Color Centers in Semiconductors for Quantum Applications

A High-Throughput Search of Point Defects in SiC

Joel Davidsson

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Front cover:

Defect hull by Joel Davidsson

A computer graphics image generated from the combined data from Figure 6.4 and Figure 6.5. Each sphere represents a calculated point defect. The x and y coordinates are the stoichiometry, and the z coordinate is the formation energy with a Fermi energy in the middle of the band gap. The colors represent the zero phonon lines (ZPLs) normalized by the PBE band gap value and color mapped using the Viridis color scheme. The brightness around each sphere represents the transition dipole moment (TDM) squared.

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Till konstanterna i livet

Abstract

Point defects in semiconductors have been and will continue to be relevant for applications. Shallow defects realize transistors, which power the modern age of information, and in the not-too-distant future, deep-level defects could provide the foundation for a revolution in quantum information processing. Deep-level defects (in particular color centers) are also of interest for other applications such as a single photon emitter, especially one that emits at 1550 nm, which is the optimal frequency for long-range communication via fiber optics.

First-principle calculations can predict the energies and optical properties of point defects. I performed extensive convergence tests for magneto-optical properties, such as zero phonon lines, hyperfine coupling parameters, and zero-field splitting for the four different configurations of the divacancy in 4H-SiC. Comparing the converged results with experimental measurements, a clear identification of the different configurations was made. With this approach, I also identified all configurations for the silicon vacancy in 4H-SiC as well as the divacancy and silicon vacancy in 6H-SiC. The same method was further used to identify two additional configurations belonging to the divacancy present in a 3C stacking fault inclusion in 4H-SiC. I extended the calculated properties to include the transition dipole moment which provides the polarization, intensity, and lifetime of the zero phonon lines. When calculating the transition dipole moment, I show that it is crucial to include the self-consistent change of the electronic orbitals in the excited state due to the geometry relaxation. I tested the method on the divacancy in 4H-SiC, further strengthening the previous identification and providing accurate photoluminescence intensities and lifetimes.

Finding stable point defects with the right properties for a given application is a challenging task. Due to the vast number of possible point defects present in bulk semiconductor materials, I designed and implemented a collection of automatic workflows to systematically investigate any point defects. This collection is called ADAQ (Automatic Defect Analysis and Qualification) and automates every step of the theoretical process, from creating defects to predicting their properties. Using ADAQ, I screened about 8000 intrinsic point defect clusters in 4H-SiC. This thesis presents an overview of the formation energy and the most relevant optical properties for these single and double point defects. These results show great promise for finding new color centers suitable for various quantum applications.

Populärvetenskaplig sammanfattning

Material har alltid varit en grundsten i mänsklighetens utveckling och historia, till den mån att vi har namngett olika tidsåldrar efter dem. Från sten- och järnåldern till nutid har vi människor lärt oss använda och anpassa olika material för att lösa problem i vår vardag. Idag har vi inte bara ett material som karaktäriserar vår tid utan många och en klass av dessa material som lagt grunden för vårt datoriserade samhälle är halvledare. Sedan de första tecknen på att halvledare existerar 1821 har utvecklingen kring halvledare haft otroliga framsteg, med uppfinnningen av transistor 1947 till dagens moderna produktion av halvledarmaterial och transistorer. Från 1965 har datorernas beräkningskapacitet (antalet transistorer i ett chip) dubblats vartannat år, även känt som Moores lag. Transistorerna har blivit mindre och mindre och idag är de bara några atomlager tjocka. Men oavsett hur bra tekniker man använder eller hur noggrann man än är kan det fortfarande bli fel. När ett material skapas kan det förekomma olika defekter. I denna avhandling ligger fokus inte på sprickor, repor eller liknande, utan på mindre defekter än så. Defekter som en atom på fel ställe eller en atom som saknas ligger i fokus.

Varför ska man studera dessa defekter? Det finns två skäl till varför det är viktigt att förstå hur defekter uppkommer och fungerar. Det första handlar om hur defekterna påverkar materialets egenskaper, det vill säga man vill förstå vilka defekter som påverkar materialet med målet att bli av med dessa så att materialets egenskaper kan nyttjas till fullo. Den andra, mindre intuitiva, skälet är att kunna använda defekters egenskaper för att skapa nya tillämpningar. En mycket intressant ny tillämpning är kvantdatorn som har möjligheten att revolutionera våra liv lika mycket som transistor har gjort. Kvantdatorer kommer förmodligen inte ersätta vanliga datorer men de skulle kunna lösa problem som inte går att lösa med dagens teknik. Ett exempel på ett sådant problem är Schrödingerekvationen som beskriver hur atomer och elektroner växelverkar. För system med många elektroner går inte denna ekvation att lösa på vanliga datorer. Men alternativa metoder har utvecklats för att kunna beräkna denna ekvation numeriskt. En av de mest kända metoderna är täthetsfunktionalsteori (DFT) som utvecklades 1964. Denna teori ger ett sätt att approximativt lösa Schrödingerekvationen på. Parallellt med utvecklingen av olika

approximationer inom DFT har också datorkraften ökat och idag har vi möjlighet att lösa DFT-problem på stor skala. Med dessa metoder är det möjligt att studera defekterna teoretiskt. Genom att använda beräkningsprogram baserade på DFT går det att simulera och beräkna defekternas optiska och magnetiska egenskaper tillräckligt nogga för att resultaten skulle kunna användas för att hitta nya defekter med intressanta egenskaper.

Eftersom det finns väldigt många olika defekter och kombinationer av dem blir det opraktiskt att göra dessa beräkningar manuellt. Därför har jag utvecklat en mjukvara som automatiskt gör allt som behövs för att förstå defekter på djupet. Mjukvaran kallas ADAQ (eng. Automatic Defect Analysis and Qualification) och kan skapa olika defekter, göra DFT-beräkningar för de viktigaste egenskaperna och samla resultaten i en sökbar databas. ADAQ är skriven för att vara en generell kod som kan göra beräkningar på vilket halvledarmaterial som helst, men som ett testmaterial används kiselkarbid. Jag har använt ADAQ för att beräkna runt 8000 defekter i kiselkarbid och hoppas att denna databas skapar bättre förståelse för de defekter som finns i kiselkarbid, vilket förhoppningsvis leder till att nya defekter kan hittas till olika tillämpningsområden.

Den främsta tillämpningen som diskuterats ovan är en defekt som kan användas för att bygga kvantdatorer, men det finns många andra tillämpningar. Bland annat skulle defekterna kunna användas för att skicka information i optiska fibrer, till sensorer med extrem noggrannhet, eller till säker kommunikation. Oavsett tillämpning är en sak säker; defekter är inte något som bara ska tas bort utan de kan också göra stor nytta. Vem vet, i framtiden kommer kanske denna tidsålder kallas defektåldern.

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Chapter 1

Introduction

*“One shouldn’t work on semiconductors, that is a filthy mess;
who knows whether any semiconductors exist.”*

Wolfgang Pauli (1902-1959)

Why should we study defects? Defects are present in most materials. They can either ruin the intended use or be a source of utility. This chapter first describes a few applications where defects are either unwanted or the main component and then follows an analogy that introduces point defects concepts in layman’s terms.

1.1 Wide Band Gap Semiconductor Applications

Semiconductor materials, like silicon, have made it possible to create transistors^[1] which have given us the modern computational world we live in today. Transistors and diodes control the flow of electricity and work great for small voltages and currents. However, when the electric current gets too large, the traditional semiconductors cannot handle the load and may explode. Another class of materials, known as wide band gap semiconductors, are needed. This class is ideal for power devices, such as diodes, which direct high currents.^{[2],[3],[4]}

In the modern world, more and more energy-demanding devices are being connected to the electric grid, which put an increasing demand on the flow of electricity. One such example is electric cars. Fast charging of the car batteries requires power converters.^[5] While driving these cars, the energy must also be transferred from the battery to the wheels efficiently.^[6] Power devices made from wide band gap semiconductors without unwanted defects, such as charge carrier lifetime killers, are one way of handling these needs. The lifetime of these power devices is limited mainly by unwanted defects present inside the material and at the interfaces.^{[7],[8]} Hence, one motivation for studying defects is to remove unwanted ones.

1.2 Point Defect Applications

As we have seen in the previous section, controlling and removing defects that interfere with the desired semiconductor properties is perhaps the most natural approach. Defects, meaning flaws and other imperfections, have a negative connotation in everyday language. However, the transistors could not have been made without the precise control of point defects (dopants) added to the semiconductors. In recent years, point defect properties have also gained remarkable interest in a diverse range of quantum applications. Instead of focusing on the material properties, the focus has shifted to the point defect properties and for what they can be used.

One area where the point defects have gained traction is the field of quantum enhanced technologies. Point defects have been suggested as qubits—the smallest quantum information processing units—in quantum computers.^[9] A quantum computer^[10] has a different architecture than a classical computer and uses quantum states to perform calculations. The quantum algorithms utilize the superposition of the quantum states to surpass their classical counterparts.^[11] One area where these quantum algorithms will provide increased performance is in simulations of quantum systems, which will accelerate the understanding and development of new materials.^[12] Other efforts focusing on using point defects to create the quantum Internet^[13] are underway.^[14] The quantum Internet will allow quantum computers to be connected over large distances and ensure secure communication. Both quantum computers and the quantum Internet will not replace their classical counterparts, but complement them.

Constructing quantum computers and the quantum Internet requires qubits. Qubits can be realized in many different physical systems but they should follow DiVincenzo's criteria.^[15] This list outlines seven criteria. Five criteria are needed for qubits to realize quantum computers, plus two additional ones needed for flying qubits—qubits that can transmit quantum information over large distances—to realize the quantum Internet. Of the five criteria related to stationary qubits, two are for the construction of quantum computers; the realization of the qubits needs to be scalable and must include universal quantum gates. The other three criteria are about the operation of quantum computers; initializing the qubits, having sufficiently long enough time (coherence time) to perform the calculations, and reading out the final result. The two criteria for flying qubits are the ability to connect stationary and flying qubits as well as to transport the information faithfully. So far, no realization of qubits that satisfies all seven criteria has been found. Point defects are a promising candidate.

The point defect that started this research is the nitrogen-vacancy center in diamond.^{[16],[17],[18],[19]} Not only is it a prime candidate for qubits^[20] but also various other point defect applications, like sensors^[21] and single photon emitters.^[22] Single photon emitter^[23] applications include quantum key distribution, quantum repeaters,

and fault-tolerant quantum computing.^[24] Some of the ideal properties of single photon emitter include stable, bright, and fast emission at room temperature which do not blink,^[24] with high efficiency and controllable properties such as photon energy, polarization, and lifetime.^[25] The nitrogen-vacancy center in diamond is the leading color center for applications but does not fulfill all of the ideal properties. Finding and identifying new point defects better suitable for single photon emitters in silicon carbide is the aim of this thesis.

1.3 Why Silicon Carbide?

Silicon carbide (SiC) is a suitable material for both power devices^{[26],[27]} and quantum devices.^{[28],[29],[30]} It is a technologically mature material with good fabrication and point defect manufacturing technologies.^[30] On the other hand, even today, there are many unknown defects whose microscopic structures have not been identified yet. All this make SiC an ideal material for searching for point defects. Another reason for choosing SiC as the test material for this study is that Linköping University is proficient in the growth and characterization of SiC.

1.4 A Popular Science Description

Now that the importance of studying point defects has been covered, let us turn to what they are. The following car analogy is presented to introduce point defects in a popular science manner. It is intended to be interpreted in the same spirit as other *gedankenexperiments* (thought experiments), such as Maxwell’s demon and Schrödinger’s cat. Before the point defect component in our analogy can be presented, the world around it and its connection to materials must first be introduced.

To understand a material, one needs to understand the electrons and how they behave. There is a complex behavior between the electrons and ions in real materials. To get an idea of how the electrons and ions interact, let us consider electrons to be cars and the ions in the material make up the roads they drive on. These cars follow some pretty strange rules compared to real-life. If a single car drives freely, not affected by any roads, it can drive at any speed, just like the cars on the Bonneville Salt Flats where land speed records are broken. However, when a single ion traps an electron, in our analogy, the car has to follow circular roads, similar to a car driving around Globen—a famous spherical arena in Sweden*. This situation will impose drastic changes to the speed limits and only certain speeds are allowed. These new speed limits are extremely precise. For example, the car is only allowed to drive at 3.14 or 16.18 km/h on these circular roads.

