

A simulation study on interactions between defects in diamond



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A thesis submitted for the degree of
Doctor of Philosophy

Hilary 2024

Acknowledgments

Everything is so sudden and unreal until I realise that I am about to submit my thesis and finish my DPhil career at Oxford. It's quite challenging for me, especially being a unique modeller in an experimental group. Fortunately, I am still survived. Here I would like to express my sincere gratitude to the Photonic Nanomaterials Group.

I would like to express my deepest gratitude to my supervisor, Jason Smith, for your invaluable guidance, support, and encouragement throughout the entire duration of my doctoral studies. I would like to thank my parents for your endless love and unconditional support. I cannot be here without you. I am truly thankful to Yuxing Zhou for your amazing advice and insightful discussion on my research project and also I cannot forget the days we spent playing basketball together. I would like to thank Dr Joseph Prentice for your patience in tutoring my simulation and giving me suggestions on my academic career.

There's a lot I am truly thankful for in Oxford. Thanks to people who would like to play with me. I do enjoy the time we spent together. Thanks to those lovely cats living in Oxford. Thanks for the music that helps me pull through my darkest time at night. I really can't survive until now without all of these. Thanks for everything.

List of Publications

- **Articles**

1. [1] *Ab initio* study of defect interactions between negatively-charged nitrogen vacancy centre and carbon self-interstitial in diamond.
Andrew R. Kirkpatrick, **Guangzhao Chen**, Helen Witkowska, James Brixey, Ben L. Green, Martin J. Booth, Patrick S. Salter, Jason M. Smith.
(<https://royalsocietypublishing.org/doi/full/10.1098/rsta.2023.0174>)
2. [2] Simulating the dynamics of NV^- formation in diamond in the presence of carbon self-interstitials.
Guangzhao Chen, Joseph C.A. Prentice, Jason M. Smith.
(<https://arxiv.org/abs/2408.05881>)
3. [3] Laser Activation of Single Group-IV Colour Centres in Diamond.
Xingrui Cheng, Andreas Thurn, **Guangzhao Chen**, Gareth Jones, Patrick Salter, Dorian Gangloff, Jason M. Smith.
(<https://arxiv.org/abs/2409.07421v1>)

- **Conference**

1. Oral presentation on the progress report of the Quantum Computing and Simulation (QCS) Hub – May 2020
2. Quantum Computing and Simulation (QCS) Hub progress report – May 2022
3. Poster presentation at PHOTON2022 – August 2022
4. Participation in the CASTEP Community Conference – July 2023
5. Poster presentation at the GAP and (M)ACE Developers and Users Conference – September 2023

Abstract

The negatively charged nitrogen-vacancy(NV^-) defect in diamond has many applications such as sensing and nanoscale imaging. It is recently becoming a promising candidate in quantum technologies such as quantum computing and quantum communication. Ultrafast laser fabrication of NV^- in diamond has proven its ability to generate NV^- with demanding position accuracy with minimal lattice damage. However, there is a possibility that the formed NV^- would be destroyed and is assumed to be the consequence of the presence of the nearby interstitial carbon. The GR1 centre in diamond is a common optical centre attributed to the neutral monovacancy of the carbon atom (V^0). In this thesis, *ab initio* simulations are conducted to investigate the ground state electronic interaction between interstitial carbon and neutral monovacancy, interstitial carbon and negatively charged nitrogen-vacancy in diamond. The results suggest that their optical properties might change due to hybridized orbitals within them. Additionally, a carbon-nitrogen machine-learning potential is developed for investigating the diffusion mechanism of interstitial carbon with the presence of NV^- centre. According to the molecular dynamics simulations, it could either diffuse away or recombine with the position of vacancy, depending on its initial position and diffusion time. Furthermore, linear-scaling time-dependent density functional theory(TDDFT) is performed, trying to interpret the changes in the optical spectrum during laser annealing where various levels of hybridized orbitals are observed, potentially mapping the difference of photoluminescence signals.

