

PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE FACULTY OF PHYSICS

# EFFECTIVE HAMILTONIANS OF THE NEGATIVELY CHARGED NITROGEN-VACANCY CENTER IN DIAMOND UNDER EXTERNAL PERTURBATIONS

by

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Thesis presented to The Institute of Physics of Pontificia Universidad Católica de Chile for the degree of Master in Theoretical Physics.

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"I have found, through painful experience, that the most important step a person can take is always the next one."

Brandon Sanderson, Oathbringer.

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### Abstract

Master in Theoretical Physics

#### by Alejandro Jiménez

Color centers in diamond are promising candidates for applications such as single photon sources, color markers for biological applications, quantum information, quantum communications and quantum sensing at the nanoscale. Such applications depend on the dynamics of the electronic spin of the center, but these dynamics are modified by different fields present in the solid. A theoretical description of the electronic spin has proven difficult as well, with different interpretations across different authors. Recent experiments have been able to access degrees of freedom of singular subspaces of the electronic spin such as the ground state, although its dynamics are affected by several other states in the system. In this thesis, we present a procedure that encompasses the effect of all higher states in the system to formulate a non-diagonal effective Hamiltonian of a particular sub Hilbert space. In this case, the ground state triplet of the center. We start by using group theory to describe the different states of the system in terms of the center symmetrize orbitals. Then we proceed to describe the different interactions in the defect such as the Coulomb interaction, spin orbit interaction, spin-spin interaction, electromagnetic field interaction and strain interaction. An effective Hamiltonian of the ground state is obtained that considers the effect of higher exited states. Finally, we compare the results with recent experimental data.

## Acknowledgements

I'd like to thank everyone who has supported me in this journey, they have been fundamental and without them I would've not been able to create this work.

I'd like to thank Dr. Jerónimo Maze and Ariel Norambuena, they have been amazing work partners and great advisors.

I'd like to thank my close family, as they have managed to tolerate my behaviour for all these years and keep giving me love.

And finally, but most important of all, I'd like to thank God, for he has given me a reason to keep on trying.

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# Abbreviations

- $\mathbf{NV}$  Nitrogen Vacancy
- SO Spin Oorbit
- SS Spin Spin

# **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	$a_B$	=	$5.2918 \times 10^{-11} \text{ m}$
Electric constant	$k_e$	=	$8.987\times 10^9~{\rm m}^{-3}{\rm kg}^{-1}{\rm s}^{4}{\rm A}^{2}$
Speed of Light	c	=	$2.997~924~58\times 10^8~{\rm ms}^{-1}$
Boltzmann Constant	$k_B$	=	$1.3806 \times 10^{-23} \text{ m}^2 \text{kgs}^{-2} \text{K}^{-1}$

# Symbols

$\omega$	Angular	Frequency	rad Hz
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- $\nu$  Linear Frequency Hz
- P power W (Js<sup>-1</sup>)

To the Giants who lent their shoulders

# Chapter 1

# Introduction

During the last decades color centers in diamond have emerged as promising candidates for applications such as electro-optical devices, single photon sources, fluorescent markers for biological measurements, quantum sensing at the atom-scale resolution, quantum information and quantum communications [2–7]. These technological applications can be realized thanks to the optical properties and room temperature stability of color centers in diamond. The existence of these possible applications have caused color centers to be the central topic of several papers [8–18]. However, many of the properties of the centers, and in particular, the ones that relate to the applications mentioned previously, are not yet understood in detail. This is the case of the effect of strain in  $NV^-$  centers.

In this thesis, we focus mainly on this problem. This chapter introduces to the general concepts of group theory. Chapter 2 gives a detailed explanation of the  $NV^-$  system, as well as explaining the interactions that we consider for this work. Chapter 3 consists in the explanation of the effective hamiltonian method and its use in the description we are building. Chapter 4 exposes experimental results found in the literature and compares them to our model. And Chapter 5 concludes this work with a summary of the main points this thesis presents and proposes possible approaches to future research.

### **1.1** Effective Hamiltonians

In quantum mechanics, the properties of a certain system are determined by its Hamiltonian. The Hamiltonian determines the energy and dynamics of the system. However, generally the complexity of the Hamiltonian exponentially increases as one increases the number of states of the system. And in many studies, one is interested in a few particular states.

Since all the states interact with each other, to get the complete picture of the states of interest, one would have to solve the Hamiltonian of the whole system, and then discard the information of the other states. This is incredibly inefficient. Therefore, most of the time, physicists look for methods that allow to summarize the effect of the other states in one simpler Hamiltonian that involves only the states of interest. This is called an Effective Hamiltonian.

As we will show in the next chapter, the NV center, despite having only four atoms, spawns a system that has fifteen states. Therefore the objective of this work is to find an effective Hamiltonian method that allows us to focus on a particular set of smaller states.

## Chapter 2

# Group Theoretical Description of the Negatively Charged Nitrogen-Vacancy Center and its Interactions

In the previous chapter we introduced the concept of effective Hamiltonians and underlined their importance. In this chapter, we will introduce the concept of group theory and the role of symmetry in describing a system. Then we will focus in our system of interest, the  $NV^-$  center, which possesses a particular set of symmetries. We will also explore how the presence of these symmetries restricts the electronic structure of the center and shapes its interactions.

### 2.1 Group Theory

In quantum mechanics, problems become exponentially difficult as one increases the number of particles of the studied system. This renders the study of a system of several particles, such as the study of solids (and more particulary, defects in solids) by a direct approach practically impossible. In studying such systems, shortcuts and clever tricks are usually employed to reduce the complexity of the task. One of those shortcuts is the exploitation of the possible symmetries a system could have.

Certain systems have properties that remain unchanged when certain transformations are applied. These transformations are associated to symmetries of the system. Group Theory



Figure 2.1: Left: Structure of the NV center in diamond; The carbons of the structure and their neighbours (cyan spheres) and the Nitrogen (blue sphere) are shown. The electronic distribution (red lobes) and the bonds that form the defect levels (in yellow) are also shown (Image taken from Ref. [1] without permission). The three orbitals  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$  and  $\sigma_n$  (which is near the nitrogen) form linear combinations that produce the symmetrized single electron orbitals (equations 2.13-2.16). Right: Same structure from a perspective perpendicular to the plane formed by the three carbons. Note that applying the rotations  $C_3^+$  and  $C_3^-$  (in orange) do not change the configuration of the system. The same applies for the reflections over the planes  $\sigma_v$ ,  $\sigma'_v$  and  $\sigma''_v$ .

is a powerful method that takes advantage of these symmetries to characterize the system. One of the properties that remain unchanged when a symmetry operator is applied is the Hamiltonian. This also implies that the symmetry operator commutes with the Hamiltonian.

$$RH = HR, (2.1)$$

where R is the symmetry operator and H is the Hamiltonian. This equation is the basis of group theory. On Appendix A we give a detailed development of this formalism and derive properties that we use in following chapters.

### 2.2 The Negatively Charged Nitrogen Vacancy System

Diamonds are crystals formed by a tetrahedrical array of carbon atoms. An NV center on the other hand, is a defect in diamond created when one of those carbon atoms is replaced by a nitrogen atom, forming the structure shown in Figure 2.1. This figure also shows the electronic distribution of the orbitals of the structure. In the diamond, when one of the carbons is replaced by a nitrogen, the structure rearranges itself, changing the position of the atoms. The place where the lost carbon was is called vacancy. And the axis that is formed between the vacancy and the nitrogen is referred to as the NV-axis.

This color center remains unchanged if a rotation of  $2\pi/3$  radians along the NV-axis, either clockwise or counterclockwise is performed, this is also true for reflections over the three planes perpendicular to the plane that contains the three carbons, and that contain one of the carbons and the nitrogen. These transformations are respectively called  $C_3^+$ ,  $C_3^-$ ,  $\sigma_v$ ,  $\sigma'_v$ and  $\sigma''_v$ .

In group theory, a group is a set of operations. These operations also have to follow certain rules. The application of two operations within the set can be summarized by the application of only one operation that is also within the set. Each element of the set must have an inverse within the set. The application of operations must follow associativity. And the set must contain the identity operation. In conjunction with the identity,  $C_3^+$ ,  $C_3^-$ ,  $\sigma_v$ ,  $\sigma'_v$  and  $\sigma''_v$  follow these rules. And these elements form the group known as  $C_{3v}$ .

It is important to note that these transformations can be represented by matrices, but they require a base. For example, we can express the three orbitals  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$  and  $\sigma_n$  by the orthonormal vectors (1, 0, 0, 0), (0, 1, 0, 0), (0, 0, 1, 0) and (0, 0, 0, 1), respectively. The representation of the  $C_{3v}$  group elements in this orbital base is,

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad C_3^+ = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad C_3^- = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (2.2)$$

$$\sigma_v = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \sigma_v' = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (2.3)$$

$C_{3v}$	E	$2C_3$	$3\sigma_v$	
$A_1$	1	1	1	$z, x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$
$\mid E$	2	-1	0	$x, y, R_x, R_y$

**Table 2.1:** Character Table for  $C_{3v}$ . In the top row, E is the identity,  $C_3$  are the two rotations, and  $\sigma_v$  are the three reflections. In the leftmost column,  $A_1$ ,  $A_2$  and E are the possible irreducible representations. In the rightmost column we display some functions that transform as the corresponding irreducible representation.

This is called a representation of the group. But it is not unique. Another representation can be made using a coordinate system on which the z-axis is equivalent to the NV-axis and the x-axis contains one of the carbons. The representation of this coordinate system in the  $C_{3v}$  group is as follows,

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3^+ = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3^- = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2.4)$$

$$\sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma'_v = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma''_v = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$
(2.5)

From the last example we note that the matrices of that representation can be decomposed in two block matrices that lie in the diagonal. One in the upper left corner of dimension 2, and another one in the bottom right corner of dimension 1. These block matrices are representations of the group, and when a representation can be decomposed in such manner it is said to be reducible.