*even though the scale between a car and Globen is not correct compared to the scale between the electron and ion

When multiple electrons and ions are put together, even stranger behavior emerges. In materials, there is an enormous number of electrons and ions. Different atoms and their corresponding arrangement give rise to different materials. In our analogy, a single ion forms circular roads, multiple ions will form a network of roads, like a city grid. As the cars drive in these cities, they are forced to follow some strange speed limits. The exact rules depend on the city. For example, if the roads have no speed limit, like the cities on the Isle of Man, the cars can accelerate and decelerate as they interact with each other. This behavior corresponds to a metal, where the electrons move around more or less freely. However, in our analogy, there exist cities that have a peculiar speed limit, at least compared to ordinary life. In these cities, cars are allowed to travel, for instance, either 0-40 km/h or 60-80 km/h but are not allowed to travel 40-60 km/h. These strange laws are not decided by the police but arise from the roads themselves. If the roads are fully occupied, all cars follow the 0-40 km/h speed rule and since no one is allowed to exceed this speed limit, everyone stays in their lane. To overtake another car, a car at 40 km/h needs external help, some form of extra energy, to get to the 60-80 km/h speed limit. These cities correspond to the behavior in a semiconductor. Here, there are forbidden energy levels for the electrons, just like the cars' speed limits. This forbidden energy range is called the band gap, and its value depends on the atoms present in the material and how they are arranged. These energies are forbidden as long as all the atoms are in their correct positions.

Now, let us turn to the defects. Just like regular roads, materials can have defects. Many different defects can occur, like cracks, but let us consider the simplest one—a pothole. Contrary to real-life potholes, which are usually smaller than the car, in our analogy, they are large enough so that one or a few cars can get stuck in them. When a car gets stuck in a pothole, they start going around in circles similar to going around Globen as mentioned before. Just as the speed limit change to be a precise value for the car traveling around Globen, it also changes for the car in the pothole. Here, the car keeps driving in circles with a speed determined by the pothole. This speed can now fall inside the forbidden speed range, forbidden for all other electrons, but now accessible to the car stuck in the pothole. One can then imagine what would happen if two potholes were close together and the cars can jump between them. This jump would still require some external help. If there are too many potholes, the external help needed will get smaller and the cars jump in and out of them easier, leading to the fixed speed limits no longer being followed. Instead of nice roads, they now look more like gravel roads.

At the beginning of making semiconductors, the material looked like these gravel roads—filled with potholes. It was extremely hard to figure out why they acted as they did. Every sample was different from the next. This unreliability was what Wolfgang Pauli was referring to when he said not to work with semiconductors. When he made his statement, semiconductor production was in its infancy and

the quality was poor. However, just like the construction of real-life roads has seen vast improvement, so has the production of semiconductors. Today, the high-quality production of semiconductors can manufacture reliable materials. Here, the properties of the semiconductor are realized.

The potholes discussed in our analogy are the point defects in semiconductors. Even if the production of semiconductors has seen great improvement, there can still be some unwanted point defects left that can affect the properties. As mentioned before, studying the point defects in semiconductors is done for two reasons; either because we want to get rid of them and use the semiconductor properties or because we want to use the properties of the point defects themselves in applications. An application of the first kind is power devices that direct electric power, which can be explained in our road analogy. When electricity is passed along a metal wire, like copper, one can imagine it as a highway with fast driving cars. This works fine as long as they stay on the highway. However, when they exit the highway, they need to be gently guided off. Here is where the semiconductor material comes in, either as an interface between the metal wire and the device or in the device itself. If the exit turns onto a road with too many potholes, the transition is not smooth. This “friction” causes energy losses (heating in the material) and degrade the material over time. Here, one sees how unwanted point defects cause the degradation of the device. Applications of the second kind where the properties of the point defects are used are diverse, but let us look at single photon emitters. Here, there are two different circles in the pothole, in which the car can drive around. Jumping between them produces a single photon. Unfortunately, it does not pay to continue with the road analogy further to understand them. Instead, the required concepts are presented in the rest of this thesis.

Chapter 2

Defects

“Crystals are like people, it’s the defects in them that make them interesting.”

Sir Charles Frank (1911-1998)

There are many different defects one can consider and study, from point to line to surface defects. This thesis limits the analysis to point defects and their clusters (0D defects). What are point defects and how can they be modeled? Before we get to the necessary nomenclature and theory used for point defects, let us begin with the material which hosts the point defects.

2.1 Host Material

Point defects exist in most materials. However, the intricacy of the point defects emanates from the complexity of the material. The focus of this thesis is to provide a code that can analyze point defects in bulk semiconductor materials. To avoid limiting the intricacy and focusing on special cases of point defects, it is key to choose a material complex enough to provide a general procedure for handling defects. The material complexity originates from the number of atomic elements and different symmetry positions. The host material of choice in this thesis, SiC, satisfies these two prerequisites. SiC has two different atomic elements and comes in many different *polytypes*—different stackings of the layer with the same atoms. Both features add to the total number of possible point defect clusters.

2.1.1 Polytypes

SiC is a material that consists of layers of silicon and carbon atoms. When these layers are stacked on top of each other, they can rotate compared to the previous

layer. A 60° rotation changes how the bonds align in the material and gives rise to the different polytypes. SiC has more than 250 different polytypes^[31] but the most important ones are 3C, 4H, and 6H^{[32],[33]} which are shown in Figure 2.1. The main focus in this thesis lies on the 4H-SiC polytype since it is the most commonly grown and used for applications.

Figure 2.1 – The unit cells of the three most common polytypes of SiC: 3C, 4H, and 6H. They all have different stackings: 3C has ABC stacking; 4H has ABCB stacking, where the hexagonal-like and cubic-like layers are denoted with k and h , respectively; 6H has ABCACB stacking, where the two cubic-like layers are denoted with k_1 and k_2 .

2.1.2 Space Group

Different materials and polytypes have different symmetry operations that transform the crystal lattice onto itself. For example, a 120° rotation along the c -axis of the unit cells in Figure 2.1 or a translation along any lattice vectors result in the exact same structure. To keep track of all the symmetry operations, they are grouped together. The group of all the possible rotations, reflections, inversions, and translations is called a *space group*.^[34] There is only a fixed number (230) of space groups in 3D.^[34]

The space group of 4H-SiC is No. 186, which is taken from the International Tables for Crystallography.^{[35],[36]} Important symmetry properties are extracted from the space group. For example, all positions in the crystal lattice can be described by *Wyckoff positions*, which describe the site symmetry of a particular point. Table 2.1 shows the Wyckoff positions for the space group which describes 4H-SiC, conveniently looked up using the online service of Bilbao crystallographic server.^{[37],[38],[39]} The Wyckoff positions can be either points, lines, planes, or the entire space itself. The last is always included.

Wyckoff letter	Multiplicity	Position	Coordinates
<i>a</i>	2	line	$(0, 0, z)$ $(0, 0, z+1/2)$
<i>b</i>	2	line	$(1/3, 2/3, z)$ $(1/3, 2/3, z+1/2)$
<i>c</i>	6	plane	$(x, -x, z)$ $(x, 2x, z)$ $(-2x, -x, z)$ $(-x, x, z+1/2)$ $(-x, -2x, z+1/2)$ $(2x, x, z+1/2)$
<i>d</i>	12	space	(x, y, z) $(-y, x-y, z)$ $(-x+y, -x, z)$ $(-x, -y, z+1/2)$ $(y, -x+y, z+1/2)$ $(x-y, x, z+1/2)$ $(-y, -x, z)$ $(-x+y, y, z)$ $(x, x-y, z)$ $(y, x, z+1/2)$ $(x-y, -y, z+1/2)$ $(-x, -x+y, z+1/2)$

Table 2.1 – Wyckoff positions for space group No. 186, ordered from highest to lowest symmetry.

Figure 2.2 shows the Wyckoff positions in the 4H-SiC unit cell. Here, the silicon and carbon atoms are placed at the highest symmetry positions in this space group, along the *a* and *b* lines, see Table 2.1. Thus, the same element is found in different symmetry positions. The Wyckoff positions are important for the defect generation, which is discussed further in Sec. 6.3.1.

Figure 2.2 – The Wyckoff positions in 4H-SiC unit cell. The silicon and carbon atoms are placed along the Wyckoff lines *a* and *b*, shown with green lines. There are several Wyckoff planes *c* in the unit cell, two examples are shown here, and the remaining points are the Wyckoff space *d*.

2.2 Point Defects

Once the host material is selected, the point defects can be discussed. *Intrinsic* point defects are defects that consist of elements only present in the host material. Analogously, the point defect is called *extrinsic* if the other elements are present. Point defects come in three main varieties and are abbreviated in this thesis as follows:

- A *vacancy* defect is a missing atom and is denoted Vac_X where X is the element removed.
- A *substitutional* defect is an atom that replaces another atom at the same position. It is denoted X_Y , where X is the element that replaces the element Y . If the replacing atom is an intrinsic element of the host material, it is also called an *antisite*.
- An *interstitial* defect is an extra atom added to the material but not at a position in the original lattice. They are denoted Int_X where X is the element added.

These are known as the *single* point defects. Hereinafter, the term *defect* is dropped and the defects are referred to as vacancies, substitutionals, and interstitials. The three varieties can be combined and form point defect clusters, like a vacancy and interstitial cluster, also known as a Frenkel pair. To keep track of the kind of point defect, the clusters (including single defects) are called the *defect type* in this thesis.

The defect types can be separated based on their *stoichiometry*—the quantity of different elements. A silicon vacancy can never transform into a carbon vacancy by simply rearranging the atoms because they have different stoichiometries. However, the silicon vacancy can transform into a carbon vacancy-antisite pair. The stoichiometry is denoted $X:x_Y:y$, where the upper case letter stands for the element and the lower case letter is the number of added or removed elements. For example, the silicon vacancy has the stoichiometry $\text{Si:1}_\text{C:0}$ whereas a vacancy and interstitial cluster (Frenkel pair) has the same stoichiometry as the host material $\text{Si:0}_\text{C:0}$. Here, the notation for added (-1) and removed (+1) elements is chosen to align with the notation used for the formation energy, see Sec. 2.5.1.

If the host materials have different layers or symmetric positions for the same atomic element, different *configurations* of the same defect type may exist. To separate the multiple configurations of a defect type, a parenthesis is added after each defect type to indicate which layer the defect originates from. As examples, the different configurations of two important point defects in SiC are presented.

2.2.1 Silicon Vacancy

In 4H-SiC, there are two different symmetry positions for the silicon and carbon atoms, as can be seen in Figure 2.2 where the elements are placed on different Wyckoff lines. The different positions give rise to different local environments. There is a hexagonal-like environment h and a cubic-like environment k , see Figure 2.1. For the silicon vacancy, there are two different configurations which are denoted $\text{Vac}_{\text{Si}}(h)$ and $\text{Vac}_{\text{Si}}(k)$. Similarly, in 6H-SiC, there are three different configurations. The silicon vacancy has shown to be useful in applications like magnetometers,^[40] nanothermometers,^[41] masers,^[42] qubits,^[43] and single photon emitters.

2.2.2 Divacancy

The divacancy is a point defect cluster of nearest neighbors, namely a combined silicon and carbon vacancy ($\text{Vac}_{\text{Si}}\text{Vac}_{\text{C}}$). This defect type has four different configurations depending on which layers the silicon and carbon are removed from. In 4H-SiC, the configurations are hh , hk , kh , and kk , see Figure 2.1 for the different layers. In 6H-SiC, there are six different configurations. The divacancy properties closely resemble the properties of the NV-center in diamond.^[44] It has a slightly longer coherence time^{[45],[46]} than the NV-center, making it a suitable candidate for qubits. It can also be used as a single photon emitter.^[46]

2.3 Defect States

When a point defect is introduced in the semiconductor, localized (defect) states may appear. These localized states may interact with electromagnetic fields, such as light. These interactions are measured in various experiments and are discussed in detail in Chapter 5.

Depending on the number of defect states in the band gap and the Fermi energy, the point defect may capture or release extra electrons. This catch or release will change the *charge state* of the point defect and consequently its properties. If a point defect captures an extra electron, it is referred to as the negatively charged version of the point defect.

Since the electrons are quantum particles and have spin, multiple spin arrangements of the same point defect might exist. Thus, a point defect can have different *spin states* of the same defect type. The spin of the point defect depends on the number of unpaired electrons x and is denoted $\text{spin-}x/2$. The spin state also varies depending on the charge state of the point defect.

2.4 Theoretical Approach

So far, the point defects have been imagined as a single defect in an infinite crystal. However, in most practical calculations, it is not possible to handle the point defects in this manner. One approach to solve this is to use a supercell—multiple copies of the unit cell—with periodic boundary conditions. A supercell with a point defect is therefore modeled as a repeating point defect. But if the supercell is large enough, the point defect will not interact with itself, *i.e.*, the point defect self-interaction is negligible. How the electronic structure and energy are found for the supercells is discussed in detail in Chapter 4.

2.5 Thermodynamical Stability

In general, when a point defect is introduced in a perfect material, this tends to increase the energy of the system. The energy needed to create a point defect is known as the formation energy. It indicates how stable the point defect is and which charge and spin state is the most probable. By comparing the binding energy between point defects, one can also see if a point defect cluster is stable or if it prefers to separate into its constituents.