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List of Abbreviations

Abbreviation	Definition
NV	Nitrogen Vacancy
SiV	Silicon Vacancy
CVD	Chemical Vapour Deposition
GeV	Germanium Vacancy
SnV	Tin Vacancy
PbV	Lead Vacancy
PE-CVD	Plasma-Enhanced Chemical Vapour Deposition
PL	Photoluminescence
ML	Machine Learning
DFT	Density Functional Theory
TDDFT	Time-Dependent Density Functional Theory
CN-GAP	Carbon-Nitrogen Gaussian Approximation Potential
AIMD	Ab Initio Molecular Dynamics
GAP	Gaussian Approximation Potential
EPR	Electron Paramagnetic Resonance
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
B3LYP	Becke, 3-parameter, Lee-Yang-Parr Hybrid Functional
HSE	Heyd-Scuseria-Ernzerhof Hybrid Functional
PBE0	Perdew-Burke-Ernzerhof Hybrid Functional
CI	Configuration Interaction
ZPL	Zero Phonon Line
N_s	Substitutional Nitrogen
V	Vacancy
N₂	Nitrogen Dimer
N₂V	Nitrogen Dimer with a Vacancy

V₂	Divacancy
C_i	Interstitial Carbon
HSE06	Screened Hybrid Functional (HSE with 2006 parameters)
DFTB	Density Functional Tight Binding
FF	Force Field
GDML	Gradient Domain Machine Learning
NNPs	Neural Network Potentials
PES	Potential Energy Surface
SOAP	Smooth Overlap of Atomic Positions
CASTEP	Cambridge Serial Total Energy Package
BFGS	Broyden-Fletcher-Goldfarb-Shanno Algorithm
MP	Materials Project
GR1	Green Luminescence 1 (related to NV centers in diamond)
CP2K	A Molecular Simulation Software Package
NVT	Constant Number of Particles, Volume, and Temperature Ensemble
MPI	Message Passing Interface
HPC	High-Performance Computing
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
MAE	Mean Absolute Error
RMSE	Root Mean Square Error
ASE	Atomic Simulation Environment
NEB	Nudged Elastic Band
ONETEP	Order-N Electronic Total Energy Package
QUIP	A software package for interatomic potentials
NGWFs	Nonorthogonal Generalized Wannier Functions
DOS	Density of States

Chapter 1

Introduction

1.1 NV centre in diamond

Diamond is known not only as the hardest naturally occurring substance but also as a promising candidate for quantum sensing, quantum networks, etc. when desirable defects are built inside. Those defects are usually known as colour centres since it had the capability of generating single photons under large band gap materials like diamonds. There are several diamond defects have been studied for quantum applications, such as the most famous negatively charged nitrogen-vacancy(NV^-) centre[17][18] and other defects like SiV^- , SiV^0 and NV^0 [19][20][21]. Further reasons for colour centres in diamond that can be applied in the quantum technology area is that diamond is not only a large bandgap material but also optically transparent. This provides a platform for colour centres to initialize and read out the single-photon source with recorded spin coherence properties. Also, its high Debye temperature and magnetically quiet nature provide an ideal environment for quantum technology

There are many applications for NV centres in diamond. For example, an NV centre can be applied in quantum sensing by coupling to its surrounding environment [22]. This can be achieved by coupling its electronic spin state to the electric field[23], magnetic field[24][25], temperature[26] and strain[27]. This results in energy shifts among spin sub-levels and alterations in transition rates, detectable through optical spin polarization, coherent microwave manipulation, and optical readout. The colour centre in diamond, also known for its long spin coherence time and efficient optical transitions, represents an excellent candidate for quantum networks. In classical optical communication, amplifiers play a crucial role in compensating for signal losses during transmission. However, rather than relying on direct transmission, 'quantum repeater' schemes expand the scope of communication by leveraging remote entanglement distribution as a valuable resource for teleportation[28]. Such strategies need a long-lived quantum memory, identical photons through all nodes and an effective spin-photon interface. NV colour centres have been utilized to successfully demonstrate several essential components of quantum repeaters [29][30].