It is possible to summarize most of the information of a representation in the traces of the elements. In group theory, these traces are referred as to characters. And a table that contains the characters of the irreducible representations of a group is called the character table of a group. The group  $C_{3v}$  possesses 3 irreducible representations, and its character table is shown in Table 2.1.

When the  $C_{3v}$  group is present in a system, it restricts the orbitals to form distributions that are also symmetric. To calculate these distributions one uses the projection operator, that is related to one particular irreducible representation, and it is defined in Equation 2.6,

$$\mathcal{P}^{(j)} = \frac{l_j}{h} \sum_R \chi^{(j)}(R) P_R, \qquad (2.6)$$

where the index j refers to the irreducible representation related to the projection operator,  $l_j$  is the order of the irreducible representation, h is the number of symmetries present in the system, R is an element of the representation,  $\chi^{(j)}(R)$  is the character associated with the representation j; and  $P_R$  is the operator related to R.

It is important to note that  $P_R$  will depend on the nature of what is being projected. For example, we could try to find which irreducible representation a rotation along the z axis  $(R_z)$  transforms as. In this case, it is not difficult to see that E and  $C_3$  do not affect  $R_z$ . However,  $\sigma_v$  does, as the inversion changes the rotation from clockwise to counter clockwise and viceversa. Therefore,

$$P_E R_z = R_z, (2.7)$$

$$P_{C_3}R_z = R_z, (2.8)$$

$$P_{\sigma_v} R_z = -R_z. \tag{2.9}$$

And,

$$\mathcal{P}^{(A_1)}R_z = \frac{1}{6}(R_z + R_z + R_z - R_z - R_z - R_z) = 0, \qquad (2.10)$$

$$\mathcal{P}^{(A_2)}R_z = \frac{1}{6}(R_z + R_z + R_z + R_z + R_z + R_z) = R_z, \qquad (2.11)$$

$$\mathcal{P}^{(E)}R_z = \frac{1}{3}(2R_z - R_z - R_z) = 0.$$
(2.12)

Therefore  $R_z$  transforms as the irreducible representation  $A_2$ .

Now, using the projection operator for all the irreducible representations in one of the orbitals, we can generate symmetrized single electron orbitals,

$$a = \frac{\alpha}{\sqrt{3}} \left( \sigma_1 + \sigma_2 + \sigma_3 \right) + \beta \sigma_n, \qquad (2.13)$$

$$a' = \alpha \sigma_n + \frac{\beta}{\sqrt{3}} \left( \sigma_1 + \sigma_2 + \sigma_3 \right), \qquad (2.14)$$

$$e_x = \frac{1}{\sqrt{6}} (2\sigma_1 - \sigma_2 - \sigma_3),$$
 (2.15)

$$e_y = \frac{1}{\sqrt{2}} (\sigma_2 - \sigma_3),$$
 (2.16)

where a and a' transform as  $A_1$ ,  $e_x$  and  $e_y$  transform as E (a visual representation of  $e_x$  and  $e_y$  is shown in Figure 2.2), and  $\alpha$  and  $\beta$  are constants whose value is set by the Coulomb interaction. It is important to note that if we only apply group theory,  $\alpha$  and  $\beta$  can acquire any normalized value. However, the presence of the Coulomb interaction sets the values of these constants [19].

Over these symmetrized orbitals, the electrons of the molecule are distributed, as shown in figure 2.2. Now, if two more electrons were added to the system, the wavefunction of the defect would be a singlet with a totally symmetric spatial wavefunction, equivalent to the state of an atom with a filled shell [20][21]. Therefore, the electronic configuration of this defect can be modelled by two holes occupying the orbitals in equations 2.13-2.16 (The presence of symmetry applies further restrictions in how these orbitals are filled. We explore these restrictions in section 2.4). This hole formulation is equivalent to an electronic formulation and it makes it easier to describe the system. However, we have to be careful because in this formulation some interactions change sign [20]. This is because, as we are using holes instead of electrons, the holes would actually behave as having a positive charge instead of a negative one. This is not a problem for the interactions between the two holes, as the multiplication would eliminate the change of sign. But in the interactions that affect the holes separatedly, such as the Spin Orbit interaction, the change of sign would prevail.



Figure 2.2: Left: Example of distribution of the electrons along the symmetrized orbitals. This distribution is actually forbidden due to the effect of the symmetries, but it serves as a visual example for the electrons occupying the orbitals. Right: A visual representation of how the symmetrized orbitals  $e_x$  and  $e_y$  look like.

### 2.3 The configurations of the system

As we said in the previous section, the system can be modelled by holes in the symmetrized orbitals, as opposed to a model based on electrons. In this description we can generate three configurations. First, the ground state  $(e^2)$ , that exists when the two holes are on the  $e_x$  and  $e_y$  orbitals. Second, the exited state (ae), that can be generated from the ground state by promoting an electron from the *a* orbital to the  $e_x$  or  $e_y$  orbitals. This is equivalent to demoting a hole from the orbitals  $e_x$  or  $e_y$ , to the orbital *a*. Finally, we have the second exited state  $(a^2)$ , that promotes another electron from the *a* orbital, or, in other words, demotes another hole to the *a* orbital. Another configuration could also be made by considering the a' orbital, however, this is not considered because of the high energy separation between this orbital and the others. Each of these configurations can form triplets or singlets, with the exception of  $a^2$  which can only form a singlet. Therefore it is possible to have several different wavefunctions for each configuration.

Now, we would like to study one of these configurations in isolation from the others. Particularly, we would like to find a Hamiltonian in terms of spin operators to describe the triplet states of each configuration because many important optical properties could be derived from it. One of the problems that arises when trying to describe the configurations in isolation is that the configurations get mixed by interactions. Therefore, the states mix and change their energies in the presence of different configurations. Then, to find an effective spin Hamiltonian of a configuration in isolation, we must consider the effect of all the configurations that compose the system, and effective Hamiltonians are used to take these configurations into account.

### 2.4 States of the system

In order to find the symmetrized states of the system, we need to start with a possible wavefunction of the system (from now it will be called test function), on which we will apply the projection operator. This projection operator is different from the one we applied before, because for the case of several electrons (or holes), each one with spin, the  $P_R$  will be different. Explicitly, if we apply the projection operator to a wavefunction of the form  $|\Psi\rangle = |\psi_1 \otimes \chi_1 \otimes \psi_2 \otimes \chi_2\rangle$ , where  $\psi$  refers to an orbital function and  $\chi$  refers to a spin function, the result would be as follows[19],

$$\mathcal{P}^{(j)} |\Psi\rangle = \mathcal{P}^{(j)} |\psi_1 \otimes \chi_1 \otimes \psi_2 \otimes \chi_2\rangle = \frac{l_j}{h} \sum_R \chi^{(j)}(R) \left(T_R |\psi_1\rangle \otimes U_R |\chi_1\rangle \otimes T_R |\psi_2\rangle \otimes U_R |\chi_1\rangle\right),$$
(2.17)

where  $T_R$  is the matrix representation of a tridimentional rotation  $(SO_3)$ , associated with the  $C_{3v}$  element R, and  $U_R$  is the matrix representation of the rotation of the spins  $(SU_2)$ , associated with the  $C_{3v}$  element R.

It is important to note that the resulting wavefunction will preserve its original configuration because the application of the operators that belong to  $C_{3v}$  do not mix a with  $e_x$  and  $e_y$ . Hence, for each configuration we will need a different test function. This is also true for the spin, if we start with a test function that has certain spin for an electron pair, we will not be able to produce a symmetrized state that contains on its terms that electron pair coupled with a different spin.

The final consideration that we have to make before finding the symmetrized states is that the irreducible representation E has two partner functions associated for each test function. However, the application of the projection operator only provides one of them. To find the other one, it is possible to use the projection operator defined in Equation 2.18 in combination with the diagonal elements of a matrix representation of E (we use the one found in [22])

$$\mathcal{P}_{\nu\kappa}^{(i)} = \frac{l_i}{h} \sum_R \Gamma^{(i)}(R)_{\nu\kappa} P_R.$$
(2.18)

Configuration	State	Irreducible Representation
	$ ^{3}A_{2-}\rangle =  e_{x}e_{y} - e_{y}e_{x}\rangle \otimes  \downarrow\downarrow\rangle$	$E_1 + E_2$
$e^2(T)$	$  ^{3}A_{20}\rangle =  e_{x}e_{y} - e_{y}e_{x}\rangle \otimes  \uparrow\downarrow + \downarrow\uparrow\rangle$	$A_1$
	$ ^{3}A_{2+}\rangle =  e_{x}e_{y} - e_{y}e_{x}\rangle \otimes  \uparrow\uparrow\rangle$	$E_1 - E_2$
	$ ^{1}E_{1}\rangle =  e_{x}e_{x} - e_{y}e_{y}\rangle \otimes  \uparrow\downarrow - \downarrow\uparrow\rangle$	$E_1$
$e^2(S)$	$   ^{1}E_{2}\rangle =  e_{x}e_{y} + e_{y}e_{x}\rangle \otimes  \uparrow\downarrow - \downarrow\uparrow\rangle$	$E_2$
	$  ^{1}A_{1}\rangle =  e_{x}e_{x} + e_{y}e_{y}\rangle \otimes  \uparrow\downarrow - \downarrow\uparrow\rangle$	$A_1$
	$ A_1\rangle =  E\rangle \otimes  \uparrow\uparrow\rangle -  E_+\rangle \otimes  \downarrow\downarrow\rangle$	$A_1$
	$ A_2\rangle =  E\rangle \otimes  \uparrow\uparrow\rangle +  E_+\rangle \otimes  \downarrow\downarrow\rangle$	$A_2$
ea(T)	$ E_1\rangle =  E\rangle \otimes  \downarrow\downarrow\rangle -  E_+\rangle \otimes  \uparrow\uparrow\rangle$	$E_1$
	$ E_2\rangle =  E\rangle \otimes  \downarrow\downarrow\rangle +  E_+\rangle \otimes  \uparrow\uparrow\rangle$	$E_2$
	$ E_y\rangle =  Y\rangle \otimes  \uparrow\downarrow + \downarrow\uparrow angle$	$E_1$
	$ E_x\rangle =  X\rangle \otimes  \uparrow\downarrow + \downarrow\uparrow\rangle$	$E_2$
ea(S)	$ ^{1}E_{x}\rangle =  ae_{x} + e_{x}a\rangle \otimes  \uparrow\downarrow - \downarrow\uparrow\rangle$	$E_1$
	$   ^{1}E_{y}\rangle =  ae_{y} + e_{y}a\rangle \otimes  \uparrow\downarrow - \downarrow\uparrow\rangle$	$E_2$
$a^2(S)$	$ ^{1}A_{1}\rangle =  aa\rangle \otimes  \uparrow\downarrow - \downarrow\uparrow\rangle$	$A_1$

With this in mind, we find all the 15 states as shown in Table 2.2.

