamond we can expand the strain Hamiltonian in the following two-fold degenerate basis

$$|e\rangle = \{e_{ux}, e_{uy}\}, \text{ excited state}$$
(5.9)

$$|g\rangle = \{e_{gx}, e_{gy}\}, \text{ ground state.}$$
 (5.10)

In order to consider the symmetry properties of these excited and ground states it is convenient to expand the strain tensor into irreducible representations of the symmetry group of the SiV⁻ center. The symmetry group associated with the SiV⁻ center is the C_{3v+i} group. The strain Hamiltonian can be symmetrically expanded as follow

$$H_{\text{strain}} = \sum_{r,\alpha,\beta} \langle \alpha | V_r | \beta \rangle \, \hat{\gamma}_r | \alpha \rangle \, \langle \beta | \,, \qquad \alpha, \beta = \{ e_{ux}, e_{uy}, e_{gx}, e_{gy} \}, \tag{5.11}$$

where $\hat{\gamma}_r$ is the symmetric strain tensor associated with irreducible representation of the group C_{3v+i} . The C_{3v+i} group has irreducible representations labelled by $r = \{A_{1g}, A_{2g}, E_g, A_{1u}, A_{2u}, E_u\}$ (see character table (5.1)). In this notation, the symmetry groups C_{3v+i} and D_3 are isomorphic, *i.e* $C_{3v+i} \simeq D_{3d}$ (but the irreducible representations A_1 and A_2 are swapped).

Physically, local strain or local distortions in the SiV^- structure generates a collective displacement of the defect atoms. This leads to a change in the potential seen by the each atom and results in a modification of the electronic distribution of the defect via electron-ion interaction. To first order in the ion displacements and in the Born-Oppenheimer approximation, this local distortion effect can be modeled by the strain Hamiltonian

$$\hat{H}_{\text{strain}} = \sum_{i,j,\alpha,\beta} |\alpha\rangle \langle \alpha| |V_{ij}|\beta\rangle \langle \beta| \hat{\gamma}_{ij}.$$
(5.12)

Here, $|\alpha\rangle$ is the electronic basis and V_{ij} are couplings that involve the electron-ion Coulomb interaction [41]. For the SiV⁻ center the matrix associated to the strain tensor can be expressed in terms of matrices that transform according to the irreducible representations of the C_{3v+i} group. This mathematical decomposition can be achieved by projecting the matrix

Table 5.1: Character table of the group C_{3v+i} . The first column are the irreducible representations of the C_{ev+i} group $(A_{1g}, A_{2g}, E_g, A_{1u}, A_{2u}, E_u)$. The index g and u denote the german word "gerade" (symmetric) and "ungerade" (antysimmetric) representations. The first row is a list of the symmetry operations of the group C_{3v} ordered by the classes of the group $(E, 2C_3, 3C_2, i, 2S_6, 3\sigma)$.

	E	$2C_3$	$3C_2$	i	$2S_6$	3σ	linear	quadratic
A_{1g}	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	-1	1	1	-1	R_z	
E_g	2	-1	0	2	-1	0	(R_x, R_y)	$(x^2 - y^2, xy), (xz, yz)$
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	z	
E_u	2	-1	0	-2	1	0	(x,y)	

given in Eq. (5.7) in each irreducible representation by applying the following formula [40, 41]

$$\hat{\gamma}_r = \frac{l_r}{h} \sum_{g \in C_{3v+i}} \chi^r(g) R^{\dagger}(g) \,\hat{\gamma} \, R(g), \qquad \hat{\gamma} = \begin{pmatrix} \hat{\gamma}_{xx} & \hat{\gamma}_{xy} & \hat{\gamma}_{xz} \\ \hat{\gamma}_{xy} & \hat{\gamma}_{yy} & \hat{\gamma}_{yz} \\ \hat{\gamma}_{xz} & \hat{\gamma}_{yz} & \hat{\gamma}_{zz} \end{pmatrix}, \tag{5.13}$$

where $\hat{\gamma}_r$ is the projection of the strain tensor into the irreducible representation r. Here, l_r is the dimension of the r-th irreducible representation, h is the order of the group (number of elements), $\chi^r(g)$ is the character of the group element g in the irreducible representation r, and R(g) is the matrix representation of the group element g (see Character Table (5.1)). Using the formula given in Eq. (5.13) we can find that the strain tensor can be decomposed as

$$\hat{\gamma} = \hat{\gamma}_{A_{1g}} + \hat{\gamma}_{E_g},\tag{5.14}$$

where

$$\hat{\gamma}_{A_{1g}} = \begin{bmatrix} \frac{1}{2} (\gamma_{xx} + \gamma_{yy}) & 0 & 0\\ 0 & \frac{1}{2} (\gamma_{xx} + \gamma_{yy}) & 0\\ 0 & 0 & \gamma_{zz} \end{bmatrix}, \quad (5.15)$$

$$\hat{\gamma}_{E_g} = \begin{bmatrix} \frac{1}{2} (\gamma_{xx} - \gamma_{yy}) & \gamma_{xy} & \gamma_{xz} \\ \gamma_{xy} & \frac{1}{2} (\gamma_{yy} - \gamma_{xx}) & \gamma_{yz} \\ \gamma_{xz} & \gamma_{yz} & 0 \end{bmatrix}.$$
(5.16)

See Supporting Material D.1 for further details of the algorithm and code used for the symmetric decomposition. Due to the inversion symmetry of the SiV^- center, the orbital degrees of freedom of the states within the ground and excited subspaces are characterized

by parity [40]. As a consequence, the expectation values of the form $\langle \alpha | V_{iz} | \alpha \rangle$ (i = x, y, z) vanish in both ground and excited subspaces. Therefore, in the electronic basis spawned by $\{|e_{gx}\rangle, |e_{gy}\rangle\}$, the strain Hamiltonian can be written as [92]

$$\hat{H}_{\text{strain}} = \begin{bmatrix} \delta & 0\\ 0 & \delta \end{bmatrix} + \begin{bmatrix} \alpha & \beta\\ \beta & -\alpha \end{bmatrix}, \qquad (5.17)$$

with $\delta = \lambda_0 (\hat{\gamma}_{xx} + \hat{\gamma}_{yy})$, $\alpha = \lambda_1 (\hat{\gamma}_{xx} - \hat{\gamma}_{yy})$ and $\beta = \lambda_2 \hat{\gamma}_{xy}$. Here, λ_0, λ_1 , and λ_2 are coupling constants. The first term of the strain Hamiltonian is the energy shift induced by symmetry local distortions and can be neglected. Now, the spin-orbit Hamiltonian of the SiV⁻ center is given by [36] (see Supplemental Material)

$$\hat{H}_{\rm SO} = -\lambda_{\rm SO} \hat{L}_z \hat{S}_z = -\frac{\lambda_{\rm SO}}{2} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -\frac{\lambda_{\rm SO}}{2} \begin{pmatrix} 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \\ -i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}, \quad (5.18)$$

where $\lambda_{\rm SO} > 0$ is the spin-orbit coupling constant. The eigenstates of the above Hamiltonian are given by $|1\rangle = |e_{-},\downarrow\rangle$, $|2\rangle = |e_{+},\uparrow\rangle$, $|3\rangle = |e_{+},\downarrow\rangle$, and $|4\rangle = |e_{-},\uparrow\rangle$, where $|e_{\pm}\rangle = (|e_x\rangle \pm i |e_y\rangle)/\sqrt{2}$ are the eigenstates of \hat{L}_z . Finally, if we write the strain Hamiltonian using the basis spawned by the eigenstates of the spin-orbit coupling we obtain

$$\hat{H}_{\text{strain}} = \begin{pmatrix} 0 & \alpha - i\beta \\ \alpha + i\beta & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = g_1 \left(\hat{\gamma}_{xx} - \hat{\gamma}_{yy} \right) \left(\hat{L}_- + \hat{L}_+ \right) - ig_2 \hat{\gamma}_{xy} \left(\hat{L}_- - \hat{L}_+ \right),$$
(5.19)

where $\hat{L}_{+} = |3\rangle \langle 1| + |2\rangle \langle 4| = \hat{L}_{-}^{\dagger}$ are the raising (\hat{L}_{+}) and lowering (\hat{L}_{-}) orbital momentum operators of the ground state, and $g_{1,2}$ are the strength of the couplings to the strain field. This strain-induced Hamiltonian was used in the following work [12]. We observe that the electron and the lattice can exchange orbital angular momentum via the strain-induced Hamiltonian.

5.4 Conclusions

We have presented a microscopic approach to the problem of modeling the strain-induced interaction between the SiV^- center in diamond and the distortions of the lattice. We take

advantage of the symmetrized orbital states of the color center as well as the symmetric decomposition of the strain tensor. Group theoretical arguments are presented in order to find the symmetric form of the final strain-induced Hamiltonian. This approach can be used to characterize new strain-induced Hamiltonians of solid-state systems with different symmetries.

Chapter 6

Conclusions and outlook

The goal of this thesis was to study the effect of phonons on the optical, electronic and spin properties of color centers in diamond. We started our analysis with a theoretical description of the effect of phonons on the photoluminescence spectrum of negatively charged siliconvacancy centers in diamond. The main motivation of this project was to understand the crucial difference between the observed PL spectra of the NV⁻ center and SiV⁻ center at the same temperature. As we discussed in Chapter 2, the NV-center has a broad emission ranging from 637 nm zero-phonon line (ZPL) to 750 nm; meanwhile, the emission of the SiV⁻ has a width of few nanometers at the same temperature [14]. Motivated by this experimental evidence, our fundamental question was to understand the role of symmetry on the optical features of color centers in diamond. In terms of symmetry, the only difference between the NV⁻ center and the SiV⁻ center is the additional inversion of the SiV-center. On the other hand, from the old theory described in the Frank-Condon principle [97] used in molecular spectroscopy, we knew that the electron-phonon interaction will determine the shape of the PL spectrum, in particular, the phonon sideband contribution.