1.2 Fabrication of NV in diamond

As demonstrated in the preceding section, the NV centre boasts numerous applications. It is challenging to fabricate NV colour centres in diamond. This part will mainly focus on the techniques for engineering NV centres in diamond. In order to generate NV centres in diamond, three steps are typically required: nitrogen doping, vacancy generation, and annealing to create NV centres.

The N(nitrogen)-doped diamond can be made by ion implantation or CVD(Chemical Vapor Deposition) growth. Ion implantation is a widely recognized technique extensively employed in the semiconductor industry and has proven highly valuable for creating colour centres[31]. It has been applied in creating different kinds of colour centres in diamond such as NV, SiV, GeV SnV and PbV which can potentially be used in quantum technology[32]. In the process of ion implantation, the ion is given kinetic energy to collide with electrons and nuclei and eventually be ‘pumped’ into the diamond lattice. Due to the collision between atoms through the implanted path, additional defects would always be created during the procedure which could potentially produce damage in the lattice. Another method of creating nitrogen-doped diamond is PE-CVD(plasma-enhanced chemical vapour deposition)[33]. This is a bottom-up technique which can dope nitrogen gently and equip it with well-controlled depth localisation. This procedure will produce less damage compared to ion implantation and it is also successfully applied in creating NV centres in diamond[34][35].

Vacancy creation is the next step after obtaining a nitrogen-doped diamond. The main techniques for generating vacancies in a diamond lattice are electron irradiation,

ion implantation and laser writing. The electron irradiation method involves the application of high-energy electrons, which are significant enough to displace carbon atoms from their original lattice positions, as discussed in the work by Delgado et al.[36]. In the context of ion implantation, as previously explained in the section on nitrogen doping, it's worth noting that the doping process can lead to the generation of vacancies as well. The laser writing part will be discussed below together with the generation of NV colour centres.

This paragraph will mainly illustrate two techniques for the creation of NV centres in diamond which are thermal treatment and laser writing. From the previous paragraph, vacancies are generated within the diamond lattice and to create an NV colour centre, we need to diffuse vacancies and combine one nitrogen and one vacancy. During the procedure of thermal treatment, ideally annealing the diamond lattice with the temperature of 1100-1200 °C would enable sufficient migration of vacancies and remove most of the undesired defects at the same time[32][37]. In terms of ultrafast laser processing, one significant advantage compared to other treatments is that the nonlinearity of interaction between laser and atoms in diamond could provide high accuracy of localization on the positions of defects in three dimensions. As shown in Figure 1.1, the laser treatment can be generally divided into two parts[38]. In the first part, which is presented on the left side of the figure, one relatively strong laser pulse, called 'seed pulse', is applied to create Frenkel defects, typically like interstitial carbons and vacancies. This procedure is followed by a diffusion pulse train with lower energy where the created vacancies can move and generate NV centre in the diamond.

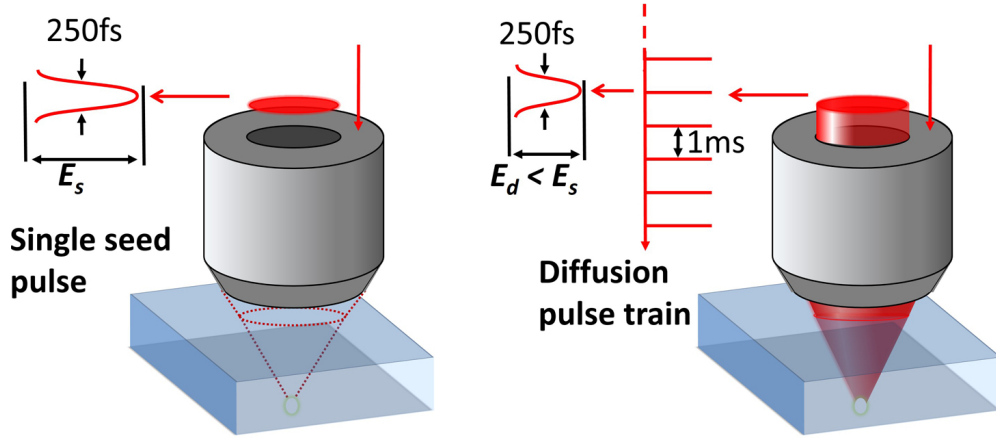


Figure 1.1: A graph illustrating the deterministic creation of NV^- colour centres in diamond through laser writing. The left part of the figure depicts the formation of Frenkel defects using a strong pulsed laser, while the right side illustrates the annealing process, which is accompanied by a series of constant diffusion laser pulses.