**Table 2.2:** All the symmetrized states of the  $NV^-$  in terms of the orbitals found in equations 2.13-2.16. Here,  $|E_{\pm}\rangle = |ae_{\pm} - e_{\pm}a\rangle$ ,  $|e_{\pm}\rangle = \mp |e_x \pm ie_y\rangle$ ,  $|X\rangle = |E_- - E_+\rangle/2$  and  $|Y\rangle = |E_- + E_+\rangle i/2$ . The first column indicates the configuration of the states, which can be  $e^2$  for the ground state, ea for the first exited state and  $a^2$  for the second exited state. The parenthesis represents the multiplicity character of the states, e.g singlet (S) or triplet (T). Finally, the third column indicates the irreducible representation the state transforms as. This table matches the results found in [19].

An example of the derivation of one of these states is shown at the end of Appendix A.

### 2.5 Interactions

Now that we have found the symmetrized states, we can start describing the different interactions in terms of their matrix elements. In general, we analyze element by element which matrix element is 0 by looking at forbidden transitions with group theory. A matrix element is 0 if an interaction M follows equation Equation 2.19

$$\langle \psi_i | M | \psi_j \rangle \not\subseteq A_1. \tag{2.19}$$

#### 2.5.1 Coulomb Interaction

Since it is the most relevant for this work as the energies related to it are of the order of hundreds of Terahertz, we start with the Coulomb interaction  $(H_0)$ , which in its most elemental form is (in cgs units),

$$H_0 = \sum_{j < j'} \frac{Z_j Z_{j'} e^2}{|R_j - R_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{|r_i - R_j|} + \sum_{i < i'} \frac{e^2}{|r_i - r_{i'}|},$$
(2.20)

where R represents the position of the ions, r represents the position of the electrons, Z is the atomic number, j labels for the ions, and i is a label for the electrons.

Using equation 2.19, and the fact that this interaction transforms as  $A_1$ , we deduce that the only non-zero matrix elements are  $\langle {}^{1}E_1|H_0|{}^{1}E_x\rangle$ ,  $\langle {}^{1}E_2|H_0|{}^{1}E_y\rangle$  and  $\langle {}^{1}A_1(e^2)|H_0|{}^{1}A_1(a^2)\rangle$ , and the diagonal elements. As they share the same orbital part of the wavefunction, all the diagonal elements from the ground state triplet share the same energy, as the first exited state triplet and exited state singlet also does. Additionally, using equation 2.18, it can be shown that  $E_1$  and  $E_2$  diagonal element of the ground state singlet have the same energy and that the  $A_1$  diagonal element has twice that energy. Finally, also using equation 2.18, it can be shown that  $\langle {}^{1}E_1|H_0|{}^{1}E_x\rangle = \langle {}^{1}E_2|H_0|{}^{1}E_y\rangle$ . This also makes sense considering that if we expand  $|X\rangle$  and  $|Y\rangle$ , those two elements are an interaction of states with similar orbitals.

#### 2.5.2 Spin-Orbit Interaction

The Spin-Orbit interaction is a relativistic interaction that arises from the relative motion between the electrons and the nuclei. Its Hamiltonian is [19],

$$H_{SO} = \sum_{k} \frac{1}{2c^2 m_e^2} \mathbf{O}_k \cdot \mathbf{S}_k, \qquad (2.21)$$

where c is the speed of light,  $m_e$  is the electron mass,  $\mathbf{O}_k = \nabla_k V \times \mathbf{p}_k$ ,  $V = e\phi$  is the nuclear potential energy,  $\mathbf{p}_k$  is the momentum operator of the k-th electron and  $\mathbf{S}_k$  is the Spin operator of the k-th electron. This description allows us to generate a matrix representation of the Hamiltonian just by finding the matrix elements of the O operator, since the Spin operators are known.

Using equations 2.6, 2.18 and 2.19, we can find the matrix representation of the O operators components in the basis  $\{e_x, e_y, a\}$ . For example, project the irreducible representation  $A_1$ on the element  $\langle a|O_z|a\rangle$ , taking in consideration that  $P_R$  operates on  $O_z$  in the same manner as a rotation in the z - axis, and that, when applied to an expectation value, it operates on both states and the operator separatedly  $(P_R \langle a|O_z|a\rangle = (P_R \langle a|)(P_RO_z)(P_R|a\rangle))$ , then,

$$\mathcal{P}^{(A_1)}\langle a|O_z|a\rangle = \frac{1}{6}(\langle a|O_z|a\rangle + \langle a|O_z|a\rangle + \langle a|O_z|a\rangle - \langle a|O_z|a\rangle - \langle a|O_z|a\rangle - \langle a|O_z|a\rangle) = 0.$$
(2.22)

Therefore,  $\langle a|O_z|a\rangle$  does not belong to the  $A_1$  representation and it has a value of 0. Applying the same process to every element, we get,

$$O_x = \begin{pmatrix} 0 & iC & 0 \\ iC & 0 & iA \\ 0 & -iA & 0 \end{pmatrix},$$
(2.23)

$$O_y = \begin{pmatrix} iC & 0 & -iA \\ 0 & -iC & 0 \\ iA & 0 & 0 \end{pmatrix},$$
(2.24)

$$O_z = \begin{pmatrix} 0 & iB & 0 \\ -iB & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$
(2.25)

where A and B are unknown real constants. C is also a real number, and to maintain hermiticity, it must be 0. Also, the fact that different expectation values yield the same results is because they are partners belonging to the same irreducible representation. And partners have the same expectation values [23].

It is now possible to calculate the  $15 \times 15$  matrix representation of this interaction by using the Kronecker product with the matrices we found and computing the expectation values using the states of table 2.2. This matrix can be found in Appendix B.

The end result is that the diagonal elements are largely unaffected, with the exception of the elements associated to the states  $|A_1\rangle$ ,  $|A_2\rangle$ ,  $|E_1\rangle$  and  $|E_2\rangle$ , which acquire an energy of B for the first two, and -B for the latter two. Other than that, the states with non zero magnetic moment of the ground state mix with the exited singlet states and with the states  $|E_x\rangle$  and  $|E_y\rangle$ . There is also mixings among  $|{}^{3}A_{20}\rangle$ ,  $|{}^{1}A_1(e^2)\rangle$  and  $|A_1\rangle$ .  $|{}^{1}E_1\rangle$  and  $|{}^{1}E_2\rangle$  mix with  $|E_1\rangle$  and  $|E_2\rangle$  respectively. And finally,  $|A_1(e^2)\rangle$  mixes with  $|{}^{1}A_1(a^2)\rangle$ .

#### 2.5.3 Spin-Spin Interaction

The Spin-Spin interaction is a two-particle interaction that arises from the magnetic field generated by the Spin of one of the particles acting upon the Spin of the other particle. As it was the case for the Spin-Orbit interaction, the Spin-Spin Hamiltonian in terms of position and Spin operators is known [24],

$$H_{SS} = -\frac{\mu_0 g^2 \mu_B^2}{4\pi r^3} \left( 3 \left( \mathbf{s}_1 \cdot \hat{r} \right) \left( \mathbf{s}_2 \cdot \hat{r} \right) - \mathbf{s}_1 \cdot \mathbf{s}_2 \right),$$
(2.26)

where  $\mu_0$  is the magnetic permeability of free space, g is the Landé factor for the electron,  $\mu_B$  is the Bohr magneton and  $\mathbf{r} = r\hat{r}$  is the relative position between electrons.

As the interaction is a two-particle interaction, it is not possible to find matrices involving one orbital as we did with the Spin-Orbit interaction, but it is possible to find the matrix elements of this interaction analysing each of the  $15 \times 15$  elements one by one. It is also possible to separate the part involving the orbital operators and the spin operators, and reordering in terms that transform as the irreducible representations, as shown in the following equation,

$$h_{ss} = -\frac{\mu_0 g^2 \mu_B^2}{4\pi} \left[ \frac{1-3\hat{z}^2}{4r^3} (S_{1+}S_{2-} + S_{1-}S_{2+} - 4S_{1z}S_{2z}) + \frac{3}{4} \frac{\hat{x}^2 - \hat{y}^2}{r^3} (S_{1-}S_{2-} + S_{1+}S_{2+}) \right] (2.27)$$
  
+ $i \frac{3}{2} \frac{\hat{x}\hat{y}}{r^3} (S_{1-}S_{2-} - S_{1+}S_{2+}) + \frac{3}{2} \frac{\hat{x}\hat{z}}{r^3} (S_{1-}S_{2z} + S_{1z}S_{2-} + S_{1+}S_{2z} + S_{1z}S_{2+})$   
+ $i \frac{3}{2} \frac{\hat{y}\hat{z}}{r^3} (S_{1-}S_{2z} + S_{1z}S_{2-} - S_{1+}S_{2z} - S_{1z}S_{2+})$ 

In this equation, the position operator of the first term transforms as  $A_1$ . The position operators of the second and third terms transform as  $E_1$ ,  $E_2$ . And the rest transform as Eas well. Using the first term as an example, we can see that  $P_R$  will not affect  $\hat{z}^2$  for any R. Therefore, after applying the projection operator, it is deduced that it transforms as  $A_1$ . This allows us to further improve the matrix elements of this interaction. The Spin-Spin Hamiltonian matrix can be found in Appendix B.