The problem of finding the PL spectrum is translated into the problem of estimating the electron-phonon coupling constants for a single SiV⁻ center embedded in a finite diamond lattice. As a first step, we developed a Hamiltonian description for the system based on the spin-boson model formalism. In Sections 2.2 and 2.3 we described both Hamiltonians associated with the SiV⁻ center and the linear electron-phonon interaction (see Appendix A.1 for further details). Using the spin-boson model and the polaron transformation we developed a model for calculating the emission spectrum of the system. In Section 2.4 we showed that the emission spectrum crucially depends on the phonon spectral density function $J(\omega)$ of

the system (see Eq. (B.27)). In order to calculate the phonon spectral density function, we elaborated a numerical method to estimate the electron-phonon coupling constants between a single SiV⁻ center and the lattice vibrations of a finite-sized crystalline structure. The vibrational properties of the whole system (diamond lattice and the individual SiV-center) were estimated using a force-constant model based on a second nearest-neighbor interaction model (see Appendix A.2). On the other hand, we implement Gaussian orbitals to describe the single sp^3 orbitals of each atom of the SiV⁻ center. From our molecular dynamic simulations we reproduced the phonon dispersion relation of a diamond lattice in a good agreement with previous experimental observations (see Fig. 2.2).

In addition, we classified all vibrational modes using the irreducible representations of the C_{3v+i} group associated with the SiV⁻ center $(a_{1g}, a_{2g}, e_g, a_{1u}, a_{2u}, e_u$ phonon modes). In the absence of ungerade (antisymmetric) perturbations on the electronic states only gerade (symmetric) modes contribute to the emission spectrum, by simple symmetry considerations (see Section 2.6). However, the observed isotopic shift of the phonon sideband suggests a strong electron-phonon interaction with a quasi-localized phonon mode with odd symmetry. To incorporate the contribution of antisymmetric phonon modes we developed the dynamical symmetry breaking mechanism in Section 2.6 and Appendix A.6. This dynamical effect is consistent with the Herzberg-Teller effect which also shows a dynamical symmetry breaking [46–48]. Using our numerical model we find a strong peak in the PL spectrum associated to an a_{1u} quasi-local phonon mode with a frequency of $\omega_{28} = 63.19$ meV, $\omega_{29} = 62.66$ meV and $\omega_{30} = 62.16$ meV for the isotopes ²⁸Si, ²⁹Si and ³⁰Si, respectively. The ratio between these energies is approximately $\omega_{28}/\omega_{29} \approx 1.01$ and $\omega_{28}/\omega_{30} \approx 1.02$ in good agreement with experimental values ($\omega_{28}/\omega_{29} = 1.016$ and $\omega_{28}/\omega_{30} = 1.036$ [45]). We remark that the isotopic shift of the phonon sideband is not possible to explain with phonons that transform evenly under inversion. Therefore, a dynamical symmetry breaking is needed, which can be caused by non-inversion preserving perturbations such as external electric fields or odd vibrational modes. As a general conclusion of this project, we recall that our results might be useful for understanding the microscopic origin of the effect of phonons on solid-state emitters, but our analysis must consider the effect or other interactions such as Jahn-Teller effect and strain.

In Chapter 3 we introduced a full theoretical description of the role of phonons on the spinlattice relaxation dynamics of individual NV^- centers in diamond. The motivation of this project was to really understand the phonon-induced spin relaxation rates and its temperature dependence for a wide range of temperature (from 1 mK to 475 K). To address this complex theoretical problem we introduced a general spin-phonon Hamiltonian for the NV^- center in diamond. Incredibly, a very recent work [98] confirmed the same Hamiltonian structure of our spin-phonon Hamiltonian introduced in Section 3.2. Moreover, we introduced both linear and quadratic interaction terms in the spin-phonon Hamiltonian. This is necessary to fully describe two-phonon processes and deduce all possible temperature scaling for the longitudinal relaxation rate. Using the Fermi golden to first and second order we analytically derived the phonon-induced relaxation rates as a function of temperature and arbitrary magnetic fields aligned with the symmetry axis of the NV⁻ center. In Section 3.3 we introduced one- and two-phonon processes with great detail, but the discussion is focused in terms of the contribution of acoustic and quasi-localized phonon modes. We neglected the contribution of optical phonon modes due to the low probability of populated high energy phonons at the experimental temperatures used in experiments. However, it is an interesting open question how optical phonons modified the temperature dependence of the spin relaxation rates. The role of optical phonons is beyond the scope of this work.

The spin-lattice relaxation dynamics of the spin degree of freedom is derived from the Markovian quantum master equation of a single NV⁻ center coupled to lattice vibrations. Here, the environment is modeled as a phonon bath in thermal equilibrium. The statistical description of phonons is an interesting way to introduce temperature effects. Basically, we use the Bose-Einstein distribution for the mean number of phonons. We phenomenologically introduced the effect of magnetic impurities by adding a Lindbadian operator associated with a stochastic magnetic noise [72]. This is a crucial point in our theoretical description since a real quantum mechanical model of the effect of magnetic impurities is still an open question in the NV-community. In fact, a full quantum description should consider the spin flip-flop processes between the NV⁻ center and the surrounding magnetic impurities (¹³C, ¹⁴Ni, ²⁹Si and other NV centers). The latter interaction is the microscopic origin of this fluctuating magnetic field that induced relaxation on the color center. The contribution of phonons is not a mystery, but a good theoretical description is needed in order to eventually describe more complex relaxation processes. Following this point of view, we think that this project is a very good starting point to really understand the relaxation dynamics of color centers in diamond for future applications in metrology and quantum communication. To study the effect of temperature and magnetic field on the longitudinal relaxation rate we separate the discussion into two important limits: low and high temperatures.

At low temperatures, we derived a set of microscopic equations (Eqs. (B.40)-(B.41))in order to study the spin-lattice relaxation dynamics induced by one-phonon processes. In this limit only one-phonon processes are relevant. Therefore, two-phonon processes can be neglected in the quantum master equation. At zero magnetic fields we analytically obtained the relaxation rate $1/T_1 = \Gamma_0(1+3\bar{n})$, where $\bar{n}(T) = (\exp(\hbar D/k_B T) - 1)^{-1}$ is the mean number of phonons at the zero-field splitting frequency $D/(2\pi) = 2.87$ GHz, and Γ_0 is constant determined by microscopic parameters. Our theoretical result is exactly the same relaxation rate predicted by experiments and *ab initio* calculations [19], as well as theoretical calculations [74]. In addition, for low magnetic fields, $\gamma_s B_0 \ll D$, we obtained the relaxation rate $1/T_1 = 2\Gamma_0(1 + 2\bar{n}) + \Gamma_B(1+2n_B)$ associated with $\langle S_z(t) \rangle$, where Γ_B scales as B_0^3 .

At high temperatures, we derived an expression for the longitudinal relaxation rate (Eq. 3.75) that consider the effect of one and two-phonon processes. In particular, the relaxation rate $1/T_1$ associated with $\langle S_z(t) \rangle$ is in agreement with experimental observations [15, 17, 18]. We included both linear and bi-linear lattice interactions that lead to several different temperature scaling in a general spin-boson model for a system with spin S = 1. Our model reproduces the observed temperature scaling T^5 at high temperatures as well as the main features for temperatures ranging from 4 K to 475 K. We think that our model can be used to understand the observed T^7 temperature dependence of the neutral siliconvacancy color center in diamond at high temperatures [73]. Finally, we recall that our model will be useful to evaluate the contribution of second-order phonon processes that give different temperature scaling (T^s, T^{s+1}, T^{s+2}) for other spin-boson systems. The power of the temperature $s = 4\nu + 2d - 3$ depends on the dimension of the system $(1 \le d \le 3)$ and the symmetry of the lattice (parameter ν).

In Chapter 4 we have presented a theoretical explanation for the absence of contrast in the ESR response at high temperatures confirming qualitative expectations for this effect [93, 94]. A model is presented to describe the dynamic Jahn-Teller effect on doubly degenerated orbital systems with a single electron spin-1/2. We consider the linear electron-phonon coupling between the orbital and lattice degrees of freedom, the spin-orbit, and Zeeman interactions, and the linear response of the system to oscillating magnetic fields (Eq. (4.1)). We analyzed the linear response of the system using the dynamical susceptibility in the limit of a weak oscillating magnetic field. In addition, we used the Markovian quantum master equation to solve the dynamics of the orbital and spin degrees of freedom when phonons are in thermal equilibrium. The spin relaxation rates of the quantum master equation and the contrast of the system. Such parameters are the magnitude of the system, the value of the spin-orbit coupling constant, the linear vibronic coupling constant associated with the

Jahn-Teller effect, and the temperature. Interestingly, and confirmed by recent experiments [95, 96], the contrast of ESR is recovered at temperatures of the order of tens-hundreds of mK where the relaxation due to phonons is suppressed.

The physical explanation of the absence of contrast in the ESR response is related with the coupling between the orbital states and phonons. When the system is driven from its equilibrium state due to the oscillating magnetic field, the relaxation dynamics of the orbital states is modified by the Jahn-Teller interaction described in Section 4.3. As a consequence of this electron-phonon coupling and the spin-orbit interaction, we observed that the spin exhibited a relaxation dynamics also. Obviously, the effect of phonons on the relaxation dynamics increases at higher temperatures. At higher temperatures the mean number of phonons increases, as a result, the phonon-induced relaxation rates also increases. In our model, when the temperature increases the absorption signal is broadened and reduced by relaxation processes induced by the dynamic Jahn-Teller effect leading to a suppression of the ESR signal. This is the microscopic origin of the phononic dynamical suppression of the electron spin resonance of $E \otimes e \otimes SU(2)$ Jahn-Teller systems. We think that this model can be used to characterize new spin-1/2 systems at low temperatures for metrology and quantum information applications.

In Chapter 5 we have presented a microscopic and group theoretical approach to the problem of modeling the strain Hamiltonian of a single SiV⁻. The main motivation of this work was to understand the strain-induced coupling of a single SiV⁻ center embedded at the end of a diamond cantilever. This system has interesting features for cooling schemes if the SiV⁻ center is coupled to a magnetic tip and controlled by two lasers. In particular, the cooling of the bending mode of the cantilever can be achieved using this system [12]. In our theoretical description, we take advantage of the symmetrized orbital states of the color center as well as the symmetric decomposition of the strain tensor into irreducible representations of the group C_{3v+i} .

We have seen that the electronic, optical, and spin properties of color centers are modified by phonons. Many of these effects are related to the electron-phonon coupling, Jahn-Teller effect or strain-induced interactions. Such interactions depend on the symmetry of the color center and the electronic distribution (localized or delocalized). The community has been started to explore new physical properties at low temperatures, where the role of vibrations can be studied with a great detail. Finally, a big challenge is the microscopic modeling of the magnetic field fluctuations of the environment. A detailed description of the relaxation processes is required for future applications in quantum sensing and quantum information processing.