1.3 Problems and motivations

As discussed in the previous section, NV colour centres can be generated through either thermal annealing or laser treatment. The photoluminescence(PL) technique can be applied in supervising the formation of NV colour centre in real-time[38] which is illustrated in Figure 1.2. This is shown in the signal of photoluminescence that a stable photon count rate occurs with a duration of around 10 seconds(from 28s to 38s) at the top of Figure 1.2. This style of PL signal corresponds to a determined transition energy between the ground state and the excited state of an NV defect which means an NV centre has been created. At the time of 40 seconds later, the strength of the signal doubles which implies two NV colour centre are generated.

Apart from the ideal situations in which NV colour centres are successfully formed, the PL signal also reveals conditions under which NV centres are unstable or may be destroyed after their formation. To be more specific, in the top graph of Figure

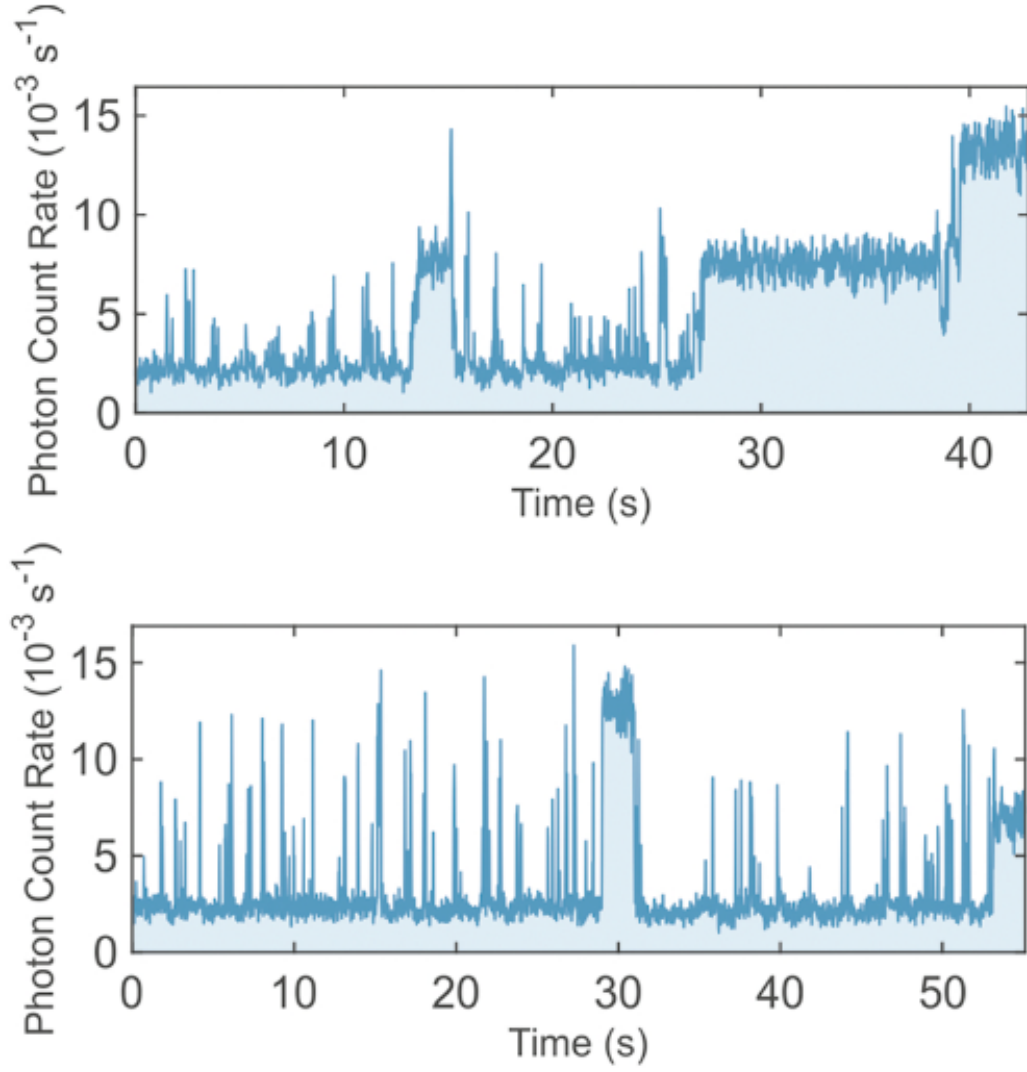


Figure 1.2: Real-time fluorescence signal in controlling NV centre generation. The top graph trace presents two NV centres created after 40 seconds while the bottom one shows the creation and destruction of an NV centre.

1.2, there are some unknown blinking PL signals before the steady platform presents between 0 seconds and around 25 seconds where an NV colour centre is formed and destroyed. This phenomenon occurs more frequently in the bottom graph of Figure 1.2, where blinking signs appear prominently, potentially indicating a significant influence on the manipulation of NV colour centres in diamond. This unusual behaviour raises the main interest of this thesis.

The source of those blinking phenomenon is unknown so far. It is significant to understand the dynamics behind this to engineer NV colour centres in a more scientific method. As mentioned in the previous part, during the procedure of ‘seed pulse’, Frenkel defects including vacancies and interstitial carbons will be constructed. While vacancies will combine with nitrogen and form an NV centre, interstitial carbons can accommodate themselves nearby, hypothetically causing the blinking signal and turning on and off the PL results. Also, the dynamics of interstitial carbons would potentially affect the formation of NV centres. This thesis will apply density functional theory (DFT) to calculate the electronic structure of various stable ensembles’ defective structures and use machine learning (ML) potentials to study the movement of these defects under thermal or laser treatment.