In contrast with the Spin-Orbit interaction, all of the diagonal elements of the matrix are non zero, acquiring a different energy for every configuration. In the ground state triplet, an energy shift takes place between the states  $|{}^{3}A_{20}\rangle$  and  $|{}^{3}A_{2\pm}\rangle$  that is associated with the zero-field splitting. Shifts also happen in the exited state triplet, however, they are also accompanied with a mixing between the states that transform as the irreducible representation E. The singlets change their energy but they do not suffer from splitting, although a separation may still occur if we consider that the  $|{}^{1}A_{1}\rangle$  states from both the  $e^{2}$  and  $a^{2}$  configurations mix. Finally, the states with non-zero magnetic momentum of the ground state triplet mix with the elements of the exited state triplet that transform as the irreducible representation E.

#### 2.5.4 Strain Field Interaction

Strain refers to a change in the distance of the orbitals relative to the original distance between them due to an external force. This means it is a dimensionless tensor expressing the fractional change under stretching,

$$\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial (\delta R_i)}{\partial R_j} + \frac{\partial (\delta R_j)}{\partial R_i} \right), \qquad (2.28)$$

where  $\delta R_i$  is the change in longitude in the *i* direction, and  $R_i$  is the variable related to the axis in the same direction. It can be produced by stress (forces applied to the solid structure), electric field (via the piezoelectric effect) or temperature.

As this deformation modifies the distance between the nuclei, it also modifies the interactions that depend on them, namely, the Coulomb interaction. This interaction was previously defined in Equation 2.20. This equation can be rewritten as,

$$H = H_N + H_e + H_{e-N} + H_s, (2.29)$$

where  $H_N$  represents the nuclear part of the Hamiltonian,  $H_e$  represents the electronic part of the Hamiltonian and  $H_{e-N}$  represents the interaction between nuclei and electrons considering the nuclei as fixed on one point and finally  $H_s$  is the interaction that arises from the perturbation in the equilibrium position and it can be written as a Taylor approximation. Therefore, considering  $R = R_0 + \delta R$ 

$$H_s = \sum_{i} \left[ \frac{\partial (H_N + H_{e-N})}{\partial R_i} \Big|_{R_{i0}} \delta R_i \right] + O(\delta R^2).$$
(2.30)

Now we can add an antisymmetric part to the strain tensor,

$$f_{ij} = \frac{1}{2} \left( \frac{\partial (\delta R_i)}{\partial R_j} - \frac{\partial (\delta R_j)}{\partial R_i} \right).$$
(2.31)

then  $\epsilon_{ij} + f_{ij} = \frac{\partial(\delta R_i)}{\partial R_j}$ , and as both terms do not depend on the position, we can integrate formally on both sides,

$$\delta R_i = (\epsilon_{ij} + f_{ij})R_j, \qquad (2.32)$$

replacing on Equation 2.30,

$$H_s = \sum_{ij} \left. \frac{\partial (H_N + H_{e-N})}{\partial R_i} \right|_{R_{i0}} R_j (\epsilon_{ij} + f_{ij}).$$
(2.33)

We are only interested in the symmetrical part of the tensor  $\epsilon$  because the antisymmetrical part f transforms as a generator of the rotational group causing only a rotation in the structure as a whole. A rotation should not affect the eigenvalues or eigenvectors of the system.

We now conclude that the strain Hamiltonian can be modelled by,

$$H_s = \sum_{ij} \left. \frac{\partial (H_N + H_{e-N})}{\partial R_i} \right|_{R_{i0}} R_j \epsilon_{ij}.$$
(2.34)

Considering now the NV center and the 3 nearest neighbor carbon atoms, with equilibrium coordinates,

$$\vec{R}_{10} = d\left(1, 0, \frac{d_0}{d}\right), \qquad (2.35)$$

$$\vec{R}_{20} = d\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, \frac{d_0}{d}\right),$$
(2.36)

$$\vec{R}_{30} = d\left(-\frac{1}{2}, -\frac{\sqrt{3}}{2}, \frac{d_0}{d}\right),$$
(2.37)

$$\vec{R}_{40} = d_1(0, 0, -1),$$
 (2.38)

where the indices 1,2 and 3 represent the carbons and the index 4 represents the nitrogen,  $d_0$  is the distance from the vacancy to the carbon plane, d is the distance from the projected vacancy in the carbon plane to each carbon and  $d_1$  is the distance from the nitrogen to the vacancy as shown in Figure 2.3.



Figure 2.3: Definition of the coordinate system for the NV center. The z-axis aligns itself with the invisible line that connects the nitrogen (blue) and the vacancy (transparent). The origin of the system of coordinates is set to the vacancy and one of the carbons (grey), is set to the x-axis.

For the four atoms of the molecule we have to add a sum over  $\alpha$  which will label the carbons and the nitrogen:

$$H_s = \sum_{\alpha ij} \left. \frac{\partial (H_N + H_{e-N})}{\partial x_{\alpha i}} \right|_{R_{\alpha 0}} R_{\alpha j} \epsilon_{ij}.$$
(2.39)

We note that the complexity in calculating the operator that accompanies the Strain Tensor resides in calculating the derivatives of  $H_N + H_{e-N}$ , but there is a much simpler way of calculating them as group theory allows to rewrite any function in a linear combination of terms that transform as irreducible representations. Then we define,

$$H_{ij} \equiv \sum_{\alpha} \left. \frac{\partial (H_N + H_{e-N})}{\partial x_{\alpha i}} \right|_{R_{\alpha 0}} R_{\alpha j}.$$
(2.40)

Therefore,

$$H_s = \sum_{ij} H_{ij} \epsilon_{ij}.$$
 (2.41)

Now, as this equation does not depend on spin, and does not involve terms with more than one orbital function, we can reduce the dimensionality of the problem,

$$H_s = (\epsilon \otimes \mathbb{1}_{3 \times 3} + \mathbb{1}_{3 \times 3} \otimes \epsilon) \otimes \mathbb{1}_{4 \times 4}, \tag{2.42}$$

where  $\epsilon$  will have the same structure as Equation 2.41. The 3 × 3 identity matrices act upon each orbital (with the exception of a') and the 4 × 4 identity matrix acts upon both the spins. As mentioned before, the  $\epsilon$  tensor can be decomposed into terms that transform as each of the irreducible representations [19]. Furthermore, it is possible to find this decomposition in the basis  $\{e_x, e_y, a\}$ . Then,

$$\epsilon = \delta^a_{A_1} A^a_1 + \delta^b_{A_1} A^b_1 + \delta^a_{E_1} E^a_1 + \delta^a_{E_2} E^a_2 + \delta^b_{E_1} E^b_1 + \delta^b_{E_2} E^b_2, \qquad (2.43)$$

where  $\delta_{A_1}^a = (\epsilon_{xx} + \epsilon_{yy})/2$ ,  $\delta_{A_1}^b = \epsilon_{zz}$ ,  $\delta_{E_1}^a = (\epsilon_{xx} - \epsilon_{yy})/2$ ,  $\delta_{E_2}^a = (\epsilon_{xy} + \epsilon_{yx})/2$ ,  $\delta_{E_1}^b = (\epsilon_{xz} + \epsilon_{zx})/2$ ,  $\delta_{E_2}^b = (\epsilon_{yz} + \epsilon_{zy})/2$ , and,

$$A_{1}^{a} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad E_{1}^{a} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} E_{2}^{a} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$
(2.44)  
$$A_{1}^{b} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad E_{1}^{a} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} E_{2}^{a} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$
(2.45)

The strain  $15 \times 15$  interaction Hamiltonian matrix can be found in Appendix B.

#### 2.5.5 Electromagnetic Field Interaction

We can separate the electromagnetic field in an electric part and in a magnetic part. As we stated in the previous subsection, an electric field can cause strain. Furthermore, the total effect caused by the presence of an electric field can be expressed in terms of a strain field. And the strain tensor produced by it is known [25],

$$e_E = \begin{pmatrix} aE_x + bE_z & -aE_y & cE_x \\ -aE_y & -aE_x + bE_z & cE_y \\ cE_x & cE_y & dE_z \end{pmatrix},$$
(2.46)

where  $e_E$  is the strain tensor generated by the electric field, **E** is the electric field vector,  $a \approx b \approx c \approx 0.3 \times 10^{-6} (MVm^{-1})^{-1}$  and  $d \approx 3 \times 10^{-6} (MVm^{-1})^{-1}$ [19].

The magnetic field can be incorporated with the Zeeman effect [24],

$$H_{Zeeman} = \frac{\mu_B}{\hbar} \left( \mathbf{L} \cdot \mathbf{B} + g \mathbf{S} \cdot \mathbf{B} \right), \qquad (2.47)$$

where **B** is the magnetic field vector. As we have already calculated the matrices of **L**, we only have to incorporate them and we can deduce a  $15 \times 15$  Hamiltonian matrix. This matrix is shown in Appendix B.

Now that we have a full Hamiltonian description of the system, we want to find a method to study a subspace in isolation. Therefore, in the next chapter we will focus on this.

## Chapter 3

### Effective Hamiltonian method

In the last chapter we found the states of the system and described its interactions. Now, we want to describe a particular configuration of the system. In this chapter we will present a method for generating an effective Hamiltonian with the dimension of the configuration we want to describe and that has the effective effect of the full Hamiltonian. We show the validity of the method by comparing the diagonalized expectation values of both the method and the full Hamiltonian.

### 3.1 Effective Hamiltonians

As we discussed, we need a method for taking all the states of the system into consideration when attempting to describe one configuration in isolation. In order to do this we will introduce an effective Hamiltonian method. As we will show, this method will produce a description of a configuration that is approximately equivalent to the description of the complete system. Therefore the expectation values of the effective Hamiltonian, and the original Hamiltonian will approximately be the same for a particular configuration.