Appendix A

Supporting Material for Chapter 2

A.1 Electron-phonon interaction

In this section we present a more detailed derivation of the electron-phonon interaction used to model the optical properties of the SiV⁻ center. Using the normal coordinates Q_l^{Lat} defined in Eq. (2.4) the electron-phonon interaction can be expanded as follow

$$V_{\text{e-ph}}(\mathbf{r}, \{\mathbf{Q}\}) = V_0 + \sum_{l=1}^{3N_{\text{Lat}}-6} \left(\frac{\partial V_{\text{e-Ion}}}{\partial Q_l^{\text{Lat}}}\right) Q_l^{\text{Lat}} + \dots, \qquad (A.1)$$

where only the $3N_{\text{Lat}} - 6$ vibrational modes are considered, as translational and rotational modes leave invariant the electron-phonon interaction [25]. As we will focus on deep centers, *i.e.*, center whose electronic wave functions decay quickly with distance [99], it will be convenient to define local vibrational modes involving only those atoms on which the electronic wave functions are considered to be non-zero. These modes can be obtained from group theoretical considerations [25, 40] or by numerically solving a small molecular system considering only the atoms related with the defect structure using a force-constant model [100] or *ab initio* calculations. These defect normal coordinates are defined as

$$Q_{l'}^{\rm SiV} = \sum_{i=1}^{N_{\rm D}} \sum_{\alpha = \{x, y, z\}} \sqrt{M_i} u_{i\alpha} h_{i\alpha, l'}^{\rm SiV}, \qquad (A.2)$$

where $N_{\rm D}$ is the number of atoms of the defect $(N_{\rm D} < N_{\rm Lat})$, $u_{i\alpha}$ is the displacement of the i-th ion in the α direction from its equilibrium position, and $h_{i\alpha,l'}^{\rm SiV}$ are the eigenvectors l' associated to the defect molecular vibrations of the i-th ion in the α direction. The local normal coordinates of the defect can be written as a linear combination of the lattice normal modes given in Eq. (2.4)

$$Q_{l'}^{\rm SiV} = \sum_{l=1}^{3N_{\rm Lat}-6} \alpha_{l'l} Q_l^{\rm Lat},$$
(A.3)

where the parameter $\alpha_{l'l}$ is given by Eq. (2.8). $\mathbf{H}_{l'}^{\text{SiV}}$ and $\mathbf{h}_{l}^{\text{Lat}}$ are vectors with the same dimensionality and whose components are given by

$$\mathbf{H}_{l'}^{\text{SiV}} = \begin{pmatrix} h_{1x,l'}^{\text{SiV}} \\ h_{1y,l'}^{\text{SiV}} \\ h_{1z,l'}^{\text{SiV}} \\ \vdots \\ h_{N_{\mathrm{D}}z,l'}^{\text{SiV}} \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \mathbf{h}_{l}^{\text{Lat}} = \begin{pmatrix} h_{1x,l}^{\text{Lat}} \\ h_{1y,l}^{\text{Lat}} \\ h_{1z,l}^{\text{Lat}} \\ \vdots \\ h_{N_{\mathrm{D}}z,l}^{\text{Lat}} \\ h_{N_{\mathrm{D}}z,l}^{\text{Lat}} \\ \vdots \\ h_{N_{\mathrm{D}}+1x,l}^{\text{Lat}} \\ \vdots \\ h_{N_{\mathrm{Lat}}z,l}^{\text{Lat}} \end{pmatrix}$$
(A.4)

where $H_{i\alpha,l'}^{\text{SiV}}$ are obtained from group theoretical arguments and $H_{i\alpha,l'}^{\text{Lat}}$ are numerically obtained by solving the eigenvalue equation (2.5). Therefore, using the chain rule and neglecting the constant term V_0 on Eq. (A.1) we recover electron-phonon interaction given in Eq. (2.7).

A.2 Force constant model to second order nearest-neighbor

In this section we present the force constant model used to numerically solve the vibrational modes associated to the eigenvalue equation given in Eq. (2.5). Using the general valence force field for diamond [42], we can extract the vibrational dynamics of the system using the following expression for the ion-ion interaction including up to second nearest-neighbor interactions

$$V_{\text{Ion-Ion}} = \sum_{k_s \in \mathbb{K}} V_{k_s}, \qquad \mathbb{K} = \{k_r, k_{rr}, k_{r\theta}, k_{\theta}, k_{\theta\theta}\},$$
(A.5)

where the contributions to the ion-ion potential interaction are given by

$$V_{k_r} = \frac{1}{2} k_r \sum_{\langle ij \rangle} \left(\delta u_{ij} \right)^2, \qquad (A.6)$$

$$V_{k_{rr}} = k_{rr} \sum_{\langle ij \rangle, \langle kj \rangle} (\delta u_{ij}) (\delta u_{kj}), \qquad (A.7)$$

$$V_{k_{r\theta}} = bk_{r\theta} \sum_{\langle ijk \rangle} (\delta u_{ij}) (\delta \theta_{ijk}), \qquad (A.8)$$

$$V_{k_{\theta}} = \frac{1}{2} b^2 k_{\theta} \sum_{\langle ijk \rangle} \left(\delta \theta_{ijk} \right)^2, \qquad (A.9)$$

$$V_{k_{\theta\theta}} = \frac{1}{2} b^2 k_{\theta\theta} \sum_{\langle ijk \rangle, \langle ljm \rangle} \left(\delta \theta_{ijk} \right) \left(\delta \theta_{ljm} \right), \qquad (A.10)$$

where V_{k_r} is the potential energy associated with the bond-stretching of the first nearest neighbor $\langle ij \rangle$, $V_{k_{rr}}$ is the potential energy associated with bond-stretching of the bond-pair $\langle ij \rangle$ and $\langle kj \rangle$ that share the atom j, $V_{k_{r\theta}}$ is the potential energy associated with the bondstretching of the first nearest-neighbor $\langle ij \rangle$ that shares a bond with the bond-bending angle θ_{ijk} , $V_{k_{\theta}}$ is the potential energy associated with the bond-bending angle θ_{ijk} such that i and kare nearest-neighbor of j, and $V_{k_{\theta\theta}}$ is the potential energy associated with the bond-bending of the angles θ_{ijk} and θ_{ljm} when no bond is shared. The parameter b = 1.95 Å for the point defect and b = 1.54 Å for the bulk diamond. These interaction depends on the geometrical distortions of the lattice

$$\delta u_{ij} = |\mathbf{u}_i - \mathbf{u}_j|, \qquad \hat{\mathbf{u}}_{ij} = (\mathbf{u}_i - \mathbf{u}_j)/\delta u_{ij}, \qquad (A.11)$$

$$\delta\theta_{ijk} = \cos^{-1}(\hat{\mathbf{u}}_{ij} \cdot \hat{\mathbf{u}}_{kj}), \qquad (A.12)$$

and the elastic constants $k_r, k_{rr}, k_{r\theta}, k_{\theta}, k_{\theta\theta}$. These elastic constants are obtained from literature in the case of bulk-diamond [42, 43] and from *ab initio* simulations for the SiV⁻ center. In order to obtain the elastic constants $k_r^{\text{SiV}}, k_{rr}^{\text{SiV}}, k_{\theta\theta}^{\text{SiV}}$ and $k_{\theta\theta}^{\text{SiV}}$ for this point defect we fit the energy variations for each displacement mode **u** as follow

$$\delta E = E_0 + \frac{1}{2} \delta \mathbf{u}^\top \cdot \mathbf{D} \cdot \delta \mathbf{u}, \qquad (A.13)$$

where **D** is the dynamical matrix of the whole system [Eq. (2.5)]. We can calculate this variation from *ab initio* calculations by considering the same displacement mode **u**. Using the density functional theory (DFT) and the projector-augmented wave (PAW) [101, 102]



Figure A.1: Potential energy variation. Red points represent ab initio calculations of the energy variation of a supper cell with 64 atoms in which one carbon atom of the SiV-center is displacement toward the silicon atom (see SiV-center mode). The blue dashed line represent our second order nearest-neighbor model fitting.

method implemented in the Vienna ab-initio simulation package (VASP) [103–105]. We can use a plane-wave energy cutoff of 400 eV in all our calculations. The exchange and correlation energy was described within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof functional [106, 107]. The Monkhorst-Pack scheme was employed for the Brillouin-zone (BZ) integrations [108] with a mesh $8 \times 8 \times 8$, which corresponds a set of 60 special k-points in the irreducible BZ.

In order to considerer the SiV-center as a defect, we employed a $2 \times 2 \times 2$ supercell of the diamond cubic unit cell with a total of 64 atoms. Furthermore, in the calculation of equilibrium electronic structure, the geometry was relaxed until the forces over each component of atoms position were smaller than $2 \times 10^{-4} \text{ eV/Å}$. Figure A.1 shows the potential energy calculated from *ab initio* and the resulting fit using the elastic constants k_r^{siv} , k_{rr}^{siv} , k_{θ}^{siv} and $k_{\theta\theta}^{\text{siv}}$ as fitting parameters. Similar fittings can be performed for the rest of the molecular distortions. From the above methodology we find the following elastic


Figure A.2: Types of interactions present in a second nearest neighbor model for phonons. The five elastic constant $k_r, k_{rr}, k_{r\theta}, k_{\theta}, k_{\theta\theta}$ are obtained from literature in the case of bulk-diamond and from ab initio simulations for the defect.

constants for the SiV^- center

$$k_r^{\rm SiV} = 45 \text{ N/m} = 2.8087 \text{ eV/Å}^2,$$
 (A.14)

$$k_{rr}^{\rm SiV} = 17.7 \text{ N/m} = 1.1047 \text{ eV/Å}^2,$$
 (A.15)

$$k_{r\theta}^{\rm SiV} = 37.5 \text{ N/m} = 2.3406 \text{ eV/Å}^2,$$
 (A.16)

$$k_{\theta\theta}^{\rm SiV} = 3.5 \,\mathrm{N/m} = 0.2091 \,\mathrm{eV/\AA}^2,$$
 (A.17)

$$k_{\theta}^{\text{SiV}} = 47.23 \text{ N/m} = 2.9479 \text{ eV/Å}^2.$$
 (A.18)

Figure A.2 shows the molecular distortions associated with the different types of interactions introduced in the second-order nearest-neighbor interaction model.