1.4 Thesis outline

This section will describe the main structure and thesis outline of this project.

Chapter2: Literature review This chapter will review some research related to this topic, including the electronic structure of a typical NV colour centre, defect interaction simulations, and the application of machine learning potentials in molecular dynamics simulations.

Chapter3: Theoretical background

The theoretical background will demonstrate some basic concepts of theorems involved in this study. Specifically, two main parts will be presented. Firstly, Density functional theory(DFT) and Time-dependent density functional theory(TDDFT) will be introduced. DFT will be applied in calculating the electronic structure in the ground state in both Chapter 4 and Chapter 5 while TDDFT will be employed in Chapter 7 for predicting the transition energy between ground states and excited states under the various ensemble situations. The second part will primarily focus on the use of a machine learning (ML) potential, which will be utilized in Chapter 6, where large-scale molecular dynamics simulations will be performed.

Chapter4: Perturbation of a neutral vacancy with a nearby interstitial carbon

This chapter will demonstrate the interaction between one neutral vacancy and one interstitial carbon. To be more detailed, different ensembles of a neutral vacancy and split- $\langle 100 \rangle$ interstitial carbon pair will be investigated.

Chapter5: Perturbation of a negatively-charged NV with a nearby interstitial carbon

In Chapter 5, an *ab initio* method will be applied to study the strain and electronic interaction between negatively charged NV^- and split- $\langle 100 \rangle$ self-interstitial carbon.

Chapter6: CN(Carbon-nitrogen)-GAP potential and its applications

This chapter will illustrate a training algorithm that enables machine learning for a potential (CN-GAP). This potential is further applied in learning the diffusion mechanism of interstitial carbon with an NV nearby under various thermal environments.

Chapter7: Absorption properties of negatively-charged NV and interstitial carbon

The method of linear-scaling DFT will be applied in calculating the absorption properties of different combinations of an NV^- and an interstitial carbon.