2.5.1 Formation Energy

The amount of energy needed to create the point defect is given by the formation energy equation:^[47]

$$\Delta H_{D,q}(E_f, \mu) = [E_{D,q} - E_H] + \sum_i n_i \mu_i + qE_f + E_{\text{corr}}(q). \quad (2.1)$$

This equation gives the formation energy of a single defect in the infinite crystal from the periodic supercell description. Here, $E_{D,q}$ is the energy of the charged supercell with the point defect. Whereas E_H is the energy of the supercell of the perfect host material. The μ_i are the chemical potentials of the removed ($n_i > 0$) or added ($n_i < 0$) defect elements. The Fermi energy E_f is multiplied with the charge of the system q . There is also a charge correction term $E_{\text{corr}}(q)$, which accounts for the periodic repetition of any extra charge in the supercell.

Chemical Potentials

The chemical potentials should vary with pressure and temperature to describe the experimental conditions.^[47] However, the pressure and temperature in calculations are usually not representative of the experimental conditions. Thus, the total energy (at $T=0$) is used as a reference for the chemical potential.

Even if the absolute reference might be off, there are still some bounds the chemical potentials must obey.^[47] For example, an upper bound to the chemical potential of an element such as silicon μ_{Si} is found from its pure element phase, the silicon material, and is denoted $\mu_{\text{Si}}^{\text{rich}}$. The rich chemical potential for carbon is found in the same way. The lower bound is found by subtracting the upper bound of one element from the chemical potential of the combined material: $\mu_{\text{Si}}^{\text{low}} \leq \mu_{\text{SiC}} - \mu_{\text{C}}^{\text{rich}}$.

Charge Corrections

Due to the periodic repetition of the point defect in supercells, additional charges ($q \neq 0$) may interact with themselves. To correct this interaction, several different correction schemes have been suggested. The main ones are introduced here. The first suggested correction is the Markov-Payne (MP)^[48] correction, a first-order point-charge correction based on the Madelung constant. Lany-Zunger (LZ)^[49] built on the MP correction but they noticed that the third-order term, which depends on the multipole, can be rewritten to scale as the first-order term and thus suggested that the first-order term should have a different prefactor (roughly $2/3$ of the original factor) to make it more accurate. The Freysoldt-Neugebauer-Van de Walle (FNV)^[50] correction models the charges as Gaussian distributions instead of point charges and finds the correction based on electrostatic calculations. For the high-throughput results in this thesis, the LZ correction is used since it has the same expression for all defects.

2.5.2 Binding Energy

Closely related to the formation energy is the binding energy, which describes if it is energetically favorable for two point defects to stick together and form a cluster. This binding energy is modeled in a grand canonical ensemble and is defined as:^[47]

$$H^b(E_f, \mu) = \Delta H_{D,q}(E_f, \mu)[A] + \Delta H_{D,q}(E_f, \mu)[B] - \Delta H_{D,q}(E_f, \mu)[AB]. \quad (2.2)$$

Where A and B represent the separated point defects and AB is the joint cluster. A positive binding energy H^b corresponds to a stable cluster. The binding energy depends on the Fermi energy and chemical potential, which are kept fixed for all point defects included in the calculation. The charge q on the right-hand side of the equation also needs to be fixed, *i.e.*, the combined cluster has to have the same charge as the two separate point defects. For example, a negatively charged Vac_{Si} , a positively charged Vac_{C} , and the neutrally charged $\text{Vac}_{\text{Si}}\text{Vac}_{\text{C}}$ must exist for the same Fermi energy to be able to calculate the binding energy.

Chapter 3

Automatic Approach to Defects

*“To achieve great things, two things are needed;
a plan, and not quite enough time.”*

Leonard Bernstein (1918-1990)

As seen in the previous chapter, there is an enormous range of possible point defects to consider. This thesis aims to provide a systematic approach to better understand all point defect clusters in any bulk semiconductor and predict their most relevant properties. Reaching this goal requires automatic handling of the point defect clusters, as we will see in this chapter. Answers to why automatic handling is needed and how the defects are handled systematically are provided. Finally, the requirements taken into account for the design of the automatic workflows are presented, which are needed to produce a database that would help in the search for new point defects of interest for applications in, *e.g.*, quantum information.

3.1 Vision

The ambition is to build a database with the most relevant point defect properties to identify unknown defects and find those suitable for quantum applications. For the identification, a visual representation of this process is shown in Figure 3.1.

3.2 Motivation

To estimate the number of calculations required to fully characterize a point defect, *i.e.*, to know all relevant properties, let us consider one defect in one host material, the divacancy in 4H-SiC. As mentioned before, this point defect exists in 4 different *configurations*. In general, this number can be higher or lower depending on how

Figure 3.1 – A schematic picture of how the database is constructed and used to identify point defects. First, a vast array of point defects are created. These are processed in the automatic workflow that calculates the most important quantities and stores them in a database. The database results can then be compared with experimental measurements and the point defects can be identified.

complex the point defect and host material are. For each *configuration*, we consider 5 different charge states. For each *charge state*, there could be multiple spin states, a maximum of 3. For each *spin state*, there are several excitations that, in general, depend on the number of defect states. The number of excitations can vary a lot from defect to defect but is estimated to be around 10. The total number of calculations needed to fully characterize one defect is 600 ($4 \cdot 5 \cdot 3 \cdot 10$), clearly showing the need for automation.

Recall that this number is just for one defect in one host material. If we want to consider many different defects in one host material, how many point defects need to be handled? By combining vacancies, substitutionals, and interstitials into point defect clusters, one can easily generate up to 10 000 intrinsic point defects. Adding extrinsic dopants, one can easily generate 10 000 additional point defects.

3.3 Three Stages

The motivation for automation is clear. There is no way all these calculations can be done manually. Two different challenges emerge from the discussion in the previous section. First, to find and identify unknown defects, around 10 000 point defects need to be handled. Second, to have an accurate understanding of one defect, about 600 calculations are needed, even if the specific number of calculations varies a lot depending on the specific point defect.

These two requirements are handled as a three-stage rocket. In the first stage, a quick workflow screens 10 000 defects and produces the most important properties. After this stage, the most important and interesting defects are selected and processed in the next stage. In the second stage, an extensive workflow fully characterizes all the selected defects. In the final stage, for the most promising defects that have completed both workflows, a human must decide which additional manual calculations are needed to analyze the point defect further. Figure 3.2 illustrates the three stages.

Figure 3.2 – A schematic picture of the three-stage process of finding interesting point defects. First, 10 000 defects are screened, then the most interesting point defects are fully characterized, and last manual calculations are performed for the most interesting defects.

3.4 Requirements for the Automatic Workflows

The following requirements have been kept in mind while designing the automatic workflows.

- **Minimal human intervention** - The workflows should run by themselves with minimal human intervention. The only input needed is for setting up and collecting runs to and from the supercomputer.
- **General host material** - The code should be able to handle any bulk semiconductor host material. SiC is a good choice as a test material since it contains different species and symmetry points that add to the complexity that needs to be handled.
- **General point defect clusters** - It is important to include clusters since they are used in many quantum applications. The code should be able to generate point defect clusters up to an arbitrary size.
- **No assumptions** - The workflows should handle any added point defect clusters. There should be no need to remove point defects based on some assumptions beforehand.
- **Complete characterization** - After running the full characterization workflow, one should have a good qualitative understanding of the defect without requiring additional runs.
- **Most important properties** - The workflows should provide not only total energies of the point defect clusters but also other important properties to facilitate the identification of unknown defects and the search for point defects suitable for quantum applications.
- **Consistent database** - After all the calculations have finished, the results need to be consistent and collected in a database.
- **First-principle methods** - The workflows should be based on first-principle theory to avoid relying on experimental parameters.
- **Standard level of theory** - Due to the number of calculations, the level of theory can not be too computationally demanding.

In the next chapter, we will discuss the first-principles theory used to handle the vast number of point defects.

Chapter 4

Electronic Structure

“Physics is really nothing more than a search for ultimate simplicity, but so far all we have is a kind of elegant messiness.”

Bill Bryson, *A Short History of Nearly Everything* (1951-present)

Given a point defect in a material, or any set of electrons and ions, we would like to know how they behave. Their behavior is described by the Schrödinger equation. However, this equation cannot be solved directly; thus, other approaches such as density functional theory or Hartree-Fock theory are needed. These describe the electronic structure of the ground state, but, with extensions, excited states can also be handled.

4.1 Schrödinger Equation

Ordinary matter consists of electrons and ions. Their behavior and interaction with each other are described by the *Schrödinger equation*. Here, the *many-body wave function* Ψ contains all the information on the quantum mechanical properties of both electrons and ions.

$$\hat{H}\Psi = E\Psi, \tag{4.1}$$

where $\hat{H}$ is the *Hamiltonian* and E is the energy. For a material with N electrons and M ions, the Hamiltonian used in the Schrödinger equation* is (in Hartree atomic units, $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ ^[51]):

*time independent non-relativistic version

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_i}{|\mathbf{R}_I - \mathbf{r}_i|} - \sum_{I=1}^M \frac{1}{2M_I} \nabla_I^2 + \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|},$$

(4.2)

where the first two terms are the kinetic and repulsive energy terms for the electrons, the middle term is the electron-ion attraction term, and the last two terms are the kinetic and repulsive energy terms for the ions. In its present condition, solving this equation for large systems ($N > 100$) would require an infeasible amount of classical computer memory.^[52] To simplify the equation, two approximations, both based on the fact that the ions are much heavier than the electrons, are used. If the electrons find their equilibrium positions much faster than the ions move, the *Born-Oppenheimer approximation*^[53] is valid. In other words, if the electrons and ions move at different time-scales, this approximation makes the Schrödinger Equation separable, splitting the Hamiltonian into two parts, an electronic and ionic part. The electronic Hamiltonian depends parametrically on the ion positions. The ionic Hamiltonian can be simplified further by treating the ions as classical particles. In this thesis, the motion of the ions is neglected. Thus, let us consider the ions to be stationary and focus on the electrons. These approximations of treating the ions as stationary classical particles effectively turn Eq. (4.2) into:

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_i}{|\mathbf{R}_I - \mathbf{r}_i|} - \sum_{I=1}^M \frac{1}{2M_I} \nabla_I^2 + \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}.$$

(4.3)

Since the last term now refers to classical particles, it is no longer an operator and is just written as V_{II} . To abbreviate the other terms, the remaining operators are rewritten, in the same order, to be:

$$\hat{H} = \hat{T} + \hat{U} + \hat{V} + V_{II}. \quad (4.4)$$

The Born-Oppenheimer approximation simplifies the equation but it is still infeasible to solve. The most difficult part is the interacting electrons. Hence, the Schrödinger equation still cannot be solved directly using the many-body wave function for large systems; other approaches are needed.

4.2 Density Functional Theory

One successful^[54] alternative approach is density functional theory (DFT). DFT uses the electron *density* $n(\mathbf{r})$ as the variable instead of the electronic wave function. They have the following relation:

$$n(\mathbf{r}) = \int \dots \int \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N, \quad (4.5)$$

where $\mathbf{x}$ is the combination of position and spin $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$, and $\int d\mathbf{x}$ is the combination of $\int d\mathbf{r}$ and $\sum \sigma$.

Hohenberg and Kohn proved in their two famous theorems that using the electron density, the ground state can be found and that there exists a *functional*—a mathematical mapping from a function to a number—that is universal, *i.e.*, independent of the external potential which describes all the quantum mechanical effects.^[55] With the universal functional $E[n]$, the ground state energy in DFT would be the same as in the Schrödinger equation. A remarkable feat!