A.3 Numerical methodology for the molecular vibrations

In this appendix, we describe how to calculate the second order nearest-neighbor interactions for the molecular vibrations of a single defect embedded in a finite diamond lattice. First at all, given the primitive basis vector of the diamond lattice $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$, we can construct all the atomic positions \mathbf{R}_i $(i = 1, ..., N_{\text{Lat}})$ for a finite lattice with a sphere shape with a characteristic radius R_{Max} such as $|\mathbf{R}_i| \leq R_{\text{Max}} \forall i$. In this lattice, the single defect is located at the center of the structure, which is defined as the origin of our coordinate system ($\mathbf{R} = 0$). Once the finite lattice is constructed, we proceed to generate the dynamical matrix \mathbf{D} of the whole system (see Eq. (2.6)), pictorially

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}^{\text{siv}} & \mathbf{D}^{\text{I}} \\ \hline \mathbf{D}^{\text{I}} & \mathbf{D}^{\text{Bulk}} \end{pmatrix}, \qquad (A.19)$$

where \mathbf{D}^{siv} , \mathbf{D}^{Bulk} and \mathbf{D}^{I} are the dynamical matrix associated with the SiV⁻ center, bulk lattice and defect-bulk interaction, respectively. For the SiV⁻ center, the dynamical matrix is defined as,

$$D_{i\alpha,j\beta}^{\text{Defect}} = \frac{1}{\sqrt{M_i M_j}} \left. \frac{\partial^2 V_{\text{Ion-Ion}}^{\text{Defect}}}{\partial u_{i\alpha} \partial u_{j\beta}} \right|_{\text{eq}} \text{ if } i, j \le N_{\text{D}} \,\,\forall \,\alpha, \beta, \tag{A.20}$$

where $N_{\rm D}$ is the number of atoms of the defect. The internal potential interaction of the defect $V_{\rm Ion-Ion}^{\rm SiV}$ is defined as

$$V_{\text{Ion-Ion}}^{\text{SiV}} = \sum_{ks} V_{ks}^{\text{SiV}}, \qquad k_s \in \{k_r^{\text{SiV}}, k_{rr}^{\text{SiV}}, k_{r\theta}^{\text{SiV}}, k_{\theta\theta}^{\text{SiV}}, k_{\theta\theta}^{\text{SiV}}\},$$
(A.21)

where the elastic constants k_r^{SiV} , k_{rr}^{SiV} , $k_{\theta\theta}^{\text{SiV}}$, $k_{\theta\theta}^{\text{SiV}}$ are given in Eqs. (A.14)-(A.18). The potential $V_{k_s}^{\text{SiV}}$ is given by Eqs. (A.6)-(A.10). For the bulk lattice, the dynamical matrix is defined as

$$D_{i\alpha,j\beta}^{\text{Bulk}} = \frac{1}{\sqrt{M_i M_j}} \left. \frac{\partial^2 V_{\text{Ion-Ion}}^{\text{Bulk}}}{\partial u_{i\alpha} \partial u_{j\beta}} \right|_{\text{eq}} \text{ if } i, j > N_{\text{D}} \ \forall \alpha, \beta.$$
(A.22)

Analogously to the potential for the defect case given in Eq. (A.21), the bulk-potential $V_{\text{Ion-Ion}}^{\text{Bulk}}$ is calculated using the second-nearest neighbor model, but using some different bulkelastic constants $k_r^{\text{Bulk}}, k_{rr}^{\text{Bulk}}, k_{\theta\theta}^{\text{Bulk}}, k_{\theta\theta\theta}^{\text{Bulk}}$ given in [42]. Finally, we numerically solve the eigenvalue equation given in Eq. (2.5). In our approximation we assume for simplicity that the dynamical matrix associated with the atoms between the defect and the bulk is equal to the dynamical matrix of the bulk. Even with this approximations, we obtain an accurate phononic dispersion relation in comparison with *ab initio* calculations. In Figure A.3 we show the ordered phonon frequencies for a periodic diamond lattice using the force-constant model to second nearest-neighbor interaction and an *ab initio* calculation of a super cell with 63 atoms with one SiV-center.



Figure A.3: Comparison between the phonon frequencies using the force-constant model and *ab initio calculations*.

A.4 Electron-phonon coupling constants and Gaussian orbitals

The electron-phonon coupling constants given in Eqs. (2.12)-(2.13) can be numerically solved by estimating the following integral

$$\langle i | \left(\frac{\partial V_{\text{e-Ion}}}{\partial u_{i\alpha}} \right) \Big|_{\mathbf{R}_0} | j \rangle = \int_{\mathbb{R}^3} \varphi_i^*(\mathbf{r}) \left(\frac{\partial V_{\text{e-Ion}}}{\partial u_{i\alpha}} \right) \Big|_{\mathbf{R}_0} \varphi_j(\mathbf{r}) \, d\mathbf{r}, \tag{A.23}$$

where the electron-Ion potential is modeled by a screening Coulomb potential given by

$$V_{\text{e-Ion}} = -\sum_{i=1}^{N_{\text{D}}} \frac{k_e Z_i e^2}{\varepsilon_{\text{D}} |\mathbf{r} - \mathbf{R}_i|}, \quad \mathbf{R}_i = \mathbf{R}_i^{(0)} + \mathbf{u}_i, \tag{A.24}$$

where $k_e = 1/(4\pi\varepsilon_0)$ is the Coulomb constant, $\varepsilon_D = 10$ is the diamond dielectric constant, and the effective charge $Z_i = 3.25, 4.15$ for carbon and silicon atoms, respectively. The electronic wavefunctions $\varphi_i(\mathbf{r})$ are approximated by symmetrized Gaussian orbitals in order to numerically solve the integral given in Eq. (B.56). In this approximation, the single atomic orbitals for the carbon and silicon atoms are written as linear combinations of the following Gaussian orbitals,

$$s_a = \left(\frac{2a}{\pi}\right)^{3/4} \exp\left(-a|\mathbf{r} - \mathbf{r}_a|^2\right), \qquad (A.25)$$

$$p_{ak} = \sqrt{4\pi} \left(\frac{2a}{\pi}\right)^{3/4} \mathbf{e}_k \cdot (\mathbf{r} - \mathbf{r}_a) \exp\left(-a|\mathbf{r} - \mathbf{r}_a|^2\right), \qquad (A.26)$$

where $\mathbf{e}_k = {\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}}$ for $k = {x, y, z}$. The integral (B.56) can be numerically solved using spherical coordinates (r, θ, ϕ) and the seed integral is given by

$$\int_{\mathbb{R}^3} \frac{1}{r} \exp\left(-a|\mathbf{r} - \mathbf{A}|^2\right) \exp\left(-b|\mathbf{r} - \mathbf{B}|^2\right) \, d\mathbf{r} = S \, \frac{\operatorname{erf}(\sqrt{c} \, u)}{u},\tag{A.27}$$

where

$$S = \left(\frac{2\sqrt{ab}}{a+b}\right)^{3/2} \exp\left(-\frac{ab}{a+b}|\mathbf{A}-\mathbf{B}|^2\right), \qquad (A.28)$$

$$c = a+b,$$
 $u = \frac{a|\mathbf{A}| + b|\mathbf{B}|}{a+b},$ (A.29)

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^{2}} dt.$$
 (A.30)

Note that integrals involving p-orbitals can be obtained by taking the derivative of equation (A.27) with respect to some of the components of the ion positions **A** or **B**. The exponential decay constants of the Gaussian orbitals given in Eqs. (A.25) and (A.26) are determined by minimizing the error on the radial probability distribution with respect to the radial probability distribution of the Slater orbitals. We obtain a = 1.7105 Å⁻² for the carbon atoms and a = 2.9879 Å⁻² for the silicon atom.

A.5 Silicon contribution to the electronic and phonon calculations

In this section we describe the effect of a small change in the silicon mass on the phonon frequency of localized phonon modes with a predominant oscillation of the silicon atom. In



Figure A.4: Silicon contribution to the dynamical matrix. The dynamical matrix is a matrix with $3N_{\text{Lat}} \times 3N_{\text{Lat}}$ elements and the elements that contains a silicon contribution are marked by the pink regions of the matrix D^{Defect} (A.20) and the interaction matrix D^{I} (A.19).

addition, we show some numerical results in order to confirming the contribution of 2s-like atomic orbitals in the ground state configuration of the SiV⁻ center when phonons are not present. Finally, we compare our predicted phonon frequencies with *ab initio* calculations.

There are three stable silicon isotopes in the diamond lattice (²⁸Si, ²⁹Si, and ³⁰Si), and they differ each other by a small amount of mass. A small change in the silicon mass can be represent by the following transformation

$$M_{\rm Si} \longrightarrow M_{\rm Si} + \delta M_{\rm Si},$$
 (A.31)

where $M_{\rm Si}$ is the silicon mass and $\delta M_{\rm Si}$ is a small mass, i.e., $\delta M_{\rm Si} \ll M_{\rm Si}$. Under the mass transformation introduced in Eq. (A.31) the dynamical matrix $D_{i\alpha,j\beta}$ defined in Eq. (2.6) transform as

$$D_{i\alpha,j\beta} \longrightarrow D_{i\alpha,j\beta} + \delta D_{i\alpha,j\beta},$$
 (A.32)

where $\delta D_{i\alpha,j\beta}$ has the matrix structure shown in Fig. A.4, and is mathematically given by

$$\delta D_{i\alpha,j\beta} = -\frac{\delta M_{\rm Si}}{M_{\rm Si}} D_{i\alpha,j\beta}, \qquad i,j=1, \quad \alpha,\beta=x,y,z, \tag{A.33}$$

where i, j = 1 are de indices for the Silicon atom in our numerical simulations. Now we evaluate the effect of the mass transformation introduced in Eq. (A.31) on a finite sized lattice composed of N_{Lat} atoms. First, the eigenvalue equation from which we calculate the



Figure A.5: Phonon frequencies of the three stable silicon isotopes.

phonon frequencies of system can be written as

$$\mathbb{D} \cdot \mathbf{h}_l = \omega_l^2 \mathbf{h}_l, \tag{A.34}$$

where \mathbb{D} , \mathbf{h}_l and ω_l^2 are the dynamical matrix, eigenvectors, and eigenvalues, respectively. From perturbation theory we can obtain the following transformations on the eigenvalues and eigenvectors when the dynamical matrix transform as $\mathbb{D} + \delta \mathbb{D}$

$$\omega_l^2 \longrightarrow \omega_l^2 + \mathbf{h}_l^\top \cdot \delta \mathbb{D} \cdot \mathbf{h}_{0l}$$
(A.35)

$$\mathbf{h}_{l} \longrightarrow \mathbf{h}_{l} + \sum_{m \neq l} \left(\frac{\mathbf{h}_{m}^{+} \cdot \delta \mathbb{D} \cdot \mathbf{h}_{l}}{\omega_{l}^{2} - \omega_{m}^{2}} \right) \mathbf{h}_{m}.$$
(A.36)