In this chapter we will explore how these effective Hamiltonians are derived. We will describe the Hamiltonian of the complete system in the base of the symmetrized states. Finally, we will find an effective Hamiltonian for the ground state triplet of the system.

To find an effective Hamiltonian as described before, we have to start from the timeindependent Schrödinger equation [24],

$$H\psi_i = E_i\psi_i,\tag{3.1}$$

where H is the complete Hamiltonian in a Hilbert space of dimension N,  $\psi_i$  is one of its eigenvectors, and  $E_i$  its eigenvalue.

As we have a full matrix description of the Hamiltonian, it is possible to separate this matrix into blocks

$$H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix}, \tag{3.2}$$

where the sub-index *a* refers to the configuration we are interested to describe and the subindex *b* refers to the rest of the configurations. Therefore,  $H_{aa}$  is a square matrix of dimension  $M_a$  equal to the configuration we want to study and  $H_{bb}$  is also a square matrix of dimensions  $M_b = N - M_a$ .

The main requirement that this method needs to work is that the energy of each state in the configuration a must be the same, and as expected, this is not the case. However, it is possible to create a series expansion around an interaction that affects the configuration a uniformly and that is greater than the other interactions. The Coulomb interaction satisfies both conditions and allows us to develop this method without further complications. Now, to develop a formula for the effective Hamiltonian, we solve the eigenvalue problem for Equation 3.2,

$$\begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix} \begin{pmatrix} \psi_{i,a} \\ \psi_{i,b} \end{pmatrix} = \begin{pmatrix} E_i \psi_{i,a} \\ E_i \psi_{i,b} \end{pmatrix},$$
(3.3)

where the sub indices represent the subspaces previously defined. Now, solving for  $\psi_{i,b}$ 

$$H_{ba}\psi_{i,a} + H_{bb}\psi_{i,b} = E_i\psi_{i,b},$$
  
$$\psi_{i,b} = (E_i \mathbb{I}_{bb} - H_{bb})^{-1} H_{ba}\psi_{i,a},$$
(3.4)

where the exponent represent the inverse of the matrix and  $\mathbb{I}_{bb}$  is the identity matrix of dimension equal to  $H_{bb}$ .

Now for the equation of the a subspace,

$$H_{aa}\psi_{i,a} + H_{ab}\psi_{i,b} = E_i\psi_{i,a},$$
  
$$(H_{aa} + H_{ab}(E_i\mathbb{I}_{bb} - H_{bb})^{-1}H_{ba})\psi_{i,a} = E_i\psi_{i,a}.$$
 (3.5)

Comparing to the Schrödinger equation, we get,

$$H_{eff}(E_i) = H_{aa} + H_{ab}(E_i \mathbb{I}_{bb} - H_{bb})^{-1} H_{ba}.$$
(3.6)

Note that this effective Hamiltonian has  $E_i$  as a parameter, making several different effective Hamiltonians for one subspace. We solve this by writing the total Hamiltonian as  $H = H_0 + H_{int}$ , where  $H_0$  is the coulomb interaction, which is greater than any of the interactions. If we expand the energy with perturbation theory, the energies at order 0 are degenerate for the individual subspaces we want to study. Therefore we can expand equation (3.6) to any order in  $E_{i,0}$  to get different effective Hamiltonians. For order zero we have,

$$H_{eff} = H_{aa} + H_{ab} (E_{i,0} \mathbb{I}_{bb} - H_{bb})^{-1} H_{ba}.$$
(3.7)

We can also expand equation 3.6 to the first order in  $E_{i,0}$ ,

$$H_{eff}(E_i) = H_{aa} + H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-1}H_{ba} - H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-2}H_{ba}(E_i - E_{i,0}) + O(2).$$
(3.8)

If we apply this equation to the eigenvector  $\psi_{i,a}$ , in the last term, due to the Schrödinger equation, we can replace  $E_i$  with  $H_{eff}(E_i)$ . Therefore,

$$H_{eff}(E_i) = H_{aa} + H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-1}H_{ba} - H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-2}H_{ba}H_{eff}(E_i)\cdots + H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-2}H_{ba}E_{i,0} + O(2).$$
(3.9)

Solving for  $H_{eff}(E_i)$ ,

$$H_{eff} = (\mathbb{I}_{aa} + H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-2}H_{ba})^{-1}(H_{aa} + H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-1}H_{ba} + H_{ab}(E_{i,0}\mathbb{I}_{bb} - H_{bb})^{-2}H_{ba}E_{i,0})$$
(3.10)

Which is independent of the possible non-degeneracy of the final levels. This same procedure could be applied to get more precise Effective Hamiltonians.

### 3.2 Effective Hamiltonian Example

To give an example, let  $H_0$  be a Hamiltonian given by,

$$H_0 = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}.$$
 (3.11)

And  $H_{int}$  an interaction much weaker than  $H_0$  of the form,

$$H_{int} = \begin{pmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c^* & 0 & 0 \end{pmatrix}.$$
 (3.12)

Assuming that  $a \leq b$ , let us imagine that we want to calculate the effect of  $H_{int}$  on the two lower energy states. Towards this we can use Equation 3.7. Applying it to  $H_0 + H_{int}$ , we get,

$$H_{eff} = \begin{pmatrix} a + \frac{|c|^2}{a-b} & 0\\ 0 & a \end{pmatrix}.$$
 (3.13)

This is a known result of an adiabatic elimination process.

### 3.3 Spin Hamiltonian

We now describe the Spin Hamiltonian of the ground state triplet. This is done by decomposing the effective Hamiltonian matrix for the  $e^2$  configuration into Spin operators. Since the symmetrized spin operators form a complete basis, the decomposition is achieved by projecting the Hamiltonian in those operators (with an inner product defined by the trace of the matrix dot product). By applying this procedure in a Mathematica script, we get,

$$H = E_0 \mathbb{1} + \alpha S_z^2 + \beta (S_x^2 - S_y^2) + \gamma (S_x S_y + S_y S_x)$$
  
+  $\delta (S_x S_z + S_z S_x) + \epsilon (S_y S_z + S_z S_y) + \zeta S_x + \eta S_y + \gamma_e \mathbf{B} \cdot \mathbf{S},$  (3.14)

where,  $E_0$  is the base energy of the system and does not cause a splitting in the energy levels,

$$\begin{split} \alpha &= D = 2.87 \text{ GHz} & \epsilon = \frac{\sqrt{2}(\delta_{E1}^b + cE_x)\Delta_{xy}}{E_{et}}, \\ \beta &= \frac{2(\delta_{E2}^b + cE_y)\operatorname{Re}(\Delta_+) + 4\sqrt{2}A_MB_x\operatorname{Im}(\Delta_+)}{E_{et}} & \zeta = \frac{8AA_MB_x - 4A_MB_y\Delta_{xy}}{E_{et}}, \\ \gamma &= -\frac{2(\delta_{E1}^b + cE_x)\operatorname{Re}(\Delta_+) - 4\sqrt{2}A_MB_y\operatorname{Im}(\Delta_+)}{E_{et}} & \eta = \frac{8AA_MB_y - 4A_MB_x\Delta_{xy}}{E_{et}}, \\ \delta &= \frac{\sqrt{2}(\delta_{E2}^b + cE_y)\Delta_{xy}}{E_{et}}, \end{split}$$

where,  $A_M = \frac{\hbar}{2m_e^2 c^2 \mu_B} A$ ,  $B_M = \frac{\hbar}{2m_e^2 c^2 \mu_B} B$ , A and B are elements of the Spin Orbit operator (A = 7.3 GHz and B = 5.475 GHz[19]),  $\Delta_{ij}$ ,  $\Delta_+$  and  $\Delta_-$  refer to the matrix elements of the Spin Spin interaction, the  $\delta$ 's are strain parameters,  $E_{et}$  is the Coulomb energy of the exited state,  $E_i$  is an electric field in the *i* direction,  $B_j$  is a magnetic field in the *j* direction and  $c = 0.3 \times 10^{-6} (MVm^{-1})^{-1}$ .

### 3.4 Comparison between the effective Hamiltonian and the full Hamiltonian

As we said in the previous section, the effective Hamiltonian method is a perturbative method and therefore, its validity needs to be contrasted against the original full Hamiltonian. For that we need numerical values for the elements of the Spin Spin interaction. The values for  $\Delta$ ,  $\Delta'$ , and  $\Delta''$  are given by 0.5 GHz, 0.825 GHz and 0.26 GHz respectively[19]. We can also calculate  $\Delta_1 = -0.32$  GHz by the zero field splitting. Other values are picked randomly with a similar order of magnitude as the previous ones (the effect of varying these values in the error is negligible).

We make a comparison of the lowest energy level versus strain in Figure 3.1. As it can be appreciated, the percentage error in the energy of the full Hamiltonian and the effective Hamiltonian is of the order of  $10^{-6}$ , which is neglectable. The figure also includes a comparison of the lowest energy level as the magnetic field varies in Figure 3.1. The effect of a magnetic field variation is more noticeable, however the error is still small even for large magnetic fields.



Figure 3.1: Left: Error in the comparison between the lowest energy level in the full Hamiltonian and in the effective Hamiltonian of the ground state triplet as strain varies. It is not a smooth function due to the computational method used to calculate it and the behaviour near zero strain is not asymptotic. Here the strain variable can be either  $\delta_{E_1}^b$  or  $\delta_{E_2}^b$  as both of them have the same effect on the energy level. Right: Error in the comparison between the lowest energy level in the full Hamiltonian and in the effective Hamiltonian of the ground state triplet as a magnetic field aligned with the NV axis varies. In both cases, the error is calculates as  $\text{Error} = (\Delta E_i - \Delta E_{i,eff})/\Delta E_i$ , where  $\Delta E_i$  is the difference between the eigenvalue of the complete Hamiltonian of the state *i* and the eigenvalue of the isolated ground state ( $e^2$ ) configuration of the state *i*, and  $\Delta E_{i,eff}$  is the difference between the eigenvalue of the state *i*.