Chapter 2

Literature review

2.1 Introduction

This chapter will mainly review some literature related to this project and present the knowledge gap between the literature and this project. The review will initialize with some experimental research on nitrogen-vacancy colour centre generation through the methodology of laser writing. According to the previous introduction, the blinking signal coming across through the photon luminescence monitor might be the consequence of the interaction between defects. Therefore, a further review will illustrate potential defects in terms of their electronic structure on their ground state. After this, attention will move to review some up-to-date research on the interaction between point defects in diamond and their influence on the creation of NV^- colour centres in diamond. The above review provides fundamental knowledge in Chapters 4 and 5 where the electronic structure of defects interaction in the ground state will be demonstrated.

As mentioned in the thesis outline, further simulations will be conducted using molecular dynamics enabled by a machine learning potential, due to the high cost of traditional *ab initio* molecular dynamics (AIMD). Therefore, some recent potential will be reviewed. Particularly, the recently developed GAP(gaussian approximation potential) will be mainly reviewed where its application for carbon potential will be demonstrated.

2.2 Laser writing in diamond

Laser writing was initially applied to diamond to graphitize the bulk sample and construct conductive wires, which are used for optical waveguides [39][40] and particle detectors [41][42]. However, after testing these samples, it was observed that following laser writing and thermal annealing, NV^- colour centres were found near graphitized regions. This discovery is regarded as the combination of a mobile vacancy under annealing and a substitutional nitrogen which is doped in the diamond lattice, resulting in the formation of an NV^- colour centre.

This finding motivated further research endeavours aimed at utilizing laser writing to create NV^- colour centres in diamond with greater precision and control. In 2017, Chen et al. successfully demonstrated that NV^- colour centres can be effectively generated through laser writing and processing, followed by thermal annealing [43]. In their experiment, a single laser with a wavelength of 790 nm was first focused on a specific region of the diamond for 300 fs to generate Frenkel defects. After 3 hours of thermal annealing at 1000 °C, several NV^- colour centres were found and identified by their fluorescence properties. Further analysis showed that these NV^- colour centres were produced at the desired locations with an accuracy of around 200 nm in-plane and 700 nm in depth. The limitation in positional accuracy was attributed to the uncontrollable diffusion of vacancies during the annealing process. A later study by Chen et al. in 2019 [38] addressed this limitation by incorporating a fluorescence monitor during localized laser annealing, which provided real-time information on the generation of NV^- colour centres within the lattice.

Although this experiment was successful in creating NV^- colour centres at desired locations, further theoretical explanations are needed to better understand the details of what occurs during both the laser writing and annealing processes. In terms of laser writing, further research is needed to focus on the nonlinear interaction between the laser and the lattice, which would improve control over the laser energy to generate defects. Research conducted by Kurita et al. [44] shows that the pulse duration of the laser significantly influences the balance between the generation of NV^- colour centres and graphitisation. Specifically, they found that more NV^- defects were generated with a 40 fs pulse, whereas a 1 ps pulse was more likely to graphitize the diamond lattice. This research suggests that the absorption of free carriers may increase the number of biexcitons, leading to damage within the lattice. Another aspect motivating this project is understanding the dynamics of NV^- centre creation during the annealing process. As mentioned earlier, in the work of Chen et al. [38], a fluorescence monitor was used to detect the formation of NV^- centres. Observations from the fluorescence monitor clearly show that during the annealing process, NV^- centres were both created and destroyed, as illustrated in Figure 1.2. Although the truth has yet to be revealed, one possible explanation for the laser-driven dynamics is that the signal from the fluorescence monitor might be affected by the splitting of split-interstitial carbon defects [4], as demonstrated in Figure 2.2. Specifically, both split-interstitial defects and vacancies are generated during the creation of Frenkel defects in the presence of a seed pulse, as clearly illustrated in Figure 2.2. During the annealing process, both vacancies and split-interstitial carbon defects can move under a diffusion pulse with an energy of 19 nJ. According to reported studies [45]