The ground state energy E_0 , which is discussed more in Sec. 4.6, is given either by the expectation value of the Hamiltonian minimized over all many-body wave functions or from the value of the functional minimized over all possible ground state electronic densities:

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \min_n E[n(\mathbf{r})] = \min_n F_{\text{HK}}[n(\mathbf{r})] + V[n(\mathbf{r}), v(\mathbf{r})]. \quad (4.6)$$

The functional $F_{\text{HK}}[n(\mathbf{r})]$ can be divided further and one part is the kinetic energy functional. However, it turned out to be challenging to find a good approximation to this functional. The kinetic energy is a large and significant contribution to the total energy and needs to be treated accurately. To handle this, Kohn and Sham did the following ansatz. They assumed that the electron density can be mapped to a system of *non-interacting particles*, called Kohn-Sham (KS) particles.^[56] In this single-particle picture, it is easy to get the kinetic energy of the KS (non-interacting) particles ($T_s = -\frac{1}{2} \sum_{\text{occ.}} \langle \phi_i | \nabla_i^2 | \phi_i \rangle$). The ansatz also results in a set of Schrödinger-like single particle equations called the Kohn-Sham equations which are described by the Kohn-Sham orbitals ϕ_i and eigenvalues ϵ_i :

$$\left(-\frac{1}{2} \nabla_i^2 + v_{\text{eff}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \quad (4.7)$$

The first term is the kinetic energy of the non-interacting particles and $v_{\text{eff}}(\mathbf{r})$ is the effective potential the KS particles feel. The effective potential implicitly depends on the density, which is $n(\mathbf{r}) = \sum_{\text{occ.}} |\phi_i|^2$ in KS-DFT, and is explicitly defined by two functional derivatives:

$$v_{\text{eff}}(\mathbf{r}) = \frac{\delta V[n]}{\delta n(\mathbf{r})} + \frac{\delta W[n]}{\delta n(\mathbf{r})}. \quad (4.8)$$

Here, $V[n]$ is the external potential functional and is exactly $V[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}$. $W[n]$ is the internal electron-electron interaction functional that does not have an exact expression. It is commonly divided into two parts. The largest contribution is described by the *Hartree* potential $\int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$, which can be viewed as the classical repulsive electron-electron expression. The remaining part is denoted E_{xc} . The total energy functional in KS-DFT is thus:

$$E_{KS}[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + V_{II} + E_{xc}[n]. \quad (4.9)$$

Where $E_{xc}[n]$ is the *exchange-correlation functional* which consists of the remaining small, yet important, energy contribution.

4.3 The Exchange-Correlation Functional

The exchange-correlation functional accounts for the energy contributions due to the quantum mechanical effects. This functional is non-local, but it is commonly defined via the property *exchange-correlation energy per particle* $\epsilon_{xc}([n]; \mathbf{r})$ which has a spacial dependency:

$$E_{xc}[n(\mathbf{r})] = \int \epsilon_{xc}([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r}. \quad (4.10)$$

Many different approximations to the exchange-correlation energy per particle have been suggested and constructed in various ways. The first suggested exchange-correlation functional approximation was the *Local Density Approximation* (LDA),^{[55],[56]} which is the most local approximation and pointwise maps the electron density onto a homogeneous electron gas with the same density:

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}. \quad (4.11)$$

The homogeneous electron gas gives the exchange and correlation energies. The exchange contribution is expressed exactly for a homogeneous electron gas. A correlation expression is found by fitting the remaining energy contribution from quantum Monte Carlo simulations of the homogeneous electron gas.^[57] LDA turns out to work surprisingly well, not only because of an error cancellation between the exchange and correlation terms but also since LDA satisfies several exact conditions that the universal functional must fulfill.

The LDA exchange-correlation energy per particle is a local approximation that uses only the density value. To develop other exchange-correlation functionals, the exchange-correlation energy per particle was extended with the first and second derivatives of the density, with the name *general gradient approximation* (GGA).

This new kind of functionals, also known as *semi-local* functionals, can be constructed in various ways. One of the first functionals in this class was the functional PW91^{[58],[59]} that was developed by adding cutoffs to correct the errors related to the exchange hole.^[60] The PW91 functional was the starting point for advances in the semi-local functionals, spearheaded by Perdew. Perdew and coworkers continued on the idea that the functional must fulfill the exact conditions of the universal functional. Instead of satisfying all known conditions at the time; Perdew, Burke, and Ernzerhof used only the most critical energy conditions and made a smoother and more numerical stable functional, known as PBE.^[61] Today, this functional is one of the most commonly used for solid-state systems.

These are not the only functionals or approaches of constructing them. Today, there exists an abundance of different functionals, each designed in different ways. Three main design paths are:

- **Semi-empirical approach** (commonly used in chemistry) - These functionals are constructed with parameters fitted to atomic and molecular systems. One example is the BLYP functional with an exchange that has a correct $1/r$ asymptotic behavior^[62] and a fitted correlation.^[63]
- **Model system approach** - These functionals continues with the idea of mapping the electron density to a model system, like LDA, and calculate the exchange and correlation there. AM05 interpolates between the homogeneous electron gas and a surface-based model system depending on the local environment.^[64]
- **Exact condition approach** - These functionals continue on the idea that the functionals should satisfy the exact functional conditions, as discussed before. A recent development here is the SCAN functional,^[65] a meta-GGA—also uses the non-interacting kinetic energy in the functional. This functional satisfies the 17 exact conditions known for meta-GGAs.

4.4 Hartree-Fock Theory

In the next section, DFT will be combined with Hartree-Fock theory. Let us first introduce the Hartree-Fock theory, which is another approach of circumventing a direct solution to the Schrödinger equation. In the Hartree-Fock picture, the electrons are treated as independent particles. Using a single Slater determinant ensures that the wave function is antisymmetric and satisfies the Pauli exclusion principle. The many-body wave function is thus approximated as:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \dots & \phi_N(\mathbf{x}_N) \end{vmatrix}. \quad (4.12)$$

Where ϕ are the Hartree-Fock orbitals. As we discussed before, the interacting electrons are the difficult part, specifically the repulsive electron-electron interaction $\hat{U}$ in Eq. (4.4). In the Hartree-Fock picture, the electrons only interact with the average electrostatic potential of all other electrons, *i.e.*, the *mean-field*, and the $\hat{U}$ term is changed into a Coulomb interaction term J and a exchange interaction term K .^[51]

$$J = \frac{1}{2} \sum_{i,j}^{occup.} \int \int \frac{\phi_i^*(\mathbf{r}_i) \phi_j^*(\mathbf{r}_j) \phi_i(\mathbf{r}_i) \phi_j(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j, \quad (4.13)$$

$$K = -\frac{1}{2} \sum_{i,j}^{occup.} \int \int \frac{\phi_i^*(\mathbf{r}_i) \phi_j^*(\mathbf{r}_j) \phi_j(\mathbf{r}_i) \phi_i(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j. \quad (4.14)$$

Here, one electron in this wave function interacts with all other electrons via the Coulomb and exchange terms J and K but not with itself (note that J and K terms cancel each other out for $i = j$). If the K expression is used for KS-orbitals, it is called *exact exchange*. The Hartree-Fock total energy is given by the expectation value:^[51]

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_i^{occup.} \int \phi_i^*(\mathbf{r}) \left[-\frac{1}{2} \nabla_i^2 + V(\mathbf{r}) \right] \phi_i(\mathbf{r}) d\mathbf{r} + V_{II} + J + K. \quad (4.15)$$

By the variation principle, this leads to the Hartree-Fock equations:

$$\left[-\frac{1}{2} \nabla_i^2 + V(\mathbf{r}) + \sum_j^{occup.} \int \frac{\phi_j^*(\mathbf{r}_j) \phi_j(\mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|} d\mathbf{r}_j \right] \phi_i(\mathbf{r}) - \sum_j^{occup.} \int \frac{\phi_j^*(\mathbf{r}_j) \phi_j(\mathbf{r}_i) \phi_i(\mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|} d\mathbf{r}_j = \epsilon_i \phi_i(\mathbf{r}). \quad (4.16)$$

These equations share similarities with the Kohn-Sham equations (Eq. (4.7)). Next, let us consider the possibility of using Hartree-Fock like expressions in DFT.

4.5 Hybrid Functionals

There are two main motivations for combining DFT and the Hartree-Fock theory. The first comes from the energy of systems with a fractional electron number. The exact energy behavior of systems with fractional electron count is as straight lines between integer occupations with discontinuous derivatives at each integer value,^[66]

Figure 4.1 – A schematic picture of the energy behavior of fractional electrons. The exact behavior is straight lines with discontinuous derivatives. HF is Hartree-Fock, which has a concave behavior for fractional electron and discontinuous derivatives. DFT is represented by semi-local functional, which has a convex behavior. The bending of both lines is exaggerated for illustrative purposes. This illustration is inspired by Fig. 1 in Ref. 67 and Fig. 13 in Ref. 47.

see Figure 4.1. Here, Hartree-Fock theory and semi-local functionals in DFT behave oppositely; combining them should produce a result closer to the straight lines.

The second motivation comes from the *adiabatic connection*—the integral which goes from the non-interacting to interacting system by turning on the Coulomb repulsion term. Becke constructed a successful *hybrid functional* by approximating the integral, leading to mixing exact exchange and LDA half-and-half.^[68] His approach was later generalized to mix any DFT exchange-correlation with the exact exchange:^[70]

$$E_{xc} = E_{xc}^{\text{DFT}} + a_0(E_x^{\text{Exact}} - E_x^{\text{DFT}}). \quad (4.17)$$

Using the PBE functional as the DFT exchange-correlation functional, the hybrid functional PBE0 was suggested^[71] with $a_0 = 1/4$ determined from perturbation theory.^[72] Heyd, Scuseria, and Ernzerhof developed this concept further by dividing up the long-range and short-range parts of all the terms, producing a numerically fast and stable hybrid functional:^{[73],[74]}

$$E_{xc}^{\text{HSE}} = aE_x^{\text{HF,SR}}(\omega/\sqrt{2}) + (1-a)E_x^{\text{PBE,SR}}(\omega 2^{1/3}) + E_x^{\text{PBE,LR}}(\omega 2^{1/3}) + E_c^{\text{PBE}}. \quad (4.18)$$

The screening parameter ω is the amount of long-range vs. short-range, set to $0.15 a_0^{-1}$ in Ref. 74.

4.6 Ground State

A few different approaches to circumvent a direct solution of the Schrödinger equation are presented in this chapter. They all have a similar approach; given the positions of the ions (an external potential), we would like to find the minimum energy of the electronic system, E_0 . In the many-body electron wave function picture, the expectation value of the Hamiltonian is minimized with respect to the wave function,

which in DFT is the same as minimizing the energy functional with respect to the density:

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \min_n (E[n]) = \min_n F_{\text{LL}}[n(\mathbf{r})] + V[n(\mathbf{r}), v(\mathbf{r})]. \quad (4.19)$$

The minimization of Ψ uses the variation principle of Rayleigh–Ritz.^{[75],[76]} Here, F_{LL} stands for the Levy-Lieb functional. In the most modern DFT picture, this functional is minimized over all possible electronic densities.^{[77],[78]}

In regular applications, the number of electrons is an integer. The correct number of electrons is automatically handled in the many-body wave function picture, where the number of operators depends on the number of electrons, see Eq. (4.2). Whereas in DFT, the functional only depends on the density and if we minimize it as is, there is nothing that will keep the desired number of electrons constant. Hence, the density needs to be minimized under the *constraint* that the electron density corresponds to the desired number of electrons N :

$$\int n(\mathbf{r}) d\mathbf{r} = N. \quad (4.20)$$

This constraint is already mentioned in the original Hohenberg-Kohn paper.^[55] Adding this constraint to Eq. (4.19) introduces a Lagrange multiplier λ :

$$E_0 = \min_n \max_{\lambda} \left(E[n] + \lambda \left(\int n(\mathbf{r}) d\mathbf{r} - N \right) \right). \quad (4.21)$$

The Lagrange multiplier λ takes the role of the electron chemical potential of the system.

4.6.1 Constraints

Similar to constraining the number of electrons to minimize the energy, in principle, additional constraints can be added. Before going into the constraints, let us discuss the physical interpretation of the KS properties. The number of electrons and KS particles are the same by construction. The KS eigenvalues are initially said to have no physical meaning in DFT (except the highest occupied). However, in practice, they are commonly used to interpret band structure and band gap.^[79] The KS orbitals even agree with the reconstructed real space orbitals from experiments.^{[79],[80]} Some of the first additional constraints were the specific occupation of KS orbitals with *d*- or *f*-like characteristics or the total magnetization of the system.^[81] Further constraints, especially related to localizing charges in molecules, have been reviewed in Ref. 82. In that review, the authors show that these constraints are on solid theoretical ground and how the added constraints change the effective potential in the KS equations.

For example, a localizing charge constraint introduces a step-like function with a lower end on the part of the molecule where the KS particle should be localized.

These constraints are added to the KS-DFT scheme without any further modifications. The effective potential is modified, but the density is still constructed like the ground state density by using the *Aufbau principle*—filling the eigenvalues bottom-up:

$$n_{gr}(\mathbf{r}) = \sum_i^N |\phi_i|^2. \quad (4.22)$$

Since the occupation is still the ground state occupation, this constraint is called a ground state constraint in this thesis. The described state could be viewed as an excited state of the unperturbed system.^[82] However, in this thesis, excited states refer to states with a different occupation than the ground state. Excited state constraints are discussed in Sec. 4.7.2.