Now that we have found the Spin Hamiltonian for the ground state triplet, in the next chapter we make a comparison to experimental results.

# Chapter 4

# **Experimental Comparison**

### 4.1 Introduction

In the last chapter we developed a tool to find an effective Hamiltonians and used it to model the ground state triplet, also decomposing it in a Spin Hamiltonian, which is the final goal of this work. However, we still have to contrast our results against experimental findings. To do this we tabulate several results of different works regarding the effect of strain in the NV center in Table 4.1 and Table 4.2.

**Table 4.1:** Part 1 of the different results of strain in NV centers. The first column shows the Hamiltonian used to model the strain effect. The second column displays the parameters found by the experiments. The third column adds commentaries relevant for the discussion and the last column labels the results according to their authors.

Hamiltonian	Parameters	Comment	Reference
$H_{str} = \mathbf{A_1}(s_{xx} + s_{yy} + s_{zz}) + \mathbf{A'_1}(s_{yz} + s_{zx} + s_{xy}) + \mathbf{E_x}(s_{xx} + s_{yy} + 2s_{zz}) + \mathbf{E_y}\sqrt{3}(s_{xx} - s_{yy}) + \mathbf{E'_y}\sqrt{3}(s_{yz} - s_{zx}) A_1 = \langle E \mathbf{A_1} E \rangle - \langle A \mathbf{A_1} A \rangle 2A_2 = \langle E \mathbf{A'_1} E \rangle - \langle A \mathbf{A'_1} A \rangle \sqrt{2}B = \langle E \mathbf{E} E \rangle \sqrt{2}C = \langle E \mathbf{E'} E \rangle$	$\begin{array}{l} A_1 = 1.68 \times 10^{-12} \frac{\text{eV}}{\text{Pa}} \\ A_2 = 3.99 \times 10^{-12} \frac{\text{eV}}{\text{Pa}} \\ B = 1.06 \times 10^{-12} \frac{\text{eV}}{\text{Pa}} \\ C = 1.62 \times 10^{-12} \frac{\text{eV}}{\text{Pa}} \end{array}$	$A_1, A'_1$ , etc. are matrix opera- tors in the base $\{ {}^{3}A_{20}\rangle,  E_x\rangle,  E_y\rangle\}$ of Table 2.2 that transform as $A_1$ or $E$ . Here, $ E\rangle$ could be either $ E_x\rangle$ or $ E_y\rangle$ and $ A\rangle$ is $ {}^{3}A_{20}\rangle$ . $s_{ij}$ is an element of the strain tensor. The experiment was performed at room temperature applying uniaxial stress with a push-rod driven by oil pressure.	Davies 1976[26]
$\begin{split} \hbar^2 H_{str} = & d_{\parallel} \Pi_z S_z^2 \\ & -d_{\perp} \Pi_x (S_x^2 - S_y^2) \\ & +d_{\perp} \Pi_y (S_x S_y + S_y S_x) \end{split}$	$d_{\parallel}/h = 0.35 \pm 0.02 \text{Hz cm/V}$ $d_{\perp}/h = 17 \pm 3 \text{Hz cm/V}$	$\Pi$ is the addition of the electric field and the effective electric field produced by the strain. The spin oper- ators <i>S</i> are redefined. The work cites Do- herty 2011[18], how- ever there is no men- tion to the values in that reference.	Doherty 2012[27]
$H_{str} = d_{\parallel} \delta_z (S_z^2 - S(S+1)/3) + d_{\perp} \delta_x (S_x^2 - S_y^2) + d_{\perp} \delta_y (S_x S_y + S_y S_x)$	$d_{\parallel} = 0.35 \pm 0.02 \mathrm{Hz} \mathrm{cm/V}$ $d_{\perp} = 17 \pm 3 \mathrm{Hz} \mathrm{cm/V}$	These results are not derived in this paper, they are cited from Van Oort 1990[28], however, the results of that work are for electric fields, and Do- herty argues they ap- ply to strain as well. There is a difference in sign compared to Do- herty 2012.	Doherty 2013[29]
$H_{str} = \epsilon_{\parallel} \sigma_{\parallel} S_z^2$ - $\epsilon_{\perp} \sigma_x (S_x^2 - S_y^2)$ + $\epsilon_{\perp} \sigma_y (S_x S_y + S_y S_x)$	$\epsilon_{\perp} = 0.03  \frac{\mathrm{MHz}}{\mathrm{MPa}}$	The value of $\epsilon_{\parallel}$ is not derived nor cited in this paper, and the value of $\epsilon_{\perp}$ is cited from Bennett 2013[30] where it was obtained at low temperature in a mechanical res- onator.	MacQuarrie 2013[ <mark>31</mark> ]

$H_{str} = \tilde{d}_{\parallel} \epsilon_z S_z^2 - \tilde{d}_{\perp} (\epsilon_+ S_+^2 + \epsilon S^2)/2 \epsilon_{\pm} = -\epsilon_y \mp i\epsilon_x$	$\begin{split} \tilde{d}_{  } = & 5.46 \pm 0.31  \mathrm{GHz} \\ \tilde{d}_{\perp} = & 19.63 \pm 0.40  \mathrm{GHz} \end{split}$	$\epsilon_i$ is the strain on the center along the coordinate <i>i</i> . The results were obtained at room tempera- ture measuring the mechanical displace- ment of a cantilever and by diagonalizing the Hamiltonian of the model to fit the parameters.	Teissier 2014[32]
$H_{str} = d_{\parallel} \epsilon_{\parallel} S_z^2$ $-\frac{d_{\perp} \epsilon_{\perp}}{2} (e^{-i\phi_s} S_+^2 + e^{i\phi_s} S^2)$ $\epsilon_{\parallel} = \epsilon_z$ $\epsilon_{\perp} = \sqrt{\epsilon_x^2 + \epsilon_y^2}$ $\tan(\phi_s) = \epsilon_y / \epsilon_x$	$d_{\parallel} = 13.4 \pm 0.8 \mathrm{GHz}$ $d_{\perp} = 21.5 \pm 1.2 \mathrm{GHz}$	The Hamiltonian is exactly the same as Teissier 2014 and the experiment is simi- lar (the only differ- ence in setup is that Ovartchaiyapong uses a vacuum of $10^{-5}$ Torr) and yet the re- sults are different.	Ovartchaiyapong 2014[33]
$H = DS_z^2 + E(S_x^2 - S_y^2) + \gamma \mathbf{B} \cdot \mathbf{S}$	$dD/d\sigma$ =15 KHz/MPa $d\Delta/d\sigma$ =17 MHz/MPa	$\Delta$ is the shift in op- tically detected mag- netic resonance spec- tra and $\sigma$ is the stress. It is stated that the variation in <i>D</i> is only slightly affected by the stress. The exper- iment was made at room temperature and the application of uni- axial pressure. The usage of a piezomag- netic material in the sample is also noted.	Cai 2014[34]
$H_{str} = \epsilon_{\parallel} \sigma_{\parallel} S_z^2$ -\epsilon_{\perp} \sigma_x (S_x^2 - S_y^2) +\epsilon_{\perp} \sigma_y (S_x S_y + S_y S_x)	$\epsilon_{\parallel}/2\pi = 13.3 \text{GHz/Strain}$ $\epsilon_{\perp}/2\pi = 21.5 \text{GHz/Strain}$	Values for the cou- plings are cited from Ovartchaiyapong 2014[33] and the stiffness tensor is used to change from strain to stress.	MacQuarrie 2015[35]
$H = (D + \mathcal{M}_z) \left( S_z^2 - \frac{2}{3} \right) + \gamma_e \mathbf{B} \cdot \mathbf{S} - \mathcal{M}_x (S_x^2 - S_y^2) + \mathcal{M}_y (S_x S_y + S_y S_x) \mathcal{M}_x = b(2\sigma_{ZZ} - \sigma_{XX} - \sigma_{YY}) + c(2\sigma_{XY} - \sigma_{YZ} - \sigma_{ZX}) \mathcal{M}_y = \sqrt{3} (b(\sigma_{XX} - \sigma_{YY}) + c(\sigma_{YZ} - \sigma_{ZX})) \mathcal{M}_z = a_1 (\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) + 2a_2 (\sigma_{YZ} + \sigma_{ZX} + \sigma_{XY}) $	$a_1$ =4.86 MHz/GPa $a_2$ =-3.7 MHz/GPa b =-2.3 MHz/GPa c =3.5 MHz/GPa	D is the zero field splitting and $\sigma_{ij}$ is the $ij$ element of the stress tensor in the diamond lattice coor- dinate system. The results were obtained by applying uniaxial strain at room tem- perature.	Barson 2017[36]

### 4.2 Discussion of the comparison between the model and the literature

As we have presented in the previous section, there are various different results available for the parametric constants. However, there is a step in-between the raw data of the experiments and the fitting of the constants, which is the diagonalization of the Hamiltonian, and since the Hamiltonian used for the showcased models are different, it would lead to different parameters compared to us.

One of the main differences in our model compared to previous models is the lack of dependence of the  $S_z^2$  parameter related to strain parallel with the NV axis. And even after comparing the results in the table after diagonalizing every one of its Hamiltonians and our own, there is a difference that remain unexplained.

The difference might be attributed to the fact that we are not taking into account the change of the spin-spin interaction with strain. The spin-spin interaction depends on the relative position between electrons, which in turn, depend on the position of the ions and the electron cloud follows the ions.

The application of the Taylor expansion on the Coulomb interaction and not in the others is done because the Coulomb interaction is the only one that has a dependency on the position operator of the ions. Therefore, in order to capture the effect of the motion of the ions on the interactions where the Hamiltonians do not show an explicit dependency on the ion positions, we need to consider the effect on the electron wavefunctions as electrons rapidly follow the motion of the ions.