Let be $\mathbf{h}_l^{\text{loc}}$ a localized vibrational mode with a large oscillation of the silicon atom, the eigenvector representation is given by

$$\mathbf{h}_{l}^{\text{loc}} = \begin{pmatrix} h_{1,x} \\ h_{1,y} \\ h_{1,z} \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \dim \left(\mathbf{h}_{l}^{\text{loc}} \right) = 3N_{\text{Lat}}. \quad (A.37)$$

If the mass of the silicon atom increases from $M_{\rm Si}$ to $M_{\rm Si} + \delta M_{\rm Si}$ the phonon frequency of



Figure A.6: Silicon contribution to the ground state electronic state of the SiV⁻ center in diamond.

the localized phonon changes as the following

$$\omega_l^2 \longrightarrow \omega_l^2 + \left(\mathbf{h}_l^{\text{loc}}\right)^\top \cdot \delta \mathbb{D} \cdot \mathbf{h}_l^{\text{loc}}.$$
(A.38)

Using the relation given in Eq. (A.33) and the eigenvalue equation we deduce that

$$\delta \mathbb{D} \cdot \mathbf{h}_{l}^{\text{loc}} = -\frac{\delta M_{\text{Si}}}{M_{\text{Si}}} \left(\mathbb{D} \cdot \mathbf{h}_{l}^{\text{loc}} \right) = -\frac{\delta M_{\text{Si}}}{M_{\text{Si}}} \left(\omega_{l}^{2} \mathbf{h}_{l}^{\text{loc}} \right).$$
(A.39)

Therefore, the frequency of a localized phonon mode with a large vibration of the silicon atom transform as

$$\omega_l^{\text{loc}} \longrightarrow \omega_l^{\text{loc}} \sqrt{\left(1 - \frac{\delta M_{\text{Si}}}{M_{\text{Si}}}\right)}.$$
(A.40)

This result show that the phonon frequency a localized phonon mode with large vibration

of the silicon atom decreases in energy if the mass of the silicon atom increases in a small factor $\delta M_{\rm Si}$. This is the physical origin of the isotopic shift described in Section 2.6 and observed in Fig. 2.3.

From *ab initio* calculations we observe that the frequency of the phonon modes for the three stable isotopes ${}^{28}M_{\rm Si}$, ${}^{29}M_{\rm Si}$ and ${}^{30}M_{\rm Si}$ are very similar with the calculations performed in a periodic diamond lattice (see Fig. A.5). For the periodic diamond lattice we used the force constant model described in Appendix A.2. Morevoer, from *ab initio* simulations we can observe the silicon contribution to the electronic distribution for the ground state. The SiV⁻ center in diamond has a slightly distorted 2*s*-orbital, but preserving the inversion symmetry of the defect (see Figure A.6). Therefore, *ab initio* calculations support the fact that inversion symmetry is not broken if vibrations are not considered.

A.6 Dynamical symmetry breaking and spectral density function

In this section we derive the modified spectral density function due to dynamical symmetry breaking. Let $V(t) = V_u e^{-i\omega_{\rm ph}t}$ be a periodic time-dependent operator which perturbs the localized electronic degree of freedom of SiV⁻ center. Using time dependent perturbation theory we can define the electronic wavefunctions given in Eqs. (2.24)-(2.25). As a consequence of the mixing effect induced by this external perturbation the effective electronphonon coupling must be calculated as follows

$$\lambda_{\Phi_{e,l}} - \lambda_{\Phi_{g,l}} = f(\epsilon) \left[\lambda_{e,l} - \lambda_{g,l} \right] + g(\epsilon) \lambda_{e,g,l}, \tag{A.41}$$

where

$$f(\epsilon) = 1 - 2\epsilon^2, \qquad g(\epsilon) = 4\epsilon\sqrt{1 - \epsilon^2}\cos\theta.$$
 (A.42)

The coupling constants $\lambda_{g,l}$, $\lambda_{e,l}$, and $\lambda_{eg,l}$ are the electron-phonon coupling constants associated to the unperturbed electronic states $|\Psi_g^{(0)}\rangle$ and $|\Psi_e^{(0)}\rangle$, respectively. Here θ is an arbitrary phase and ϵ is a mixing parameter approximately given by

$$\epsilon \approx \frac{\langle e|V_u|g\rangle}{\hbar \left(\omega_{eg} - \omega_{\rm ph}\right)},\tag{A.43}$$

where V_u is the intensity of the periodic perturbation perturbation, $\hbar\omega_{eg}$ is the electronic gap between the excited and ground states, and $\hbar\omega_{\rm ph}$ is the energy of the phonon mode. For the SiV⁻ center $\hbar\omega_{eg} = 1.68$ eV and $V_u \ll \hbar\omega_{eg}$, therefore we expect that $|\epsilon| \ll 1$. By symmetry considerations only phonons with character odd or even contribute to the effective coupling constants $\lambda_{e,l} - \lambda_{g,l}$ or $\lambda_{e,g,l}$, respectively. As a consequence of both symmetry constraints we deduce that $(\lambda_{e,l} - \lambda_{g,l}) \lambda_{e,g,l} = 0$ for each lattice mode l. Finally, taking the limit $|\epsilon| \ll 1$ and averaging over the phase the spectral density function is

$$J(\omega) = \sum_{l} \left(\lambda_{\phi_{e,l}} - \lambda_{\phi_{g,l}} \right)^2 \delta(\omega - \omega_l) = J_0(\omega) + 8\epsilon^2 J_{eg}(\omega), \tag{A.44}$$

and we recover the spectral density function given in Eq. (2.26).

Appendix B

Supporting Material for Chapter 3

B.1 Fermi golden rule

In this section we derive the analytic form of the second-order phonon-induced spin relaxation rates introduced in Sec. III. b. To second order in time-dependent perturbation theory the transition rate between an initial $|i\rangle$ and final state $|f\rangle$ is given by

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| V_{fi} + \sum_{m} \frac{V_{fm} V_{mi}}{E_i - E_m} \right|^2 \delta(E_i - E_f), \tag{B.1}$$

where $V_{ij} = \langle i | \hat{H}_{s-ph} | j \rangle$, with \hat{H}_{s-ph} being the perturbation. In Eq. (B.1) the sum over m denotes all possible intermediate states $|m\rangle$ for which $V_{fm}V_{mi} \neq 0$. Here, E_i , E_f , and E_m are the energies of the initial, final, and intermediate states, respectively. For the Stokes transition the initial and final states are given by $|i\rangle = |m_s, n_k, n_{k'}\rangle$ and $|f\rangle = |m'_s, n_k - 1, n_{k'} + 1\rangle$. Let us write the spin-phonon Hamiltonian given in Eq. (3.6) as $\hat{H}_{s-ph} = V^{(1)} + V^{(2)}$ with $V^{(1)} = \sum_i \sum_{k \in \Gamma_i} \lambda_{k,i} (\hat{b}_k + \hat{b}_k^{\dagger}) \hat{F}_i(\mathbf{S})$ and $V^{(2)} = \sum_i \sum_{k \otimes k' \in \Gamma_i} \lambda_{kk',i} (\hat{b}_k + \hat{b}_k^{\dagger}) (\hat{b}_{k'} + \hat{b}_{k'}^{\dagger}) \hat{F}_i(\mathbf{S})$ being the linear and quadratic spin-phonon interactions, respectively. It is straightforward to verify that $V_{fm}^{(2)}V_{mi}^{(2)} = V_{fm}^{(1)}V_{mi}^{(2)} = V_{fm}^{(2)}V_{mi}^{(1)} = 0$ for every intermediate state $|m\rangle$ with initial and final states for Stokes transition, i.e., $|i\rangle = |m_s, n_k, n_{k'}\rangle$ and $|f\rangle = |m'_s, n_k - 1, n_{k'} + 1\rangle$. In other words, the contribution of the quadratic term $V^{(2)}$ is zero to second order. This implies that lower order perturbation theory combined with higher order phonon coupling wins over higher order perturbation theory state order coupling [59]. Similar arguments can be applied to the other two-phonon processes.

The non-zero contributions to the transition rate can be obtained if we expand the phonon part of the summation for the intermediate states $|n_p, n_{p'}\rangle = \{|n_k - 1, n_{k'}\rangle, |n_k, n_{k'} + 1\rangle\},$ we obtain

$$\Gamma_{m_{s},n_{k},n_{k'}}^{m'_{s},n_{k}-1,n_{k'}+1} = \frac{2\pi}{\hbar} \left| \sum_{i} g_{i}^{m'_{s},m_{s}} \lambda_{kk',i} + \frac{1}{\hbar} \sum_{m''_{s}} \sum_{i,j} \lambda_{k',i} \lambda_{k,j} \left(\frac{g_{i}^{m'_{s},m''_{s}}g_{j}^{m''_{s},m_{s}}}{\omega_{k}} - \frac{g_{i}^{m''_{s},m_{s}}g_{j}^{m'_{s},m''_{s}}}{\omega_{k'}} \right) \right|^{2} \times n_{k}(n_{k'}+1)\delta(\omega_{m'_{s},m_{s}}-\omega_{k}+\omega_{k'}),$$
(B.2)

where $g_i^{m_s,m'_s} = \langle m_s | \hat{F}_i(\mathbf{S}) | m'_s \rangle$, and the summation over *i* and *j* is over x, y, x', y', z. Here, we have used the approximation $\omega_{k,k'} \gg \omega_{m_s,m''_s}$. By taking the continuous limit and using the density of phonon states given in Eq. (3.36) we obtain

$$a_{m_s,m_s'}^{\text{Stokes}}(x_D) = \frac{2\pi D_0^2}{\hbar^3 \omega_D^{4\nu+2d-2}} \int_0^{x_D} n(x) (n(x - x_{m_s',m_s}) + 1) x^{2\nu+d-1} (x - x_{m_s',m_s})^{2\nu+d-1} \\ \times \left| \sum_{m_s'} \sum_{i,j} \lambda_{0i} \lambda_{0j} \left(\frac{g_i^{m_s',m_s'} g_j^{m_s',m_s}}{x} - \frac{g_i^{m_s',m_s} g_j^{m_s',m_s'}}{(x - x_{m_s',m_s})} \right) \right|^2 dx, \quad (B.3)$$