4.6.2 Ion Positions

Once the ground state is found, the electrons are in the lowest energy state. However, this state might not be the lowest energy with respect to the ion positions. Even if the Born-Oppenheimer approximation is used and the ion kinetic energy is set to zero, it does not mean that the ions have to be kept fixed at their positions. The force created from the electrons and ions interacting with the ions is described by the *force theorem* (also known as the *Hellman-Feynman theorem*).^{[83],[84]} The theorem shows that the force F_I is given by:

$$F_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int \frac{\partial V}{\partial \mathbf{R}_I} n(\mathbf{r}) d\mathbf{r} - \frac{\partial V_{II}}{\partial \mathbf{R}_I}. \quad (4.23)$$

Hence, the force depends on the ion positions and the electron density. The ground state of both electrons and ions is found by switching between calculating the density and updating the ion positions until the ion forces equilibrate.

4.7 Excited States

DFT is commonly viewed and used as a ground state theory. Formally, the excited state properties should be accessible since the entire Hamiltonian is determined from the density.^[85] However, the excited state properties cannot be taken directly from the KS eigenvalues since they belong to a non-interacting particle system. The KS eigenvalue differences can be viewed as a zero-order approximation to the excitation energies.^{[79],[85]} Additional methods, beyond DFT, that handle the excited states include many-body perturbation theory, configuration interaction, and coupled cluster theory. However, these methods are usually much more computationally

demanding than DFT. In this section, extensions are presented to handle excited states with roughly the same computational cost as DFT with semi-local and hybrid functionals.

4.7.1 Time-dependent DFT

Time-dependent DFT (TD-DFT) provides a formal extension to handle excited states in DFT. This approach is similar to Hohenberg-Kohn but focuses on the action instead of the energy. TD-DFT can thus handle excitations and is exact for finite systems.^[86] Here, instead of an exchange-correlation energy functional, an exchange-correlation action functional with a time dependence is required.^[87] At the moment, the two most commonly used exchange-correlation action approximations are the adiabatic LDA, which use the LDA functional for the external perturbation at that instant, and random phase approximation, which neglects the exchange-correlation effects of the external perturbation. These approximations work well to calculate electron energy loss, inelastic x-ray scattering, and compact imaging x-ray spectra but are unsatisfactory for optical spectra in semiconductors.^[87]

TD-DFT is somewhat more computationally expensive than regular DFT. It also requires simulation of the entire excitation process, even for static properties in the excited state.

4.7.2 Constraints

One approach to handle excited states, which has roughly the same computational cost as regular DFT, is to add constraints. These constraints are similar to the ground state constraints of charge localization. In the ground state, the constraints change the effective potential, which regular DFT is minimized over. In the excited state, the effective potential also needs to change to describe the excited state instead of the ground state. This change is done by constraining the KS particle to a higher orbital, which will change the density when the orbitals are added up, which in turn will change the effective potential. The resulting KS equations are solved self-consistently until the excited state is found. One gets the minimum energy which fulfills this constraint, like fulfilling other constraints also give minimum energies, but now it approximates an excited state.

This method is known as constrained DFT or $\Delta\text{SCF}^\dagger$, the latter when the total energy difference between the ground and excited state is used.^{[88],[89]} Compared to the ground state occupation, which follows the Aufbau principle, the excited state

[†]also known as ΔDFT or excited state DFT^[82]

occupation is changed to describe an excited state:

$$n_{ex}(\mathbf{r}) = \sum_i^{\infty} f_i |\phi_i|^2. \quad (4.24)$$

Where f_i is either 1 or 0 depending on if the orbital is occupied or not. These excitations describe the excited states of the non-interacting KS particles. Formally, this change breaks the condition that the KS particles have to yield the density corresponding to the minimum energy. However, Görling extended the DFT formalism to include any stationary density and used the generalized adiabatic connection to map from the non-interacting to interacting picture.^[90] This formalism introduces an orbital-dependent exchange-correlation functional, which in practical calculations is approximated by the exchange-correlation functional approximation from the standard DFT formalism.

This method works well for states separated by sufficiently large energy, which is the focus of this thesis. However, in low-lying excitations, the excited state may relax back to the ground state. In recent work, Ramos and Pavanello propose an interesting constraint scheme to handle this collapse to the ground state.^[91] In their scheme, a virtual reference space of the occupied orbitals is created, and the added constraint forces one electron to be in this virtual space, thus creating the excitation that way. This approach uses the standard DFT formalism and averts the collapse to the ground state of low-lying excitation for the 15 molecules tested in Ref. 91.

4.7.3 Ion Positions

Ion relaxation in an excited state can be considerably more difficult than in the ground state. The force theorem is still valid and the ions can be moved based on it. If the excited and ground states are well separated, the ions can relax and find their minimum energy positions in the excited state. However, if the potential energy surface of the excited and ground state are close, the ions may want to relax back into the ground state positions and change the electron configuration with it. This situation would correspond to a non-radiative relaxation back to the ground state. However, since the electron has been constrained to keep the electron configuration, there is a mismatch between the ion position and the electron configuration; thus a stable set of ion positions cannot be found for this excited state. Similar situations may also emerge between different excited states. As the ions relax with a specific occupation, the KS eigenvalues may shift and cross which could lead to another excited state being calculated.

4.8 Practicalities of DFT Calculations

While this chapter has presented the theoretical framework for DFT, there are a few other practical matters to consider when performing DFT calculations. The main goal of the DFT codes is to calculate the energy with the density and KS orbitals. Since the effective potential in KS equations depends on the density, which in itself is constructed from the KS orbitals, the KS equations need to be solved self-consistently. Starting with an initial density, the equations are iterated until a stationary density is found.

In practical calculations, the KS orbitals need to be expressed in a basis set. There are many different choices of basis sets one can use. In this thesis, the plane wave basis set is in focus, which expresses the KS orbital ϕ_j as:

$$\phi_{j\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{j\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}. \quad (4.25)$$

Where $\mathbf{G}$ are the *reciprocal lattice vectors* and $C_{j\mathbf{k}}(\mathbf{G})$ are the coefficients for a selected *k-point* $\mathbf{k}$. These coefficients, which need to be minimized, depend on the number of plane waves which, in turn, are limited by an introduced cutoff E_{cut} :

$$\frac{1}{2}|\mathbf{G} + \mathbf{k}|^2 < E_{cut}. \quad (4.26)$$

This cutoff, which corresponds to the kinetic energy of the plane waves, determines the number of plane waves. However, to correctly describe the fast varying features of the wave function would require an enormous number of plane waves, making it impractical for large systems.

There are a few solutions, which differ in various DFT codes, around this problem. This work uses the Viena Ab-initio Simulation Package (VASP),^{[92],[93]} a plane-wave code that uses the Projector Augmented-Wave method (PAW)^{[94],[95]} with the corresponding PAW pseudopotential.^[96] The PAW method separates the fast and slow varying parts of the wave function by using projector functions $\langle \tilde{p}_i |$:

$$|\phi_{j\mathbf{k}}\rangle = |\tilde{\phi}_{j\mathbf{k}}\rangle + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle) \langle \tilde{p}_i | \tilde{\phi}_{j\mathbf{k}}\rangle. \quad (4.27)$$

Here, $|\tilde{\phi}_{j\mathbf{k}}\rangle$ is the pseudo plane wave contribution that varies slowly compared to localized all-electron contributions $|\varphi_i\rangle$ and $|\tilde{\varphi}_i\rangle$. The partial wave $|\varphi_i\rangle$ is precomputed on a radial grid for a reference atom followed by a pseudization process that gives the pseudo partial wave $|\tilde{\varphi}_i\rangle$, projector function $\langle \tilde{p}_i |$, and pseudopotential. The pseudization process introduces a radial cutoff. Inside this radial cutoff, the pseudopotential is modified, whereas outside, it matches with the exact potential. It is only inside these PAW spheres that the all-electron contributions modify the pseudo plane wave

contributions. To further speed up the calculations, only the *valence* electrons are calculated. Since the *core* electrons do not contribute much to the bonding, they are kept fixed, known as the *frozen core approximation*.

When doing practical DFT calculations, not only must one choose the fundamental input like the choice of functional but also practical inputs like the size of the supercell, k-points, and various cutoffs, such as the plane wave energy cutoff, to get accurate and precise results.^[97]

Chapter 5

Magneto-Optical Properties

“The electrician is the oldest profession. When God said ‘Let there be light!’, the electrician had already finished his work and connected all the wires.”

My father (1954-present)

Like my father’s joke hints at something that happens before the light appear, so must the electronic structure be known before one can calculate the magneto-optical properties. This chapter discusses two common experiments for color centers and how the measured properties are calculated theoretically. Most of the methods have been derived and used by other researchers. My contribution to the method of calculating the transition dipole moment is described in detail in Paper I. The properties have been convergence tested for the divacancy in 4H-SiC. The results for both the divacancy and single vacancy in different polytypes are presented.

5.1 Photoluminescence

The experimental photoluminescence setup consists of an excitation laser that shines on the sample while the emitted photons are measured. If the sample contains point defects, the electrons may be excited between the defect states. In the measured spectrum, there may be sharp peaks called Zero Phonon Lines (ZPLs). These lines correspond to the transitions between different defect states and can be used to identify the defect. The intensity of the ZPLs depends on the excitation laser. A strong signal occurs when the excitation laser is tuned correctly to the defect. If the laser energy is too large, the defect may change the charge state, and the signal might disappear.

The photoluminescence spectra are temperature-dependent. In the spectra, next to the ZPLs, are the phonon sidebands that consist of phonon-assisted transitions. At high temperature, the ZPL intensity decrease and the transition move into the

phonon sideband, effectively broadening the ZPL. To prevent this decrease, the sample is often put in a cryostat and cooled down close to absolute zero to remove thermal noise. Even at absolute zero, there is some motion left (zero-point motion), but the ZPLs are the brightest under these conditions. So far, only optical transitions have been discussed. However, there is always a possibility that the electron relaxes non-radiatively back to the ground state without an optical emission.

5.1.1 Zero Phonon Lines

Figure 5.1 shows an excitation cycle for a two-defect-level system in a semiconductor. The cycle starts when an electron absorbs a photon and moves from the ground to the excited state, known as absorption. In the excited state, the Franck-Condon principle is applied. There are two versions of the Franck-Condon principle. The classical one states that the transition occurs without changing the ion positions, and the quantum one states that the transition probability is determined from the square of the overlap between the two states. In the excited state minimum, there are two possibilities of relaxing back to the ground state. The first keeps the ion positions fixed and emits a photon, known as emission. This transition is described by the classical Franck-Condon principle. The second alternative is that the electron relaxes directly back to the ground state minimum. This transition, called the ZPL, can happen since the probability of this transition is non-zero using the quantum Franck-Condon principle. The ZPL is in a narrow energy range compared to the absorption and emission that both spread out over a broad energy range due to the phonon contributions.

To calculate the ZPL, two additional approximations of a parabolic shape, as well as the same coupling between the defect and the lattice in both the ground and excited state, are made.^[98] The parabolic shape in the ground state represents a quantum harmonic oscillator. The excited state is assumed to have the same parabolic shape; however, they might differ in a real system. The energy of the ground and excited state are calculated from DFT and constrained DFT. The total energy of the ground state minimum $E_{g,min}$ is taken from regular DFT. Then the KS particle is constrained to a higher occupation to produce the excited state as discussed in Sec. 4.7.2. This constraint will change the forces on the ions, which are moved to find the minimum of the excited state and the corresponding total energy $E_{e,min}$. Once the minima of both states are found, the energy of the ZPL is given by the following equation:

$$E_{ZPL} = E_{e,min} - E_{g,min}. \quad (5.1)$$

If the excited state minimum cannot be found, it may be because the fixed occupation does not have a stable set of ion positions, indicating that this transition may relax non-radiatively. The ZPL intensity depends on the transition dipole moment.

Figure 5.1 – A schematic picture of absorption, ZPL, and emission. The left side shows how the ZPL and sidebands may look like in a measured spectra. The right side shows the two defect levels and how the electron jumps between the ground and excited state.

5.1.2 Transition Dipole Moment

In experiments, the ZPL intensity depends on different factors, like the energy of the excitation laser. However, a theoretical maximum can be calculated from the transition dipole moment (TDM) $\boldsymbol{\mu}$. Here, the Born-Oppenheimer approximation is used to separate the ionic and electronic contributions. The ionic contribution is the overlap between the ion wave functions. Whereas the electronic contributions are described by the TDM equation, which can be written in both real and reciprocal space:

$$\boldsymbol{\mu} = \langle \phi_f | q\mathbf{r} | \phi_i \rangle = \frac{i\hbar}{(\epsilon_{f,k} - \epsilon_{i,k})m} \langle \phi_{f,k} | \mathbf{p} | \phi_{i,k} \rangle. \quad (5.2)$$

Where ϕ_i and ϕ_f are the initial and final orbitals in the transition and $\epsilon_{f,k}$ and $\epsilon_{i,k}$ are the initial and final eigenvalues. Both of the orbitals and eigenvalues are taken from the KS particles. Commonly, these have been taken from the same wave function, usually the ground state. However, I showed in Paper I that it is crucial to include the orbital change due to the ion relaxation in the excited state. One orbital should be taken from the ground state wave function and one from the excited state wave function. Both the polarization and intensity are affected by this change.