[46] [47], the diffusion energies for vacancies and split-interstitial defects are 2.3 eV and 1.6 eV, respectively, making them mobile during annealing. In contrast, the activation energy for the diffusion of substitutional nitrogen atoms is 5 eV [48], which is considered to be highly immobile, allowing them to be treated as stationary. As illustrated in Figure 2.2, the laser treatment is divided into two parts. In the first part, a relatively strong pulse laser is used for the generation of Frenkel defects. During this process, vacancies and split-interstitial carbon atoms are produced, as shown in (i) in Figure 2.2. Following this, a diffusion pulse laser is employed to move the split-interstitial carbon atoms and vacancies. According to a simplified theory of strain fields, vacancies create tensile fields that can attract atoms, while split-interstitial carbon atoms and substitutional nitrogen atoms exert compressive strain, generating a repulsive force on surrounding atoms. In the presence of a diffusion pulse, both split-interstitial defects and nitrogen atoms tend to attract vacancies. As a result, when a vacancy is captured by a nitrogen atom, an NV^- centre is successfully generated, which can produce stable fluorescence that is presented in real-time monitoring. However, before a stable signal is generated, an unstable fluorescence signal occurs, which is interpreted as the influence of split-interstitial defects on the properties of fluorescence. To provide further detail, both interstitial and nitrogen atoms attract vacancies. When a vacancy is about to bind to nitrogen, but a split-interstitial defect also exists nearby, the fluorescence signal may become unstable. After the NV^- centre is created, this structure may be stable enough for split-interstitial carbon atoms to migrate far away, resulting in the production of a stable fluorescence signal. Additionally, as mentioned in Figure 1.2, after the generation of NV^- , the stable

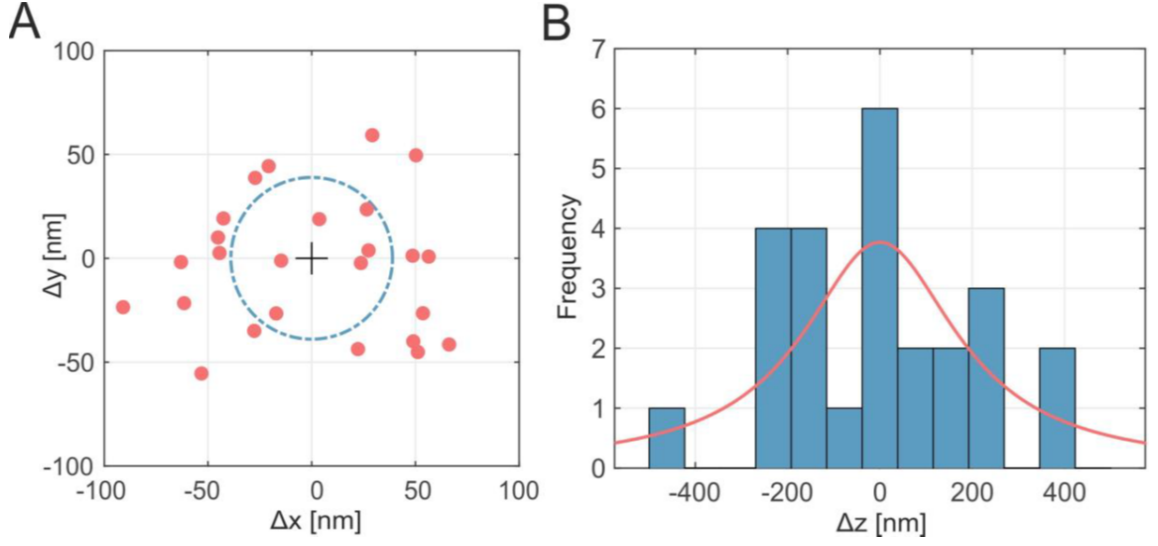


Figure 2.1: A demonstration of position accuracy of formed NV^- colour centre under laser annealing **(A)** in the image plane and **(B)** in depth[4]

fluorescence signal may be switched off. In this case, the explanation could be that diffusing interstitial carbon atoms happen to wander around the NV^- colour centre, which turns off the stable fluorescence signal.