$$b_{m_s,m_s'}^{\text{Stokes}}(x_D) = \frac{2\pi D_0^2}{\hbar^2 \omega_D^{4\nu+2d-2}} \int_0^{x_D} n(x) (n(x - x_{m_s',m_s}) + 1) x^{2\nu+d-1} (x - x_{m_s',m_s})^{2\nu+d-1} \\ \times 2\text{Re} \left[\sum_{m_s''} \sum_{i,i',j'} \lambda_{00i} \lambda_{0i'} \lambda_{0j'} \left(\frac{g_{i'}^{m_s',m_s'} g_{j'}^{m_s',m_s}}{x} - \frac{g_{i'}^{m_s',m_s} g_{j'}^{m_s',m_s}}{(x - x_{m_s',m_s})} \right) \right] dx, (B.4)$$

$$c_{m_s,m_s'}^{\text{Stokes}}(x_D) = \frac{2\pi D_0^2 \left| \sum_i g_i^{m_s',m_s} \lambda_{00i} \right|^2}{\hbar \omega_D^{4\nu+2d-2}} \int_0^{x_D} n(x) (n(x - x_{m_s',m_s}) + 1) x^{2\nu+d-1} (x - x_{m_s',m_s}) \right] dx, (B.4)$$

where for a three dimensional lattice $D_0 = \Omega \omega_D^2 / (2\pi v_s^3)$, ω_D is the Debye frequency, d is the dimension of the lattice, ν is the scaling of the spin-phonon coupling for acoustic phonons [see Eq. (3.22)]. Here, $x_D = \hbar D / (k_B T)$, $x_{m'_s,m_s} = \hbar \omega_{m'_s,m_s} / (k_B T)$, in which $\omega_{m'_s,m_s} = \omega_{m'_s} - \omega_{m_s}$, k_B is the Boltzmann constant, \hbar is the Planck constant, and T is the temperature. Similar formulas can be obtained for the other processes (Direct, Anti-Stokes and Spontaneous emission).

B.2 Quantum master equation

In this section we solve the quantum master equation for the ground state spin degree of freedom of the NV⁻ center in diamond. By solving the quantum master equation given in Eq. (3.45), for the spin populations $p_1 = \langle m_s = 1 | \hat{\rho} | m_s = 1 \rangle$, $p_2 = \langle m_s = 0 | \hat{\rho} | m_s = 0 \rangle$, and $p_3 = \langle m_s = -1 | \hat{\rho} | m_s = -1 \rangle$, we obtain

$$\dot{p}_1 = -\Gamma'_1 p_1 + \Gamma'_2 p_2 + \Gamma_3 p_3,$$
 (B.6)

$$\dot{p}_{2} = -\Gamma'_{4}p_{2} + \Gamma'_{5}p_{1} + \Gamma'_{6}p_{3},$$

$$\dot{p}_{3} = -\Gamma'_{7}p_{3} + \Gamma_{8}p_{1} + \Gamma'_{9}p_{2},$$
 (B.7)

where $\Gamma'_i = \Gamma_i + \Gamma_{\text{mag}}/2$, and the phonon-induced spin relaxation rates are given by

$$\Gamma_{1} = \Gamma_{\rm em}^{1,1-\rm ph} + \Gamma_{\rm em}^{1,2-\rm ph} + \Gamma_{\rm em}^{2,1-\rm ph} + \Gamma_{\rm em}^{2,2-\rm ph}, \qquad (B.8)$$

$$\Gamma_2 = \Gamma_{\rm abs}^{2,1-\rm ph} + \Gamma_{\rm abs}^{2,2-\rm ph}, \tag{B.9}$$

$$\Gamma_3 = \Gamma_{\rm abs}^{1,1-\rm ph} + \Gamma_{\rm abs}^{1,2-\rm ph}, \qquad (B.10)$$

$$\Gamma_{4} = \Gamma_{abs}^{2,1\text{-ph}} + \Gamma_{abs}^{2,2\text{-ph}} + \Gamma_{abs}^{3,1\text{-ph}} + \Gamma_{abs}^{3,2\text{-ph}}, \tag{B.11}$$

$$\Gamma_5 = \Gamma_{\rm em}^{2,1-\rm ph} + \Gamma_{\rm em}^{2,2-\rm ph},$$
(B.12)

$$\Gamma_6 = \Gamma_{\rm em}^{3,1\text{-ph}} + \Gamma_{\rm em}^{3,2\text{-ph}},$$
(B.13)

$$\Gamma_{7} = \Gamma_{abs}^{1,1-ph} + \Gamma_{abs}^{1,2-ph} + \Gamma_{em}^{3,1-ph} + \Gamma_{em}^{3,2-ph}, \qquad (B.14)$$

$$\Gamma_8 = \Gamma_{\rm em}^{1,1-\rm ph} + \Gamma_{\rm em}^{1,2-\rm ph},$$
(B.15)

$$\Gamma_9 = \Gamma_{\rm abs}^{3,1-\rm ph} + \Gamma_{\rm abs}^{3,2-\rm ph}.$$
 (B.16)

where $\Gamma_1 = \Gamma_5 + \Gamma_8$, $\Gamma_4 = \Gamma_2 + \Gamma_9$, and $\Gamma_7 = \Gamma_3 + \Gamma_6$, which implies that $\dot{p}_1 + \dot{p}_2 + \dot{p}_3 = 0$, and therefore, $\text{Tr}(\hat{\rho}) = 1$. The analytic solution for the populations $p_i(t)$ are determined by the following general solution

$$\begin{pmatrix} p_1(t) \\ p_2(t) \\ p_3(t) \end{pmatrix} = \sum_{i=1}^3 C_i \mathbf{v}_i e^{\lambda_i t}, \qquad (B.17)$$

where \mathbf{v}_i and λ_i are the eigenvectors and eigenvalues associated to the set of coupled linear equations of motions given by Eqs. (B.6)-(B.7). The eigenvalues are given by

$$\lambda_1 = -\frac{1}{2} \left[\Gamma_{\text{mag}} + \Gamma_{\text{ph}} + \sqrt{\Delta} \right], \qquad (B.18)$$

$$\lambda_2 = -\frac{1}{2} \left[\Gamma_{\text{mag}} + \Gamma_{\text{ph}} - \sqrt{\Delta} \right], \qquad (B.19)$$

$$\lambda_3 = 0, \tag{B.20}$$

where

$$\Gamma_{\rm ph} = \Gamma_1 + \Gamma_2 + \Gamma_7 = \sum_{i=1}^3 \left(\Gamma_{\rm abs}^i + \Gamma_{\rm ems}^i \right), \qquad (B.21)$$

is the total phonon-induced spin relaxation rate, and

$$\Delta = \Gamma_{\text{mag}}^{2} + 2\Gamma_{\text{mag}}(\Gamma_{9} - \Gamma_{8}) + \Gamma_{2}^{2} + \Gamma_{3}^{2} + (\Gamma_{1} - \Gamma_{6} - \Gamma_{9})^{2} -2\Gamma_{2}(\Gamma_{7} - \Gamma_{5} + \Gamma_{8} - \Gamma_{9} - \Gamma_{\text{mag}}) -2\Gamma_{3}(\Gamma_{5} - \Gamma_{6} - \Gamma_{8} + \Gamma_{9} + \Gamma_{\text{mag}}).$$
(B.22)

If we consider the initial condition $\rho_{00}(0) = 1$ (ground state) and considering that $\langle S_z(t) \rangle \to 0$ when $t \to \infty$, we finally obtain

$$\langle S_z(t) \rangle = e^{-\left(\Gamma_{\text{mag}} + \Gamma_{\text{ph}}\right)t} \sinh(\Delta t) \propto e^{-t/T_1}.$$
 (B.23)

Therefore, by assuming that $(2\Gamma_{\text{mag}} + \Gamma_{\text{ph}})/2 > \Delta$, we can recover the longitudinal relaxation rate given in Eq. (3.75).

B.3 Electric field fluctuations induced spin relaxation

In order to model the effect of an electric noise on the spin transitions $|m_s = 1\rangle \leftrightarrow |m_s = -1\rangle$ we introduce the following Hamiltonian for the NV⁻ center in diamond ($\hbar = 1$)

$$\hat{H} = DS_z^2 + E_x(t) \left(S_x^2 - S_y^2 \right) + E_y(t) \left(S_x S_y + S_y S_x \right) + \gamma BS_z,$$
(B.24)

where $D/2\pi = 2.87$ GHz is the zero-field splitting constant, $E_x(t)$ and $E_y(t)$ are the components of the electric field fluctuations, B is an static field aligned with the symmetry axis of the NV⁻ center, $\gamma_s/2\pi \approx 2.8$ MHZ/G is the gyromagnetic ratio, and S_x, S_y, S_z are the Pauli matrices for spin S = 1. We assume stationary stochastic processes for the components of the electric field fluctuations $E_x(t)$ and $E_y(t)$

$$\langle E_i(t) \rangle = 0, \tag{B.25}$$

$$\langle E_i(\omega)E_j(\omega')\rangle = S(\omega)\delta(\omega+\omega'), \quad i,j=x,y.$$
 (B.26)

where the spectral function is given by a Lorentzian function as the following

$$S(\omega) = \frac{\Delta^2 \tau_c}{\pi \left(1 + (\omega \tau_c)^2\right)},\tag{B.27}$$

where τ_c is the correlation time and Δ^2 is the power of the electric field fluctuations

$$\int_{-\infty}^{\infty} S(\omega) \, d\omega = \Delta^2. \tag{B.28}$$

Here, we have assumed an isotropic noise for the components of the electric field.