5.1.3 Radiative Lifetime

The electron only stays in the excited state for a limited time, called the lifetime, before returning to the ground state. It relaxes back through either nonradiative processes or radiative decay. The latter is driven by spontaneous emission, and the rate of decay depends on the radiative lifetime τ that, in turn, depends on both the ZPL frequency ν and the TDM $\bar{\mu}$ of the excitation:

$$\tau = \frac{3\epsilon_0\hbar c^3}{n^2 4\pi^3 \nu^3 |\bar{\mu}|^2}. \quad (5.3)$$

The constants in the numerator are the vacuum permittivity, Planck constant, and speed of light, respectively. The n in the denominator is the refractive index, which for 4H-SiC is 2.6473 (taken from experiment).^[99]

5.2 Electron Paramagnetic Resonance

Electron Paramagnetic/Spin Resonance (EPR/ESR) detects tiny interactions (about 10^{-4} eV) and is a powerful method for understanding point defects.^{[100],[101],[102]} The point defect needs to have unpaired electrons (non-zero spin) for the energy levels to interact with the magnetic fields. Usually, a static magnetic field is applied to split the energy levels. Then an oscillating microwave frequency magnetic field is applied to change the occupation between the split levels. Jumping between the split levels produces a single peak in the EPR spectra. If the nuclei have spin (like ^{13}C), the split electron energy levels will interact with this spin and split further; this is known as hyperfine splitting, which corresponds to many different peaks in the spectra, the height of the peaks follow the pascal triangle, at least for spin-1/2 nuclei. If the point defect has a spin larger than 1/2, additional interactions between the electron energy states themselves are possible, known as zero-field splitting.

5.2.1 Spin Hamiltonian

The experimental measurements are usually mapped to an effective Hamiltonian, called a spin Hamiltonian. To use a spin Hamiltonian, two conditions need to be valid. The included states in the spin Hamiltonian need to be well separated from the non-included states and the operators need to be able to be written with spin operators.^[100] The spin Hamiltonian H_s uses the nuclear spin operator $\hat{\mathbf{I}}$ and the electron spin operator $\hat{\mathbf{S}}$, which is a fictitious spin, but in most cases it coincide with the spin of the defect. The simplest form of the spin Hamiltonian H_s , which contains all the relevant features for this thesis, is:

$$H_s = \mu_B \mathbf{B}^T \mathbf{g} \hat{\mathbf{S}} + \hat{\mathbf{I}}^T \mathbf{A} \hat{\mathbf{S}} + \hat{\mathbf{S}}^T \mathbf{D} \hat{\mathbf{S}}. \quad (5.4)$$

The first term is the Zeeman effect, where $\mathbf{g}$ is the g-tensor (which for a free electron is the identity matrix scaled with the free electron value g_e) and μ_B is the Bohr magneton. The second term is the hyperfine coupling, where $\mathbf{A}$ is the tensor connecting the spin of the nuclei and electrons. The final term is commonly referenced as the zero-field splitting term,^[101] which does not require a magnetic field to split the defect levels when the defect spin is larger than 1/2. $\mathbf{D}$ tensor describes the electron spin-spin interaction.

Since these properties are spin-dependent, it is best to start from the Dirac equation,^{[103],[104]} not because of the inclusion of relativistic effects but because of the natural inclusion of spin.^[101]

5.2.2 Hyperfine Coupling Parameters

Starting from the Dirac equation, the contributing factors to the hyperfine tensor can be derived.^{[100],[101]} The two main contributions are the isotropic hyperfine interaction, also known as the Fermi contact term, and the anisotropic hyperfine interaction, also known as the dipole-dipole interaction term. The Fermi contact term H_{FC} is large where the spin density is large and calculated:

$$\hat{\mathbf{I}}^T \mathbf{H}_{FC} \hat{\mathbf{S}} = \frac{2\mu_0}{3} g_n \mu_N g_e \mu_B \sigma(\mathbf{R}_n) (\hat{\mathbf{I}} \hat{\mathbf{S}}). \quad (5.5)$$

Here, the σ is the spin density at the nuclei position $\mathbf{R}_n$. The dipole-dipole interaction H_{dd} is larger outside the center of the nuclei and can be written as:

$$\hat{\mathbf{I}}^T \mathbf{H}_{dd} \hat{\mathbf{S}} = \frac{\mu_0}{4\pi} g_n \mu_N g_e \mu_B \left(\frac{3(\hat{\mathbf{I}} \cdot \mathbf{r})(\hat{\mathbf{S}} \cdot \mathbf{r}) - r^2(\hat{\mathbf{I}} \hat{\mathbf{S}})}{r^5} \right). \quad (5.6)$$

In both equations, g_N and μ_N are the nuclear g-factor and magneton.

Ref. 102 outlines how the hyperfine tensor A is calculated in a plane wave code, such as VASP.^[105]

$$A_{ij} = \frac{\mu_0 g_n \mu_N g_e \mu_B}{S} \left(\int \frac{2}{3} \delta(\mathbf{r} - \mathbf{R}_n) \sigma(\mathbf{r}) + \frac{1}{4\pi} \left(\frac{3r_i r_j - r^2 \delta_{ij}}{r^5} \right) \sigma(\mathbf{r}) d\mathbf{r} \right). \quad (5.7)$$

Here, S is the total spin. The first term in the integral is the Fermi contact term, which is calculated using the frozen valence approximation and solving the KS equation for the core electrons.^[106] The second term is the anisotropic dipole-dipole interaction which is implemented as in Ref. 107.

5.2.3 Zero-Field Splitting

If the point defects have two or more unpaired electrons, the electron levels will split without a magnetic field present. This splitting is called the zero-field splitting, and the

main contribution comes from the dipole-dipole interaction of the spins:^{[100],[102],[108]}

$$\hat{\mathbf{S}}^T \mathbf{D} \hat{\mathbf{S}} = \frac{\mu_0}{4\pi} g_e^2 \mu_B^2 \left(\frac{3(\hat{\mathbf{S}}_i \cdot \mathbf{r})(\hat{\mathbf{S}}_j \cdot \mathbf{r}) - r^2(\hat{\mathbf{S}}_i \hat{\mathbf{S}}_j)}{r^5} \right). \quad (5.8)$$

Here, $\mathbf{r}$ ($r = |\mathbf{r}|$) is the distance vector between the spins, whereas $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{S}}_j$ are the spin operators. The $\mathbf{D}$ tensor is approximately calculated in DFT by taking the square of the Slater determinant of the KS orbitals $|\zeta_{i,j}(\mathbf{r}_1, \mathbf{r}_2)|^2 = \frac{1}{2} |\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) - \phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_1)|^2$ for every pair-wise interaction:^[102]

$$D_{ab} = \frac{1}{2} \frac{\mu_0}{4\pi} \frac{g_e^2 \mu_B^2}{S(2S-1)} \sum_{i < j} \chi_{ij} \int \int |\zeta_{i,j}(\mathbf{r}_1, \mathbf{r}_2)|^2 \left(\frac{3r_a r_b - r^2 \delta_{ab}}{r^5} \right) d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.9)$$

Where χ_{ij} is ± 1 for parallel and antiparallel spins, respectively. The authors of Ref. 108 implemented this equation in a stand-alone code using the pseudo part of the KS orbitals which account for 95% of the total contribution. Later, the full calculation, including the core regions, was implemented in VASP*.

5.3 Application to Defects in SiC

This section covers the convergence tests of the magneto-optical properties for the divacancy configurations in 4H-SiC. The results of these convergence tests were applied to the silicon vacancy in 4H-SiC as well as the silicon vacancy and divacancy in 6H-SiC. The results also set the foundation for the high-throughput calculations.

5.3.1 Divacancy in 4H-SiC

In Paper II, we performed extensive convergence tests for the calculations of the magneto-optical properties related to the different divacancy configurations in 4H-SiC. First, the ZPL convergence to the size of the supercell with the PBE functional was tested. Here, the ZPL results converge with a 2400 atoms supercell with Γ -point sampling. The converged ZPL results are about 0.2 eV from the experimental value. Second, smaller supercell sizes with increased k-point grids were tested, and the supercell size can be reduced to 576 with $2 \times 2 \times 2$ k-point grid without a noticeable effect on the result. Further, the choice of functional was tested. Running fully self-consistent calculations with the HSE functional is only possible for a small number of atoms (up to few hundred atoms). These calculations produce excellent ZPL results, within 50 meV compared to experimental values. However, due to the computational load, static HSE calculations on the relaxed PBE geometries were also tested. Here,

*and other codes such as Quantum espresso^[109]

the results only change slightly compared to the relaxed HSE geometries and are within 100 meV compared to experimental values. The HSE calculations on top of the PBE geometry show that the difference of 0.2 eV by using the PBE functional for the ZPL results mainly comes from the functional choice. Figure 5.2 shows the most important ZPL results from Paper II.

Figure 5.2 – ZPL results from the four different configurations of divacancy in 4H-SiC. The PBE results for 2400 atoms with Γ -point and 96 atoms with $4 \times 4 \times 4$ k-point grid are shown on the left for each configuration. These results are about 0.2 eV from the converged HSE results that, in turn, are close to the experimental measurements. The data is from Paper II.

Similar size scaling for the ZPL results is found for the hyperfine coupling parameters with the PBE functional. Here, the hyperfine coupling parameters for the closest ions to the defect also converge with a 576 supercell with $2 \times 2 \times 2$ k-point grid. Farther away from the defect, the relative error gets bigger for smaller supercells.

Comparing all converged magneto-optical properties with the experimental values, the different divacancy configurations are identified. The identification is presented in Table 5.1. To get the right identification, it is important to compare many different properties. Comparing only ZPL results would misidentify the two closest lines (hh and kk would swap places).

Divacancy Configuration	ZPL [eV]		ZFS [MHz]		Hyperfine splitting A_z [Mhz]	
	Calc.	Exp. ^[110]	Calc.	Exp. ^[110]	Calc.	Exp. ^[111]
hh	1.056	1.095	1329	1336	9.06	9.2
kk	1.044	1.096	1307	1305	9.99	10.0
kh	1.081	1.119	1314	1222	—	—
hk	1.103	1.150	1363	1334	—	—

Table 5.1 – Identification of the divacancy configurations in 4H-SiC. The data is from Paper II.

Later, I calculated the TDM for the divacancy configurations as described in Paper I. These properties also follow the same convergence as discussed above, and the converged polarization results agree well with the experimental measurements, see Figure 5.3.

These results further support the identification in Paper II. In addition to these findings, the radiative lifetimes calculated in Paper I (16 to 23 ns) are close to the experimental values (12 to 15 ns) measured at 20 K.^[112] Even if the high temperature may speed up the transition and the TDM is calculated with the PBE functional, using the HSE functional does not affect the results noticeably as discussed in Appendix A in Paper I, the calculated radiative lifetimes are remarkably good.

5.3.2 Silicon Vacancy in 4H-SiC

There have been two competing models to describe the ZPLs at 1.352 and 1.438 eV in 4H-SiC. In Paper III, we showed that these lines come from the negatively charged silicon vacancy. This identification was accomplished by calculating the magneto-optical properties using a 1532 atom supercell with Γ -point only. This supercell size is between the 576 and 2400 atoms discussed in the previous section and it is the smallest supercell where Γ -point is sufficient. The calculated ZPL, ZFS, and the hyperfine coupling parameters for the negatively charged silicon vacancy agree well with the experimental measurements. Table 5.2 presents a summary of the results. The relative error of the ZFS is quite large since the absolute value is small.

Figure 5.3 – Polarization (parallel and perpendicular to the c-axis) of the divacancy configurations in 4H-SiC. The calculated results are the a) and b) subplots, and the experimental measurements are the c) and d) subplots. For the calculated results, the x-axis is the ZPL energy, whereas the y-axis is the calculated TDM results. For the experimental measurements, the x-axis is the measured photon energy, whereas the y-axis is the counts per second for the specific photon. The data is from Paper I.

Silicon vacancy Configuration	ZPL [eV]		ZFS [MHz]		Hyperfine Si _{II} [Mhz]	
	Calc.	Exp. ^[113]	Calc.	Exp.	Calc.	Exp.
<i>h</i>	1.541	1.438	18.3	2.6	7.7	8.2
<i>k</i>	1.443	1.352	33.3	35.0	7.9	8.4

Table 5.2 – Identification of the silicon vacancy configurations in 4H-SiC. The data is from Paper III. Only the hyperfine coupling parameter for the second nearest silicon atoms Si_{II} is included, the nearest carbon atoms are presented in the paper.