Formally, this effect might be modelled by considering the change of the matrix elements with respect to a displacement of a given ion.

$$\frac{\partial \langle \Psi_i(r,R) | H(r,R) | \Psi_j(r,R) \rangle}{\partial R}.$$
(4.1)

We leave this as future work.

# Chapter 5

# Conclusions

We have described the NV<sup>-</sup> system, characterizing its states in terms of symmetrized orbitals and how the interactions affect these states. Then, we applied a method for isolating the subspaces of a system by creating an effective Hamiltonian for a subspace. Finally, we found a Spin Hamiltonian for the ground state triplet and compared it to experimental results. The conclusion of the comparison is that our model and experimentation do not match. We believe this is due to not considering the effect of the strain field on the interactions that do not show an explicit dependence on ion positions. Therefore, the next step is to transfer the dependency of ionic position operators to the electronic orbital states by modelling them as functions centered at the expectation value of the ion positions.

# Appendix A

# Introduction to Molecular Group Theory

In this appendix we will give a brief introduction to molecular group theory, following closely the derivation given in [23].

Assume you have a set of operators  $P_R$  which commute with the Hamiltonian of the system, now to be called symmetry operators. Therefore, applying this to the Schrödinger equation,

$$P_R H \psi_i = P_R E_i \psi_i, \tag{A.1}$$

$$HP_R\psi_i = E_i P_R\psi_i. \tag{A.2}$$

From this result we conclude that any function  $P_R\psi_i$  obtained by operating on an eigenfunction  $\psi_i$  by a symmetry operator from the group of the Schrödinger equation will also be an eigenfunction having the same energy as the original one. Thus, given any eigenfunction, we can generate other eigenfunctions degenerate with it by application of all the symmetry operators which commute with H.

Now, let us assume that  $E_i$  is  $l_i$ -fold degenerate. Then there are  $l_i$  orthonormal functions with energy  $E_i$ . By our previous result, if we operate  $P_R$  on any of these functions, the result must be expressed as a linear combination of these functions. This means,

$$P_R \psi_{\nu}^{(i)} = \sum_{\kappa=1}^{l_i} \psi_{\kappa}^{(i)} \Gamma^{(i)}(R)_{\kappa\nu},$$
(A.3)
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where  $\Gamma^{(i)}(R)$  is a transformation matrix. These matrices form a group, which means that if we multiply any pair of them, the result will also be in the group, there is an identity matrix in the group and every matrix in the group has its inverse also in the group. Also, these representations are irreducible since there is always an operator in the group which transforms each function into any other degenerate with it. Thus no smaller matrices could express the most general transformation.

These matrices also follow what is called the great orthogonality theorem [23], which states,

$$\sum_{R} \Gamma^{(i)}(R)^*_{\mu\nu} \Gamma^j(R)_{\alpha\beta} = \frac{h}{l_i} \delta_{ij} \delta_{\mu\alpha} \delta_{\nu\beta}, \qquad (A.4)$$

where h is the number of elements in the group and the  $\delta$ 's are Kronecher deltas. Now, we multiply equation A.3 by  $\Gamma^{(j)}(R)^*_{\kappa'\nu'}$  and sum over R, then,

$$\sum_{R} \Gamma^{(j)}(R)^*_{\kappa'\nu'} P_R \psi^{(i)}_{\kappa} = \frac{h}{l_i} \delta_{ij} \delta_{\kappa\kappa'} \psi^{(i)}_{\nu'}.$$
(A.5)

From this equation we conclude that the application of the operator,

$$\mathcal{P}_{\nu\kappa}^{(i)} = \frac{l_i}{h} \sum_R \Gamma^{(i)}(R)_{\nu\kappa} P_R,\tag{A.6}$$

to a basis function has the property of yielding zero unless the function being operated on belongs to the  $\kappa$ -th row of  $\Gamma^{(i)}$ . Moreover, if this condition is satisfied, then the result of the operation is  $\psi_{\nu}^{(i)}$ . Also it is important to remark that the application of this operator will result in functions with the same energy, as the superindex (i) does not change.

Now, if  $\nu = \kappa$  and we sum over  $\nu$ , the equation will not depend on the  $\Gamma$  matrices, but on the traces, otherwise known as characters  $\chi$  instead,

$$\mathcal{P}^{(j)} = \frac{l_j}{h} \sum_R \chi^{(j)}(R) P_R.$$
(A.7)

Finally, it is important to note that two functions belonging to different irreducible representations or representation rows are orthogonal. This again is due to the great orthogonality theorem. Moreover, if two functions have the same irreducible representation, then the multiplication will transform as the trivial irreducible representation  $A_1$ . In other words, a matrix element will be 0 if,

$$\langle \psi_i | M | \psi_j \rangle \not\subseteq A_1. \tag{A.8}$$

As an example, let us say that we want to find the states that transform as E and belong to the  $e^2(S)$  representation. As it is a singlet, it only allows wavefunctions of total spin 0 and belonging to the  $e^2$  configuration means we can only use  $e_x$  and  $e_y$ . Then, the test function to generate all possible terms should be,

$$|\Psi_{test}\rangle = |e_x e_y\rangle \otimes |\uparrow\downarrow\rangle + |e_x e_y\rangle \otimes |\downarrow\uparrow\rangle + |e_x e_x\rangle \otimes |\uparrow\downarrow\rangle + |e_x e_x\rangle \otimes |\downarrow\uparrow\rangle + |e_y e_y\rangle \otimes |\uparrow\downarrow\rangle + |e_y e_y\rangle \otimes |\downarrow\uparrow\rangle + |e_y e_y\rangle \otimes |\downarrow\downarrow\rangle + |e_y e_y\rangle \otimes |\downarrow\downarrow\rangle$$

If we use Equation A.6 on  $|\Psi_{test}\rangle$ , with  $\nu = \kappa = 1$ , with  $\Gamma$  taken from Ref. [22], the result is,

$$|e_x e_x - e_y e_y\rangle \otimes |\uparrow\downarrow - \downarrow\uparrow\rangle,$$
 (A.10)

which is the state that transforms as  $E_1$  and belongs to  $e^2(S)$  in Table 2.2. Now, if we apply the projection operator to  $|\Psi_{test}\rangle$  again, but now with  $\kappa = \nu = 2$ , we get,

$$|e_x e_y + e_y e_x\rangle \otimes |\uparrow \downarrow - \downarrow \uparrow\rangle \tag{A.11}$$

Which is the state that transforms as  $E_2$  and belongs to  $e^2(S)$  in Table 2.2.

# Appendix B

# Supplementary material for Chapter 2

In this appendix we will show the complete matrices of the interactions that act on the NV system and give a small explanation for them.

### B.1 Coulomb interaction

H			$e^2$				ae								$a^2$
		Triplet	-		Single	et			Trij	Sing					
	$^{3}A_{2-}$	${}^{1}E_{1}$	${}^{1}E_{2}$	${}^{1}A_{1}$	$A_1$	$A_2$	$E_1$	$E_2$	$E_y$	$E_x$	$^{1}E_{x}$	${}^{1}E_{y}$	$^{1}A_{1}$		
${}^{3}A_{2-}$															
${}^{3}A_{20}$															
${}^{3}A_{2+}$															
${}^{1}E_{1}$				$E_{gs}$									$E_{ss}$		
${}^{1}E_{2}$					$E_{gs}$									$E_{ss}$	
${}^{1}A_{1}$						$2E_{gs}$									$E_{se}$
$A_1$							$E_{et}$								
$A_2$								$E_{et}$							
$E_1$									$E_{et}$						
$E_2$										$E_{et}$					
$E_y$											$E_{et}$				
$E_x$												$E_{et}$			
${}^{1}E_{x}$				$E_{ss}^*$									$E_{es}$		
${}^{1}E_{y}$					$E_{ss}^*$									$E_{es}$	
${}^{1}A_{1}$						$E_{se}^*$									$E_{ee}$

The Coulomb interaction is straightforward and given by,

### **B.2** Spin-Orbit interaction

$H_{SO}$			e	2			ae								$a^2$
		Triplet		Singlet				Tripl		Sin	glet				
	$^{3}A_{2-}$	${}^{3}A_{20}$	${}^{3}A_{2+}$	${}^{1}E_{1}$	${}^{1}E_{2}$	${}^{1}A_{1}$	$A_1$	$A_2$	$E_1$	$E_2$	$E_y$	$E_x$	${}^{1}E_{x}$	${}^{1}E_{y}$	${}^{1}A_{1}$
$^{3}A_{2-}$											A	-iA	-iA	A	
$^{3}A_{20}$						2iB	-2iA								
$^{3}A_{2+}$											-A	-iA	iA	A	
${}^{1}E_{1}$									-2A						
${}^{1}E_{2}$										2iA					
$^{1}A_{1}$		-2iB					-2A								
$A_1$		2iA				-2A	В								$-2\sqrt{2}A$
$A_2$								B							
$E_1$				-2A					-B						
$E_2$					-2iA					-B					
$E_y$	A		-A										iB		
$E_x$	iA		iA											-iB	
$^{1}E_{x}$	iA		-iA								-iB				
${}^{1}E_{y}$	A		A									iB			
$^{1}A_{1}$							$-2\sqrt{2}A$								

The full Spin-Orbit matrix interaction is given by,

### **B.3** Spin-Spin interaction

The method that is used to find the Spin-Spin interaction matrix is first to develop equation 2.26 in terms that transform as irreducible representations,

$$H_{SS} = -\frac{\mu_0 g^2 \mu_B^2}{4\pi} \left[ \frac{1-3\hat{z}^2}{4r^3} (S_{1+}S_{2-} + S_{1-}S_{2+} - 4S_{1z}S_{2z}) + \frac{3}{4} \frac{\hat{x}^2 - \hat{y}^2}{r^3} (S_{1-}S_{2-} + S_{1+}S_{2+}) \right]$$

$$+ i \frac{3}{2} \frac{\hat{x}\hat{y}}{r^3} (S_{1-}S_{2-} - S_{1+}S_{2+}) + \frac{3}{2} \frac{\hat{x}\hat{z}}{r^3} (S_{1-}S_{2z} + S_{1z}S_{2-} + S_{1+}S_{2z} + S_{1z}S_{2+})$$

$$+ i \frac{3}{2} \frac{\hat{y}\hat{z}}{r^3} (S_{1-}S_{2z} + S_{1z}S_{2-} - S_{1+}S_{2z} - S_{1z}S_{2+}) \left] .$$
(B.1)