By considering that the wavefunction can be written as a linear combination of the spin states $|m_s = 0, \pm 1\rangle$ we can write

$$|\Psi(t)\rangle = c_{+}(t) |m_{s} = +1\rangle + c_{0}(t) |m_{s} = 0\rangle + c_{-}(t) |m_{s} = -1\rangle, \qquad (B.29)$$

from the Schrödinger equation $i\hbar \frac{d|\Psi(t)\rangle}{dt} = \hat{H} |\Psi(t)\rangle$ we obtain $(\hbar = 1)$

$$\dot{c}_{+} = -i(D+\gamma B)c_{+} - iE_{-}c_{-},$$
 (B.30)

$$\dot{c}_0 = 0, \tag{B.31}$$

$$\dot{c}_{-} = -i(D - \gamma B)c_{-} - iE_{+}c_{+}.$$
 (B.32)

where $E_{\pm}(t) = E_x(t) \pm iE_y(t)$. If we introduce the new variables (capital letters)

$$C_{+}(t) = e^{i(D+\gamma B)t}c_{+}(t), \qquad C_{-}(t) = e^{i(D-\gamma B)t}c_{-}(t),$$
 (B.33)

we obtain the following set of equations

$$\dot{C}_{+} = -iE_{-}e^{2i\gamma Bt}C_{-},$$
(B.34)

$$\dot{C}_{-} = -iE_{+}e^{-2i\gamma Bt}C_{+}.$$
 (B.35)

For pure states, the density matrix elements are given by

$$\rho_{11} = \langle m_s = +1 | \rho(t) | m_s = +1 \rangle = C_+(t) C_+^*(t), \qquad (B.36)$$

$$\rho_{33} = \langle m_s = -1 | \rho(t) | m_s = -1 \rangle = C_-(t) C_-^*(t), \qquad (B.37)$$

$$\rho_{13} = \langle m_s = +1 | \rho(t) | m_s = -1 \rangle = e^{-2i\gamma Bt} C_+(t) C_-^*(t), \qquad (B.38)$$

$$\rho_{31} = \langle m_s = -1 | \rho(t) | m_s = +1 \rangle = e^{2i\gamma Bt} C_{-}(t) C_{+}^{*}(t), \qquad (B.39)$$

from which it follows that

$$\dot{\rho}_{11} = -iE_{-}(t)\rho_{31} + iE_{+}(t)\rho_{13}, \qquad (B.40)$$

$$\dot{\rho}_{33} = -iE_+(t)\rho_{13} + iE_-(t)\rho_{31},$$
(B.41)

$$\dot{\rho}_{13} = -2i\gamma B\rho_{13} + iE_{-}(t)\left(\rho_{11} - \rho_{33}\right), \qquad (B.42)$$

$$\dot{\rho}_{31} = 2i\gamma B\rho_{31} - iE_{+}(t)\left(\rho_{11} - \rho_{33}\right). \tag{B.43}$$

By formal integration of Eqs. (B.42) and (B.43) and considering $\rho_{13}(0) = 0$ we obtain

$$\rho_{13}(t) = i \int_0^t E_-(t_1) e^{-2i\gamma B(t-t_1)} \left(\rho_{11}(t_1) - \rho_{33}(t_1)\right) dt_1, \quad \rho_{31}(t) = \rho_{13}^*(t), \quad (B.44)$$

replacing in Eq. (B.40) we get

$$\dot{\rho}_{11} = -\int_0^t E_+(t)E_-(t_1)e^{-2i\gamma B(t-t_1)}\left(\rho_{11}(t_1) - \rho_{33}(t_1)\right) dt_1 + c.c.$$
(B.45)

In the Markov approximation for the limit $t \gg \tau_c$ we have

$$\dot{\rho}_{11} \approx -\left(\rho_{11}(t) - \rho_{33}(t)\right) \int_0^t E_+(t) E_-(t_1) e^{-2i\gamma B(t-t_1)} dt_1 + c.c.$$
(B.46)

If we define

$$\gamma(t) = \int_0^t E_+(t) E_-(t_1) e^{-2i\gamma B(t-t_1)} dt_1, \qquad (B.47)$$

we get the following set of linear equations

$$\dot{\rho}_{11} = -\Gamma(t)\rho_{11} + \Gamma(t)\rho_{33},$$
 (B.48)

$$\dot{\rho}_{33} = \Gamma(t)\rho_{11} - \Gamma(t)\rho_{33},$$
 (B.49)

(B.50)

where $\Gamma(t) = \gamma(t) + \gamma^*(t)$. The above system of linear equations can be written as

$$\vec{\rho} = L(t)\vec{\rho}(t), \qquad \vec{\rho}(0) = \vec{\rho}_0,$$
 (B.51)

where

$$\vec{\rho}(t) = \begin{pmatrix} \rho_{11} \\ \rho_{33} \end{pmatrix}, \qquad L(t) = \begin{pmatrix} -\Gamma(t) & \Gamma(t) \\ \Gamma(t) & -\Gamma(t) \end{pmatrix}$$
(B.52)

The formal solution of Eq. (B.51) is given by

$$\vec{\rho}(t) = \exp\left(\int_0^t L(t_2) \, dt_2\right) \vec{\rho_0},\tag{B.53}$$

Since the electric field fluctuations are very small we can expand the exponential to first order. Taking the average we obtain

$$\langle \vec{\rho}(t) \rangle \approx \left(1 + \int_0^t \langle L(t_2) \rangle \, dt_2 \right) \vec{\rho_0}.$$
 (B.54)

The elements of the above integral are given by

$$\int_0^t \langle \Gamma(t_2) \rangle \, dt_2 = \int_0^t \langle \gamma(t_2) \rangle \, dt_2 + c.c. \tag{B.55}$$

Using Eq. (B.47) we get

$$\int_{0}^{t} \langle \gamma(t_2) \rangle \, dt_2 = \int_{0}^{t} dt_2 \int_{0}^{t_2} dt_1 \langle E_+(t_2) E_-(t_1) \rangle e^{-2i\gamma B(t_2 - t_1)}, \tag{B.56}$$

From Eq. (B.26) we can write

$$\langle E_{+}(t_{2})E_{-}(t_{1})\rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle E_{x}(\omega)E_{x}(\omega')\rangle e^{i\omega t_{2}} e^{i\omega' t_{1}} d\omega d\omega', \qquad (B.57)$$

$$= \frac{1}{\pi} \int_{-\infty}^{+\infty} e^{i\omega(t_2 - t_1)} S(\omega) \, d\omega, \qquad (B.58)$$

$$= \frac{\Delta^2 \tau_c}{\pi^2} \int_{-\infty}^{+\infty} \frac{e^{i\omega(t_2 - t_1)}}{1 + (\omega \tau_c)^2} d\omega$$
(B.59)

$$= \frac{\Delta^2}{\pi} e^{-|t_2 - t_1|/\tau_c}.$$
 (B.60)

In order to solve the integral in Eq. (B.56) we introduce the new variables $\tau = t_2 - t_1$ and $T = (t_1 + t_2)/2$. Because of the short correlation time and shape of the correlation function

[see Eq. (B.60)] we can extend the limits of the integral over τ from $-\infty$ to $+\infty$

$$\int_0^t \langle \gamma(t_2) \rangle \, dt_2 \approx \frac{\Delta^2}{\pi} \int_0^t dT \int_{-\infty}^{+\infty} d\tau e^{-|\tau|/\tau_c} e^{-2i\gamma B\tau} = \frac{\Delta^2 t}{\pi} S(2\gamma B), \tag{B.61}$$

where $S(\omega)$ is the spectral function given in Eq. (B.27). Therefore, the relaxation rate induced by electric field fluctuations between $|m_s = -1\rangle \leftrightarrow |m_s = +1\rangle$ is determined by the spectral function $S(\omega)$, and is given by

$$\gamma = \int_0^t \langle \gamma(t_2) \rangle + c.c. = \frac{2\Delta^2}{\pi} S(2\gamma B).$$
 (B.62)

Appendix C

Supporting Material for Chapter 4

C.1 Linear response function and absorption spectrum

The operator $\hat{A} = \sum_{ij} g_{ij} |i\rangle \langle j|$ can be written as

$$\hat{A} = \sum_{i} g_{ii}\hat{\pi}_i + \sum_{i \neq j} g_{ij}\hat{\pi}_{ij}, \qquad (C.1)$$

where $\hat{\pi}_i = |i\rangle \langle i|$ is an projector operator and $\hat{\pi}_{ij} = |i\rangle \langle j|$ $(i \neq j)$. We obtain the following sets of equations for the projector operators

$$\dot{\hat{\pi}}_{1} = \left(\Gamma_{21} + \frac{1}{2}\Gamma_{mag}\right)\hat{\pi}_{2} - \left(\Gamma_{21} + \Gamma_{31} + \Gamma_{41} + \frac{1}{2}\Gamma_{mag}\right)\hat{\pi}_{1} + \Gamma_{31}\hat{\pi}_{3} + \Gamma_{41}\hat{\pi}_{4},$$

$$\dot{\hat{\pi}}_{2} = \left(\Gamma_{12} + \frac{1}{2}\Gamma_{mag}\right)\hat{\pi}_{1} - \left(\Gamma_{12} + \Gamma_{22} + \Gamma_{42} + \frac{1}{2}\Gamma_{mag}\right)\hat{\pi}_{2}$$

$$(C.2)$$

$$\Gamma_{2} = \left(\Gamma_{12} + \frac{1}{2} \Gamma_{mag} \right) \pi_{1} - \left(\Gamma_{12} + \Gamma_{32} + \Gamma_{42} + \frac{1}{2} \Gamma_{mag} \right) \pi_{2} + \Gamma_{32} \hat{\pi}_{3} + \Gamma_{42} \hat{\pi}_{4},$$
(C.3)

$$\dot{\hat{\pi}}_{3} = \left(\Gamma_{43} + \frac{1}{2}\Gamma_{\text{mag}}\right)\hat{\pi}_{4} - \left(\Gamma_{13} + \Gamma_{23} + \Gamma_{43} + \frac{1}{2}\Gamma_{\text{mag}}\right)\hat{\pi}_{3} + \Gamma_{13}\hat{\pi}_{1} + \Gamma_{23}\hat{\pi}_{2},$$
(C.4)

$$\dot{\hat{\pi}}_{4} = \left(\Gamma_{34} + \frac{1}{2}\Gamma_{\text{mag}}\right)\hat{\pi}_{3} - \left(\Gamma_{14} + \Gamma_{24} + \Gamma_{34} + \frac{1}{2}\Gamma_{\text{mag}}\right)\hat{\pi}_{4} + \Gamma_{14}\hat{\pi}_{1} + \Gamma_{24}\hat{\pi}_{2}.$$
(C.5)