5.3.3 Divacancy and Silicon Vacancy in 6H-SiC

In Paper IV, we investigated the divacancy and silicon vacancy in 6H-SiC. Here, the size of the supercell is similar to the size used for the silicon vacancy in 4H-SiC. The number of atoms is 1536. Since there are more configurations for both defect types, the identification is harder. The identification that fits all the data best for the divacancy is presented in Table 5.3, and for the silicon vacancy is presented in Table 5.4. The hyperfine splitting is difficult to measure for the low symmetry configurations of the divacancy, which is why these values are not present in the table. For the silicon vacancy, only the hyperfine values for the carbon atom above the vacancy are presented with the values parallel and perpendicular to the *c*-axis. The hyperfine values for the carbon atoms below the vacancy are found in Paper IV.

Divacancy Configuration	ZPL [eV]		ZFS [MHz]		Hyperfine Si _{IIa} [Mhz]	
	Calc.	Exp. ^[110]	Calc.	Exp. ^[110]	Calc.	Exp. ^[111]
<i>k1k1</i>	0.939	1.088	1300	1300	12.70	12.7
<i>hh</i>	0.933	1.092	1342	1334	11.72	12.5
<i>k1h</i>	0.948	1.103	1335	1236	–	–
<i>k2k1</i>	0.944	1.119	1343	1317	–	–
<i>hk2</i>	0.961	1.134	1355	–	–	–
<i>k2k2</i>	0.972	1.134	1374	1347	11.72	13.3

Table 5.3 – Identification of the divacancy configurations in 6H-SiC. The data is from Paper IV. Only hyperfine for the second nearest silicon atom Si_{IIa} is included, the other silicon atoms are presented in the paper.

Silicon vacancy Configuration	ZPL [eV]		ZFS [MHz]		Hyperfine C _{top} [Mhz]	
	Calc.	Exp. ^[114]	Calc.	Exp. $ D $	Calc. A , A _⊥	Exp. A , A _⊥
<i>k1</i>	1.207	1.368	-26.7	13.9	84.3, 30.3	80.5, 33.6
<i>k2</i>	1.197	1.398	97	64.0	83.3, 33.2	80.5, 33.0
<i>h</i>	1.244	1.434	3.7	13.3	84.6, 31.2	80.5, 33.6

Table 5.4 – Identification of the silicon vacancy configurations in 4H-SiC. The data is from Paper IV. Only hyperfine for the nearest carbon above the silicon vacancy C_{top} is included, the other nearest carbon atoms below the silicon vacancy are presented in the paper.

5.3.4 Conclusion

The magneto-optical results for these two defects, the divacancy and silicon vacancy, in two polytypes of SiC provide an excellent start for designing the high-throughput calculations. First, the ZPL results are good enough to identify the defect type, but additional properties like hyperfine coupling parameters, ZFS, and polarization are required to identify the different configurations.

Second, the PBE functional captures the main contributions for all these properties at a low computation cost, making it ideal for high-throughput calculations. However, this will introduce a systematic shift (about 0.2 eV) of the ZPL, which seems to be the case for all the tested defects regardless of polytype and charge state.

Finally, the supercell size and k-points need to be set. From the supercell size convergence tests in Paper II, the 576 atom supercell with $2 \times 2 \times 2$ k-point set is chosen as a good compromise between calculation speed and a small self-interaction of the defect.

Chapter 6

High-Throughput Calculations

“Shut up and calculate!”

Richard Feynman (1918-1988)

What is needed to calculate the electronic structure and magneto-optical properties for a vast number of point defect clusters? In high-throughput calculations of many different defect systems, every calculation must be converged to get reliable results. One also needs an algorithm that handles the possible scenarios a calculation may encounter. Three general guidelines to consider when doing high-throughput calculations are:

- The convergence settings need to be high enough to handle the most demanding systems.
- The manual input needs to be minimal, *i.e.*, an algorithm that a computer can execute autonomously.
- The edge cases, such as non-converging calculations, need to be handled.

6.1 Convergence

Akin to other high-throughput endeavors, like the search for new materials pioneered by the Materials Project^[115] and continued by similar efforts,^{[116],[117]} convergence is a priority. The convergence settings must be increased to handle the most demanding materials in order to get dependable results. The plane wave cutoff used in Paper II, Paper III, and Paper IV was 420-480 eV. However, when starting doping with various elements, the plane wave cutoff needs to be increased to converge all elements the same. Hence, the plane wave cutoff was raised to 600 eV to produce a database of calculations, all using consistent convergence settings.

6.2 Algorithm

During the manual calculations in Paper I, Paper II, Paper III, and Paper IV; the relevant excitations are found by ocular inspection of the defect states and their energy levels. However, this approach is not easy to program into an automatic algorithm. It might not even work because it is sometimes difficult, even for a human, to know if a state is a defect state when it is close to either the conduction or valence band edges. To solve this, we use the Inverse Participation Ratio (IPR)^{[118],[119]}—a measurement of how localized the states are—to identify the defect states as presented in Paper V. If the IPR of a state is above a set threshold, the state is considered a defect state. Once the defect states are identified, all the single excitations are found and calculated. Additional details about the implementation and algorithm is found in Paper V. In this paper, a collection of workflows, called Automatic Defect Analysis and Qualification (ADAQ), have been implemented using the High-Throughput Toolkit (*httk*).^[120]

6.2.1 Handle Failing Runs

In manual calculations, if something fails, one can look at it and perhaps fix it. However, in automatic calculations, even if there is just a 1% chance of failure, for 10 000 calculations, it means that 100 runs will fail. To avert manually handling failed runs, a process for handling the edge cases is needed.

Included in *httk* are checkers that monitor the calculations and kill any calculation that breaks the predetermined rules. The checkers keep track of runs that break and also tries to fix them whenever it is possible. One can write additional checkers with predetermined rules to handle edge cases for specific workflows. For the defect workflow, there are two cases where additional checkers are needed. As discussed before in Sec. 4.7.3, the constrained excited state may not have a stable set of ion positions. Another case is if the starting geometry is too far from any stable set of ion positions. To avoid wasting time trying to converge these runs, a checker kills the calculation if convergence seems to take too long time. Here, the rule is that if the steps in the electronic convergence become greater than the smallest previous number of steps by a buffer of 5 steps, the job is killed.

6.3 ADAQ - A Collection of Workflows

ADAQ is presented in detail in Paper V. In brief, it is a collection of workflows designed to automate point defect calculations in semiconductors. ADAQ can relax the unit cells, construct point defect clusters, screen and fully characterize point defects.

The full characterization workflow is the most accurate one and follows the conclusions found in Sec. 5.3.4. Using a 576 atom supercell and $2 \times 2 \times 2$ k-point grid, the different defect configurations can be identified using the calculated magneto-optical properties. The hyperfine coupling parameters and zero-field splitting are calculated for the ground states. The excited states include all single excitations between defect states as well as the excitations to and from the conduction and valence band edges. It performs these calculations for five different charge states and the different spin states of the point defect, as discussed in Sec. 3.2. All these calculations produce a coherent picture of the point defect.

However, it is quite expensive to run approximately 400 000 core hours per defect*. Because this level of accuracy is not needed for every point defect, the screening workflow was constructed. This workflow reduces the k-point grid to only Γ -point and decreases the ion relaxation accuracy to speed up the calculations. The magneto-optical property is limited to only ZPL. All ZPL transitions are found from the KS eigenvalue difference, and the most promising is calculated by relaxing the excited state, see Appendix B in Paper V for more details. From the screening workflow, the point defect ground state energy and an ZPL estimate are found. The ZPL estimate is in a ± 0.1 eV range compared to the full characterization workflow.

ADAQ is not the only automatic point defect workflow.^{[121],[122]} However, it is unique in its focus on magneto-optical properties and the ability to construct general point defect clusters.

6.3.1 Defect Generation

The following approach is used to construct the point defect cluster supercells. The host material is analyzed with respect to symmetry and the non-equivalent atoms are found. From this information, the single vacancies and substitutionals are created. A larger challenge is posed by where to place the interstitials.

Two seemingly natural approaches of placing the interstitials are either to use Wyckoff positions or to determine suitable positions from a Voronoi tessellation of the unit cell. The first method uses the symmetry information and works fine when the Wyckoff positions are points. However, when they are lines, planes, or the whole space itself, they are only specified to these degrees of freedom. In Ref. 121, it was suggested dividing up the cell by Voronoi tessellation^{[123],[124]} and placing interstitials at the points, the midpoints of edges, and the center points of faces. I expanded on this idea and mapped these Voronoi points to the Wyckoff positions. This way, the interstitials are placed at the highest symmetry positions first, limiting the number of interstitial locations since a new interstitial location must be at least 0.5 Å from any old locations and its symmetric copies. Figure 6.1 shows the different interstitial positions found by this method for 4H-SiC.

*this particular value is for one divacancy configuration

Figure 6.1 – The interstitial positions in 4H-SiC. The interstitial positions along the Wyckoff lines are shown in a), in the Wyckoff planes are shown in b), and in the Wyckoff space are shown in c). The Voronoi points, the midpoint of the edges, and the center points of the faces are represented by green, blue, and orange, respectively.

For the point defect clusters, the point defects are combined based on non-equivalent atoms and the interstitial positions. Two parameters were added to avoid creating too many clusters. These are a maximum pair-wise defect distance to avoid creating defects that are too far from each other and a minimum distance between vacancies and interstitials to avoid them recombining into substitutionals. I also added a descriptor to avoid duplicates of the same clusters. For further details, see Appendix A in Paper V.

When it comes to creating point defect clusters, it is vital to sample the space of possible defects well. Due to the criterion on convergence of the checker: the job will be killed if it takes too long to relax. An alternative would be to converge each supercell with stricter ion relaxation parameters, but this still does not guarantee that all defect clusters are found. Sampling the defect cluster space well also helps avoid getting stuck in local minima of the point defects. When a great variety of different structures are tested, it is easier to find the point defect cluster with the lowest energy (the global defect minimum).

6.4 Screening Results

First, I present the different generated point defect clusters, then an overview of all the data the screening workflow generates, followed by an example of a database search to show how point defects can be identified.

6.4.1 Defects

I generated a database of intrinsic point defect clusters in 4H-SiC containing 8355 defects and consisting of single and double defects. See Table 6.1 for the number of defects in each defect type. These structures are processed in the screening workflow.

Defect type	Single	Vac _{Si}	Vac _C	Si _C	C _{Si}	Int _{Si}	Int _C
Vac _{Si}	2	4	5	5	5	132	132
Vac _C	2	0	4	6	5	140	140
Si _C	2	0	0	4	0	146	146
C _{Si}	2	1	0	5	4	139	139
Int _{Si}	26	9	3	3	9	1788	1788
Int _C	26	9	3	3	9	1721	1788

Table 6.1 – The number of different point defect clusters in 4H-SiC. The single column shows the number of single defects. The remaining columns show the number of double defects, which is the row combined with the column. All together, these add up to 8355 defects.

6.4.2 Overview

The ADAQ screening workflow was executed for the defects present in the database. Of these 8355 defects in the database, 898 finished the workflow and produced results. The others were stopped by the checkers. Figure 6.2 shows the total spin of the lowest energy spin state, which is calculated by the difference in occupation in the two spin channels.

Figure 6.2 – The percentages of different spin states for the finished calculated point defects. The majority of point defects have either none or one unpaired electron. A few have two unpaired electrons (spin-1), but then it drops off quite fast. It remains to see if the higher spin states (like spin- $5/2$) are related to one defect cluster or if these are the combination of two other spin defects.

Next, the stability of the point defects is presented. The most stable point defects have the lowest formation energy, calculated with Eq. (2.1). Before looking at all the point defects, let us study a subset more closely. The point defects are divided up based on their stoichiometry, which means that all the point defects with the same stoichiometry can transform into each other. As an example, Figure 6.3 shows the point defects with Si:1_C:0 stoichiometry. Here, all the calculated point defects with this stoichiometry are plotted for the various charge and spin states. The different configurations of the same defect type produce lines that collect closely. For example, the carbon vacancy antisite pair (CAV, $\text{Vac}_\text{C}\text{C}_\text{Si}$) has four configurations which give rise to a clustering of four lines. Furthermore, the positively charged CAV has the lowest formation energies for the small Fermi energies. As the Fermi energy increase, the negatively charged silicon vacancy (Vac_Si) becomes the lowest in formation energy. Thus, both the silicon vacancy and CAV are on the *defect hull*—the point defects with the lowest formation energy per Fermi energy in each stoichiometry. Note that the screening workflow only calculates three charge states ($-$, 0 , $+$) per defect. Other charge states for these, or other, point defects may end up on the defect hull.