The position part of the first term transforms as  $A_1$  and the others transform as E. We then figure out each of the matrices for the position part and then multiply with the spin part, the result is,

$H_{SS}$			$e^2$				ae								$a^2$
	Triplet			Singlet			Triplet						Sing		
	$^{3}A_{2-}$	${}^{3}A_{20}$	${}^{3}A_{2+}$	${}^{1}E_{1}$	${}^{1}E_{2}$	${}^{1}A_{1}$	$A_1$	$A_2$	$E_1$	$E_2$	$E_y$	$E_x$	$^{1}E_{x}$	${}^{1}E_{y}$	$^{1}A_{1}$
$^{3}A_{2-}$	$-4\Delta_1$								$\Delta_+$	$-\Delta_+$	$i\Delta_{xy}$	$\Delta_{xy}$			
${}^{3}A_{20}$		$5\Delta_1$													
$^{3}A_{2+}$			$-4\Delta_1$						$\Delta_+$	$\Delta_+$	$i\Delta_{xy}$	$-\Delta_{xy}$			
${}^{1}E_{1}$				$\Delta_1$									$\Delta_{1x}$		
${}^{1}E_{2}$					$\Delta_1$									$\Delta_{1x}$	
$^{1}A_{1}$						$\Delta_1$									$\Delta_{1e}$
$A_1$							$\Delta - \Delta'$								
$A_2$								$\Delta + \Delta'$							
$E_1$	$\Delta_+^*$		$\Delta_+^*$						$\Delta$		$\Delta^{\prime\prime}$				
$E_2$	$-\Delta^*_+$		$\Delta_+^*$							$\Delta$		$-i\Delta''$			
$E_y$	$-i\Delta_{xy}$		$-i\Delta_{xy}$						$\Delta^{\prime\prime}$		$-2\Delta$				
$E_x$	$\Delta_{xy}$		$-\Delta_{xy}$							$i\Delta''$		$-2\Delta$			
${}^{1}E_{x}$				$\Delta_{1x}^*$									$\Delta_{es}$		
$^{1}E_{y}$					$\Delta_{1x}^*$									$\Delta_{es}$	
$^{1}A_{1}$						$\overline{\Delta_{1e}^*}$									$\Delta_{2e}$

### B.3.1 Strain field

The full matrix for the Strain Hamiltonian is,

$H_{Strain}$			$e^2$				ae								
		Triplet	,	5	Single	t			Т	riplet			Sin	glet	
	$^{3}A_{2-}$	${}^{3}A_{20}$	${}^{3}A_{2+}$	${}^{1}E_{1}$	${}^{1}E_{2}$	${}^{1}A_{1}$	$A_1$	$A_2$	$E_1$	$E_2$	$E_y$	$E_x$	$^{1}E_{x}$	${}^{1}E_{y}$	$^{1}A_{1}$
$^{3}A_{2-}$	$\delta_3$						$\frac{1}{2}i\delta^b_E$	$-rac{1}{2}i\delta^b_E$	$-\frac{1}{2}i\delta^b_E$	$-\frac{1}{2}i\delta^b_E$					
${}^{3}A_{20}$		$\delta_3$									$\delta^b_E$				
${}^{3}A_{2+}$			$\delta_3$				$-\frac{1}{2}i\delta^b_E$	$-\frac{1}{2}i\delta^b_E$	$\frac{1}{2}i\delta^b_E$	$-\frac{1}{2}i\delta^b_E$					
${}^{1}E_{1}$				$\delta_3$		$\delta_3'$							$\delta^b_E$		
${}^{1}E_{2}$					$\delta_3$	$\delta_3''$								$\delta^b_E$	
${}^{1}A_{1}$				$\delta'_3$	$\delta_3''$	$\delta_3$							$\delta^b_E$		
$A_1$	$-\frac{1}{2}i\delta^b_E$		$\frac{1}{2}i\delta^b_E$				$\delta''$		$\frac{1}{2}\delta'_3$	$-\frac{1}{2}i\delta_3''$					
$A_2$	$\frac{1}{2}i\delta^b_E$		$\frac{1}{2}i\delta^b_E$					$\delta''$	$\frac{1}{2}i\delta_3''$	$-\frac{1}{2}\delta'_3$					
$E_1$	$\frac{1}{2}i\delta^b_E$		$-\frac{1}{2}i\delta^b_E$				$\frac{1}{2}\delta'_3$	$-\frac{1}{2}i\delta_3''$	$\delta''$						
$E_2$	$\frac{1}{2}i\delta^b_E$		$\frac{1}{2}i\delta^b_E$				$\frac{1}{2}i\delta_3''$	$-\frac{1}{2}\delta'_3$		$\delta''$					
$E_y$		$\delta^b_E$									$\delta'' - \frac{1}{2}\delta'_3$	$\frac{1}{2}\delta_3''$			
$E_x$											$\frac{1}{2}\delta_3''$	$\delta'' + \tfrac{1}{2} \delta'_3$			
$^{1}E_{x}$				$\delta^b_E$		$\delta^b_E$							$\delta'' + \frac{1}{2}\delta'_3$	$\frac{1}{2}\delta_3''$	$\sqrt{2}\delta^b_E$
${}^{1}E_{y}$					$\delta^b_E$								$\frac{1}{2}\delta_3''$	$\delta'' - \tfrac{1}{2}\delta'_3$	
${}^{1}A_{1}$													$\sqrt{2}\delta^b_E$		$2\delta^b_{A_1}$

where,  $\delta_3 = 2\delta^a_{A_1}$ ,  $\delta'_3 = 2\delta^a_{E_1}$ ,  $\delta''_3 = 2\delta^a_{E_2}$ ,  $\delta^b_E = \delta^b_{E_1} + \delta^b_{E_2}$  and  $\delta'' = \delta^a_{A_1} + \delta^b_{A_1}$ .

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$a^2$		$^{1}A_{1}$													$16iA_mB_y$	$-16iA_mB_x$	
ae	Singlet	$^{1}E_{y}$				$8i\sqrt{2}A_mB_x$	$8i\sqrt{2}A_mB_y$	$-8i\sqrt{2}A_mB_x$							$-8iB_mB_z$		$16iA_mB_x$
		$^1E_x$				$8i\sqrt{2}A_mB_y$	$-8i\sqrt{2}A_mB_x$	$8i\sqrt{2}A_mB_y$								$8iB_mB_z$	$-16iA_mB_y$
	Triplet	$E_x$		$8i\sqrt{2}A_mB_x$					$-\sqrt{2}B_x$	$i\sqrt{2}B_y$	$-\sqrt{2}B_x$	$-i\sqrt{2}B_y$	$8iB_mB_z$				
		$E_y$		$8i\sqrt{2}A_mB_y$					$-\sqrt{2}B_y$	$-i\sqrt{2}B_x$	$\sqrt{2}B_y$	$-i\sqrt{2}B_x$		$-8iB_mB_z$			
		$E_2$	$4i\sqrt{2}A_mB$		$-4i\sqrt{2}A_mB_+$						$2B_{m0}B_z$		$i\sqrt{2}B_x$	$i\sqrt{2}B_y$			
		$E_1$	$4i\sqrt{2}A_mB$		$4i\sqrt{2}A_mB_+$							$2B_{m0}B_z$	$\sqrt{2}B_y$	$-\sqrt{2}B_x$			
		$A_2$	$-4i\sqrt{2}A_mB_+$		$4i\sqrt{2}A_mB$				$-2B_{mz}$				$i\sqrt{2}B_x$	$-i\sqrt{2}B_y$			
		$A_1$	$4i\sqrt{2}A_mB_+$		$4i\sqrt{2}A_mB$					$-2B_{mz}$			$-\sqrt{2}B_y$	$-\sqrt{2}B_x$			
e <sup>2</sup>	Singlet	$^{1}A_{1}$													$-8i\sqrt{2}A_mB_y$	$8i\sqrt{2}A_mB_x$	
		${}^{1}E_{2}$				$-16iB_mB_z$									$8i\sqrt{2}A_mB_x$	$-8i\sqrt{2}A_mB_y$	
		${}^{1}E_{1}$					$16iB_mB_z$								$-8i\sqrt{2}A_mB_y$	$-8i\sqrt{2}A_mB_x$	
	Triplet	$^{3}A_{2+}$		$-\sqrt{2}B_+$	$-2B_z$				$-4i\sqrt{2}A_mB_+$	$-4i\sqrt{2}A_mB_+$	$-4i\sqrt{2}A_mB$	$4i\sqrt{2}A_mB$					
		$^{3}A_{20}$	$-\sqrt{2}B_+$		$-\sqrt{2}B_{-}$								$-8i\sqrt{2}A_mB_y$	$-8i\sqrt{2}A_mB_x$			
		$^{3}A_{2-}$	$2B_z$	$-\sqrt{2}B_{-}$					$-4i\sqrt{2}A_mB$	$4i\sqrt{2}A_mB$	$-4i\sqrt{2}A_mB_+$	$-4i\sqrt{2}A_mB_+$					
$H_B/7$			$^{3}A_{2-}$	${}^{3}A_{20}$	${}^{3}A_{2+}$	$^1E_1$	$^{1}E_{2}$	$^{1}A_{1}$	$A_1$	$A_2$	$E_1$	$E_2$	$E_y$	$E_x$	$^{1}E_{x}$	$^{1}E_{y}$	$^{1}A_{1}$

where  $B_+ = (B_x + iB_y)$ ,  $B_- = (B_x - iB_y)$ ,  $B_{mz} = (4B_mB_z + B_z)$  and  $B_{m0} = (1 - 4B_m)$ .

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