By writing the above set of equations in a matrix form, we obtain

$$\frac{\mathrm{d}\hat{\vec{\Pi}}}{\mathrm{d}t} = \mathbf{G}\hat{\vec{\Pi}}, \quad \hat{\vec{\Pi}} = \begin{pmatrix} \hat{\pi}_1(t) \\ \hat{\pi}_2(t) \\ \hat{\pi}_3(t) \\ \hat{\pi}_4(t) \end{pmatrix}, \quad (C.6)$$

where \mathbb{G} is the matrix associated with the linear set of differential equations, and given by

$$\mathbb{G} = -\frac{\Gamma_{\text{mag}}}{2} \begin{pmatrix} \mathbb{A} & 0\\ 0 & \mathbb{A} \end{pmatrix} + \mathbb{D}_{\text{diag}} + \mathbb{D}_{\text{off-diag}}, \tag{C.7}$$

where

$$\mathbb{A} = \begin{pmatrix} 1 & -1 \\ 1 & -1 \end{pmatrix},$$
(C.8)

$$\mathbb{D}_{\text{diag}} = \begin{pmatrix} \Gamma_1 & 0 & 0 & 0 \\ 0 & \Gamma_2 & 0 & 0 \\ 0 & 0 & \Gamma_3 & 0 \\ 0 & 0 & 0 & \Gamma_4 \end{pmatrix},$$
(C.9)

$$\mathbb{D}_{\text{off-diag}} = \begin{pmatrix} 0 & \Gamma_{21} & \Gamma_{31} & \Gamma_{41} \\ \Gamma_{12} & 0 & \Gamma_{32} & \Gamma_{42} \\ \Gamma_{13} & \Gamma_{23} & 0 & \Gamma_{43} \\ \Gamma_{14} & \Gamma_{24} & \Gamma_{34} & 0 \end{pmatrix}.$$
(C.10)

By solving the eigenvalue equation

$$\mathbb{G}\vec{v}_i = \lambda_i \vec{v}_i,\tag{C.11}$$

the general solution for each projector is given by

$$\hat{\pi}_i(t) = \sum_j C_{ij} e^{i\lambda_i t} \hat{\pi}_j, \qquad (C.12)$$

where λ_i are the eigenvalues of \mathbb{G} and $C_{ij} = C_j(\vec{u}_j \cdot \hat{e}_i)$ are the elements of the eigenvectors \vec{v}_k multiply by a factor $C_j \in \mathbb{C}$, being \hat{e}_i the vector basis for \mathbb{R}^4 , i.e., $\hat{e}_1 = (1, 0, 0, 0)$, $\hat{e}_2 = (0, 1, 0, 0)$, $\hat{e}_3 = (0, 0, 1, 0)$, and $\hat{e}_4 = (0, 0, 0, 1)$. The operators $\hat{\pi}_{ij}$ satisfy the following equations

$$\dot{\hat{\pi}}_{ij} = \gamma_{ij}\hat{\pi}_{ij}, \quad \hat{\pi}_{ij}(t) = e^{\gamma_{ij}t}\hat{\pi}_{ij}, \tag{C.13}$$

where we have neglected the effect of the magnetic relaxation rate Γ_{mag} and we consider that $\hat{\pi}_{ij}(0) = \hat{\pi}_{ij}$. The relaxation rates Γ_{ij}^{tot} are given by

$$\gamma_{ij} = -\frac{1}{2} \sum_{k \neq i,j} (\Gamma_{ki} + \Gamma_{kj}) + i(E_i - E_j),$$
(C.14)

where Γ_{ij} are the one-phonon relaxation rates given in Eq. (4.32) and E_i are the energy levels of the Hamiltonian \hat{H}_0 . By replacing the solution for $\hat{\pi}_i(t)$ and $\hat{\pi}_{ij}(t)$ we obtain

$$\hat{A}(t) = \sum_{i,j} g_{ii} C_{ij} e^{\lambda_j t} \hat{\pi}_j + \sum_{i \neq j} g_{ij} e^{\gamma_{ij} t} \hat{\pi}_{ij}, \qquad (C.15)$$

using the initial condition $\hat{A}(0) = \sum_{ij} g_{ij} |i\rangle \langle j|$ and the orthogonality $\langle i|j\rangle = \delta_{ij}$, we obtain

$$\langle \hat{A}(t)\hat{A}(0)\rangle = \sum_{i} |g_{ii}|^2 e^{\lambda_i t} + \sum_{i \neq j} |g_{ij}|^2 e^{\gamma_{ij} t},$$
 (C.16)

where we have used the properties $g_{ji} = g_{ij}^*$ and $g_{ii} \in \mathbb{R}$. The linear response function for $t \ge 0$ is given by

$$R(t) = 2\mathrm{Im}\left(\sum_{i} |g_{ii}|^2 e^{\lambda_i t} + \sum_{i \neq j} |g_{ij}|^2 e^{\gamma_{ij} t}\right),$$

$$= \sum_{i \neq j} |g_{ij}|^2 e^{-2\Gamma_{ij}^{\mathrm{tot}} t} \sin(\omega_{ij} t).$$
 (C.17)

The imaginary part of λ_i is zero, therefore, the only contribution to the absorption spectrum comes from the term $e^{\gamma_{ij}t}$. By written $\gamma_{ij} = -2\Gamma_{ij}^{\text{tot}} + i\omega_{ij}$ and using the linear response function given in Eq. (C.17) we can recover the absorption spectrum shown in Eq. (??) if we solve the integral given in Eq. (4.28).

Appendix D

Supporting Material for Chapter 5

D.1 Matlab Code: Strain Decomposition for the SiV⁻ center

```
function StrainSiV
1
2
3 syms a b c d e f
4 assume(a, 'real')
5 assume(b, 'real')
6 assume(c, 'real')
7 assume(d, 'real')
  assume(e, 'real')
8
   assume(f, 'real')
9
10
11 % Strain matrix (real and symmetric)
  epsilon = [a b c; b d e; c e f];
12
13
14 % Matrix representation of the elements of the C_{3v+i} group
15 R\{1\} = [1 \ 0 \ 0; \ 0 \ 1 \ 0; \ 0 \ 1];
                                                                                         % E
16 R\{2\} = [-1/2 - 1/2 \times \text{sqrt}(3) \ 0; +1/2 \times \text{sqrt}(3) -1/2 \ 0; \ 0 \ 0 \ 1];
                                                                                        % C13
17 R{3} = [-1/2 + 1/2 \times \text{sqrt}(3) \ 0; \ -1/2 \times \text{sqrt}(3) \ -1/2 \ 0; \ 0 \ 0 \ 1];
                                                                                         % C23
18 R{4} = [+1/2 + 1/2 \times \text{sqrt}(3) 0; +1/2 \times \text{sqrt}(3) -1/2 0; 0 0 -1];
                                                                                         % C2
19 R{5} = [+1/2 - 1/2 \times \text{sqrt}(3) 0; -1/2 \times \text{sqrt}(3) -1/2 0; 0 0 -1];
                                                                                        % C2'
20 R\{6\} = [-1 \ 0 \ 0; \ 0 \ 1 \ 0; \ 0 \ -1];
                                                                                         % C2''
21 R\{7\} = [-1 \ 0 \ 0; \ 0 \ -1 \ 0; \ 0 \ 0 \ -1];
                                                                                         % i
```

```
22 R\{8\} = [+1/2 + 1/2 \times \text{sqrt}(3) 0; -1/2 \times \text{sqrt}(3) + 1/2 0; 0 0 - 1];
                                                                        % S16
23 R{9} = [+1/2 - 1/2 \times \text{sqrt}(3) 0; +1/2 \times \text{sqrt}(3) +1/2 0; 0 0 -1];
                                                                        % S56
24 R\{10\} = [-1/2 - 1/2 \times \text{sqrt}(3) \ 0; \ -1/2 \times \text{sqrt}(3) \ +1/2 \ 0; \ 0 \ 0 \ 1];
                                                                        % sd
25 R{11} = [-1/2 + 1/2 \times \text{sqrt}(3) \ 0; +1/2 \times \text{sqrt}(3) + 1/2 \ 0; \ 0 \ 0 \ 1];
                                                                        % sd'
26 R\{12\} = [1 \ 0 \ 0; \ 0 \ -1 \ 0; \ 0 \ 0 \ 1];
                                                                        % Sd''
_{27} h = 12;
28
  % Character vector associated to the Irreducible Representations for each
29
  % element of the group C_{3v+i}
30
  GammaAlg = [1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1
                                      1 1 1
                                               1
                                                   1];
31
  GammaA2g = [1 \ 1 \ 1 \ -1 \ -1 \ -1 \ 1 \ 1 \ -1 \ -1 \ -1];
32
                                                0 0];
  GammaEg = [2 -1 -1 0 0 0 2 -1 -1 0]
33
  34
  1
                                                   1];
35
  GammaEu = [2 -1 -1 0 0 0 -2 1 1 0 0 0];
36
37
  % order of each Irreducible Representation
38
  lA1q = 1; lA2q = 1; lEq = 2;
39
  lA1u = 1; lA2u = 1; lEu = 2;
40
41
  % Initial strain matrices associated to the Irreducible
42
  % Representation decomposition
43
  epsilonA1g = zeros(3,3); epsilonA2g = zeros(3,3);epsilonEg = zeros(3,3);
44
  epsilonAlu = zeros(3,3); epsilonA2u = zeros(3,3);epsilonEu = zeros(3,3);
45
46
  % Numerical projective operator formula
47
  for g=1:h
48
       epsilonA1g = epsilonA1g + lA1g/h*(GammaA1g(g)*R{g}'*epsilon*R{g});
49
       epsilonA2g = epsilonA2g + lA2g/h*(GammaA2g(g)*R{g}'*epsilon*R{g});
50
       epsilonEg = epsilonEg + lEg/h*(GammaEg(g)*R{g}'*epsilon*R{g});
51
52
       epsilonAlu = epsilonAlu + lAlu/h*(GammaAlu(g)*R{g}'*epsilon*R{g});
53
       epsilonA2u = epsilonA2u + lA2u/h*(GammaA2u(q)*R{q}'*epsilon*R{q});
54
       epsilonEu = epsilonEu + lEu/h*(GammaEu(g)*R{g}'*epsilon*R{g});
55
  end
56
57
  % Simplify
58
  epsilonAlg = simplify(epsilonAlg);
59
60 epsilonA2g = simplify(epsilonA2g);
  epsilonEg = simplify(epsilonEg);
61
62
63 epsilonAlu = simplify(epsilonAlu);
```

```
64 epsilonA2u = simplify(epsilonA2u);
65 epsilonEu = simplify(epsilonEu);
66
  % Final decomposition of the strain matrix into irreducible representations
67
68
  epsilonA1g
69
70 epsilonA2g
  epsilonEg
71
72
73 epsilonAlu
74 epsilonA2u
75
  epsilonEu
76
77
  % Check properties
78
  M = epsilonA1g + epsilonA2g + epsilonEg + ...
79
             epsilonAlu + epsilonA2u + epsilonEu;
80
81
  % This difference must be equal to zero
^{82}
  ZERO = M-epsilon
83
84
85
86 end
```

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