Figure 6.4 shows an overview of the formation energy of all the calculated point defects divided based on stoichiometry. In the middle is the host material stoichiometry (Si:0_C:0) which corresponds to the Frenkel pairs. Although there are many formation energy lines in these plots, many of which arise from defect types containing interstitials due to the large variations of available configurations, see Table 6.1. Most of the lines are of no discernible focus; only a few are relevant to look more closely at. The point defects with the lowest formation energy lines in each stoichiometry make up the defect hull. The defect hull provides a quick overview of the most stable defects. It also gives hints of which combinations of point defects can be stable, *i.e.*, relative energy between combined and separate defects. For example, the double silicon vacancy ($\text{Vac}_\text{Si}\text{Vac}_\text{Si}$), which is on the defect hull in the Si:2_C:0 stoichiometry, has a quite large formation energy compared to two silicon vacancies in the Si:1_C:0 stoichiometry. This relative energy difference suggests that a double silicon vacancy cluster is unlikely to be found in SiC. It will separate into two silicon vacancies, which, in turn, might separate further into the CAV depending on the Fermi energy. The shape of the defect hull and the comparison between defect types based on their composing components and stoichiometries provide these observations and general trends.

Figure 6.3 – Formation energy for all calculated point defects with Si:1_C:0 stoichiometry, *i.e.*, the host SiC stoichiometry with one missing silicon atom. The x-axis is the Fermi energy, which is plotted across the calculated PBE band gap. The y-axis is the formation energy. Green, orange, and blue lines represent positively, neutrally, and negatively charged defects, respectively, with corresponding (+, 0, -) slope. At every Fermi energy, the most relevant information is the lowest formation energy which correspond to the most stable defect. Hence, in this stoichiometry, the carbon vacancy antisite pair (Vac_CC_{Si}) is the most stable defect at low Fermi energies, whereas the silicon vacancy (Vac_{Si}) is the most stable defect at high Fermi energies. The transition between the two defect types is marked by the vertical line.

Figure 6.4 – Overview of all formation energies for the calculated intrinsic single and double point defects in SiC. Each subplot is one instance of Figure 6.3, where the x-axis is the Fermi energy and the y-axis is the formation energy. The subplots are arranged based on their stoichiometry, with the center subplot being the stoichiometry of the host material. Going left or right corresponds to adding or removing silicon atoms, conversely up and down for carbon atoms.

Of the 898 converged point defect clusters, the screening workflow predicts 2283 ZPLs. After removing the higher energy spin state of the same defects, 1762 remain which are plotted in Figure 6.5.

Figure 6.5 – The ZPLs that the screening workflow predicted for single and double point defects in 4H-SiC. Only ZPLs for the lowest energy spin state is included regardless of the formation energy of the defect. The orange dotted line shows the least square fit. The x-axis shows the ZPL energy up to the band gap energy, and the y-axis shows TDM.

The y-axis in Figure 6.5 shows the TDM (μ) which is calculated from Eq. (5.2). This equation depends on the eigenvalue difference between the two states, which is close to the ZPL energy ($\mu \propto 1/ZPL$). Hence, the TDM can be approximated as C/ZPL , where the constant C is determined from the calculated data. Since there is a $1/ZPL$ dependency, only ZPLs above 0.1 eV are used to determine the constant C . A least-square fit produces the value 1.43 used in Figure 6.5 and fits the trend nicely. Using other statistic methods gave large values (median 4.4 and average 5.4 over all the data), which overestimated the trend.

Figure 6.6 – The radiative lifetime of the predicted ZPLs plotted on a log scale. The x-axis shows the ZPL energy up to the band gap energy and the y-axis shows radiative lifetime between *ms* and *ns*.

Figure 6.6 shows the radiative lifetimes calculated with Eq. (5.3). Here, the radiative lifetime also scales inversely depending on the ZPL energy. This equation has two factors in the denominator that depend on the ZPL energy: ν^3 and $|\boldsymbol{\mu}|^2$. Where ν is the ZPL energy and $\boldsymbol{\mu}$ depends on the inverse of the ZPL energy, as discussed in the previous paragraph. Hence, the radiative lifetime also scales as $\tau \propto 1/ZPL$. In contrast to the TDM, the radiative lifetimes span several orders of magnitude from *ms* down to *ns* and further. Note in this figure that the non-radiative processes are not included in the radiative lifetime calculation. For small ZPL values ($ZPL \lesssim 0.5$ eV), the radiative lifetime is not expected to be accurate compared with experiments because many phonons can bring the excited state back to the ground state non-radiatively.

6.4.3 Search

To find a point defect for a specific application or to understand experimental results, one can query the database and find interesting defects. One example is to use the database to identify the ZPL lines seen in experiments. Consider as an example if it was unknown that the divacancy was related to the four lines around 1.1 eV. Searching for spin-1 defects in the calculated range 0.7-1.3 eV with 1 eV distance to the defect hull, only the divacancy is found with these search criteria. Because this is the only defect among the single and double defects that fulfill these search criteria, this finding further supports the identification of the divacancy presented in Paper I and Paper II.

6.5 Limitations

ADAAQ handles only bulk point defects at the moment. There are other scenarios where point defects can occur. For example, they could occur in stacking faults as discussed in Paper VI. Here, the divacancy is present in a layer of 3C-SiC included as a stacking fault in 4H-SiC (effectively making it a local “6H-SiC”-like environment). The stacking fault acts as a quantum well and slightly modifies the divacancy properties, which accounts for two lines seen in experiments. These lines are not found in the database of 8355 defects discussed above because the structures are not included. The limiting factor to be able to include these in ADAAQ is the defect generation. The defect generation uses the space group and places the defects in the middle of the cell and would have to be modified to create point defects in stacking faults or other interfaces. Once it is possible to create these structures, it is straightforward to run them in the screening or full workflow.

Similarly, it is currently not possible to model 2D materials or surfaces. Apart from that the defect generation code needs to be updated to handle placing defects in 2D materials, the workflows themselves may need an update. Additional testing of the effect of the exchange-correlation functional on the energy and magneto-optical properties for 2D materials is required.

Another scenario where the PBE functional is not accurate enough is point defects with d - and f -elements. It is well known that the PBE functional struggle to provide accurate results for materials with d - and f -orbital physics. If the point defect or host material contains such an element, the results produced by ADAAQ may not be generally trusted. To handle these cases, a more accurate functional must be used. However, the functional cannot be too computational heavy, preventing it from running in a high-throughput manner. A good starting point would be to test DFT+U. This method introduces a Hubbard-like interaction term, which penalizes occupied d - and f -orbitals, to the semi-local functionals in DFT. However, both the energetics and magneto-optical properties must be carefully evaluated with the DFT+U before running these calculations in a high-throughput manner.

6.6 Future Development of ADAAQ

This thesis has presented ADAAQ, a collection of automatic workflows, which is written to be a general software that can take a semiconductor material, generate defects, and screen the most important properties. So far, it has only been tested for 4H-SiC. Hence, the next step is to try it on another host material. If one stays within the realm of semiconductor materials for quantum applications or qubits, many relevant host materials have been suggested.^[125] In Ref. 125, the authors reduce 100 000+ candidates down to 541 host materials suitable for quantum devices. Even with the limitation of using the PBE functional in ADAAQ, there are still 288 host

materials (materials without d - or f -elements) that can be processed with the current capabilities present in ADAQ.

Furthermore, there are additional features that would be useful to add to ADAQ. One of these features is group theory analysis of the defect states and the allowed transitions. To better understand a point defect and its possible applications, the symmetry of the many-body wave function would be analyzed with group theory.

A second feature to add is an easier way to combine the theoretical prediction with experimental data to identify the point defects. There is a vast amount of data present in the database, and finding the right defect corresponding to given experimental results is difficult and time-consuming. Usually, different data comes from different experiments, like photoluminescence and EPR. It is challenging to know if the results come from the same or different defects. Even just with photoluminescence, multiple lines could belong to the same or different defects. To handle this systematically, a matching algorithm is needed. This algorithm would take all experimental data available from a sample and compare it to the database results. The output would be the defects that best describes the experimental data with a probability measure. This algorithm would speed up the identification of defects.

Finally, the data provided by ADAQ is a good starting point, but if more accurate results are needed, the more computationally demanding methods are still calculated manually. However, nothing stops one from adding additional workflows to ADAQ when further accuracy is needed. For example, a workflow to calculate results with the HSE functional for selected transitions would be useful.

Chapter 7

Conclusion

*“It’s tough to make predictions,
especially about the future.”*

Niels Bohr (1885-1962)

To identify and understand different point defects requires a diverse range of magneto-optical properties. These properties include zero phonon lines with the corresponding polarization, intensity, and lifetime characteristics, as well as hyperfine coupling parameters and zero-field splitting. Comparing the experimental measurements of these properties with the calculated first principle values, it is possible to identify the different point defect configurations. This approach has successfully identified the divacancy in 4H-SiC, 6H-SiC, and a 3C stacking fault inclusion in 4H-SiC, as well as the silicon vacancy in 4H-SiC and 6H-SiC. In all these cases, it is important to compare an assorted range of properties to get a rigorous identification and find which configurations best explain the overall data.

In general, finding a point defect that can explain all the features of an experiment is arduous. Many unknown defect lines in 4H-SiC have not been identified yet, and to find appropriate candidates is as hard to find as hay in a pile of needles. The number of different point defects in one host material is vast. Not only are there different defect types but also different configurations of the same type. Each may have multiple charge and spin states. Calculating magneto-optical properties for all these variations is a mammoth task.

ADAQ was developed for this reason. It is a collection of automatic workflows that can systematically investigate any point defect by creating them and calculating their magneto-optical properties. With 4H-SiC as a test material, the single and double intrinsic defects are created and the roughly 8000 point defects are processed in the screening workflow that calculates the most important energy and optical properties. For these 8000 defects, about 900 converged. By arranging the formation energy diagrams based on the stoichiometry of the point defect, one can get a good

overview of all the defects, especially the most stable ones. Apart from the energy of the defect, the optical properties show zero phonon lines spanning the entire range of the band gap with lifetimes from ms to ns. This screening data provides an excellent start for finding and identifying new point defect in 4H-SiC.

The screening data can be used to identify new point defects and search for point defects with interesting properties. I hope that ADAQ will facilitate the search for new exciting point defects in SiC and many other host materials relevant for quantum applications.

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Chapter 8

List of Included Publications and my Contributions

[I] **Theoretical Polarization of zero phonon lines in point defects**

Joel Davidsson

Journal of Physics: Condensed Matter **32** 385502 (2020)

I conceived the project, performed the calculations and wrote the manuscript.

[II] **First principles predictions of magneto-optical data for semiconductor point defect identification:**

the case of divacancy defects in 4H-SiC

Joel Davidsson, Viktor Ivády, Rickard Armiento, Nguyen T. Son, Adam Gali, and Igor A. Abrikosov

New Journal of Physics **20** 023035 (2018)

I performed the majority of the calculations and wrote the manuscript with contributions from the other authors.

[III] **Identification of Si-vacancy related room-temperature qubits in 4H silicon carbide**

Viktor Ivády, Joel Davidsson, Nguyen T. Son, Takeshi Ohshima, Igor A. Abrikosov and Adam Gali

Physical Review B **96** 161114 (2017)

I contributed to the calculations and the manuscript as well as discussion and analysis of the data.

[IV] **Identification of divacancy and silicon vacancy qubits in 6H-SiC**

Joel Davidsson, Viktor Ivády, Rickard Armiento, Takeshi Ohshima, Nguyen T. Son, Adam Gali and Igor A. Abrikosov

Applied Physics Letters **114** 112107 (2019)

I performed the calculations and wrote the manuscript with contributions from the other authors.

[V] **ADAP: Automatic workflows for magneto-optical properties of point defects in semiconductors**

Joel Davidsson, Viktor Ivády, Rickard Armiento, and Igor A. Abrikosov

Submitted (arXiv preprint available arXiv:2008.12539 (2020))

I designed, tested, and implemented the software as well as wrote the manuscript with contributions from the other authors.

[VI] **Stabilization of point-defect spin qubits by quantum wells**

Viktor Ivády, Joel Davidsson, Nazar Delean, Abram L. Falk, Paul V. Klimov, Samuel J. Whiteley, Stephan O. Hruszkewycz, Martin V. Holt, F. Joseph Heremans, Nguyen T. Son, David D. Awschalom, Igor A. Abrikosov and Adam Gali

Nature communications **10** 1-8 (2019)

I contributed to the calculations and the manuscript as well as discussion and analysis of the data.

Chapter 9

Related, not included publications

1. **Energy-surfaces from the upper bound of the Pauli kinetic energy**
Kati Finzel, Joel Davidsson and Igor A .Abrikosov
International Journal of Quantum Chemistry **116** 1337-1341 (2016)
2. **Semi-Local Parameterization of the Electron Localization Function in Second-Order Density Gradients**
Alexander Lindmaa, Joel Davidsson, Ann E. Mattsson and Rickard Armiento
arXiv preprint arXiv:1908.06947 (2019)

Chapter 10

Papers

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Papers

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