This interpretation of the dynamics of the diffusion process is plausible and clearly explains the situations that can be inferred from the fluorescence signal. However, the specific relationship between the fluorescence signal and the underlying structure remains unknown. Further research is required to support this hypothesis. For example, the presence of interstitial carbon strongly influences the stability of NV^- centres in the diamond lattice, which, in turn, significantly impacts the electronic structure of NV^- . Additionally, the complexity of NV^- formation near an interstitial needs to be verified. These two issues are the primary focus of this project. The following review will concentrate on the electronic structure of the NV^- colour centre, the potential defects created in the lattice, and research examining the interactions between defects

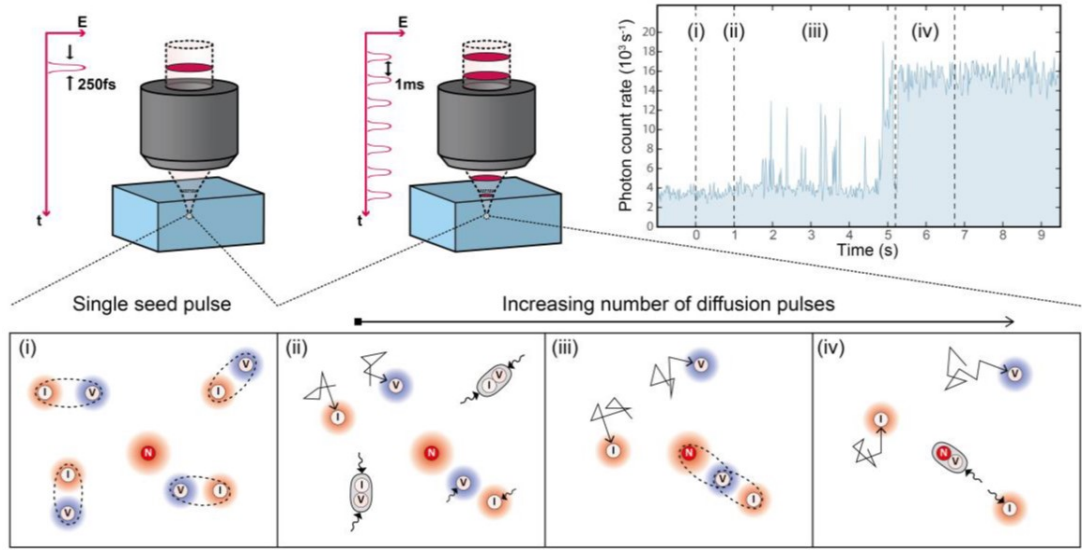


Figure 2.2: Hypothetical dynamic in the process of creation of NV⁻ centres under laser writing.[4]

from both experimental and simulation perspectives.

2.3 Electronic structure of NV^- colour centre

Before conducting in-depth research on the factors that might influence the stability of NV^- colour centres during the annealing process, it is useful to review the structural properties of NV centres. To be more precise, since the fluorescence signal primarily results from the electronic structure of the NV^- colour centre, the electronic structure of an NV^- colour centre will be reviewed in the following section from both experimental and theoretical perspectives. To begin with, the NV^- colour centre is formed by one substitutional nitrogen atom and a nearby vacancy, which was previously a carbon site in the diamond lattice, as shown in Figure 2.3. The NV^- colour centre contains six localized electrons, as demonstrated in the research by Loubser and Van Wyk[49][50]. Their interpretation of the signal observed from EPR is that the electronic structure of the NV^- colour centre is formed by two molecular orbitals: $A_1(a_1, a'_1)$ and the degenerate $E(e_x, e_y)$. This molecular orbital comprises six electrons, two of which come from the dangling bond of nitrogen, while the other four are derived from the carbon atoms surrounding the vacancy. Since it is a six-electron structure, one extra electron is donated by the lattice. This interpretation was later confirmed by a study using both EPR and *ab initio* calculations[51][52][53]. For each molecular centre, two electrons can be accommodated, as demonstrated in Figure 2.4. For the ground state of NV^- colour centre, the a_1, a'_1 molecular orbitals are fully occupied while the degenerate E orbitals are not fully occupied. The electron occupation of the ground state is referred to as 3A_2 , while the first excited state, where one spin-down electron is promoted from a_2 to either e_x or e_y , is regarded as the 3E state. Cur-

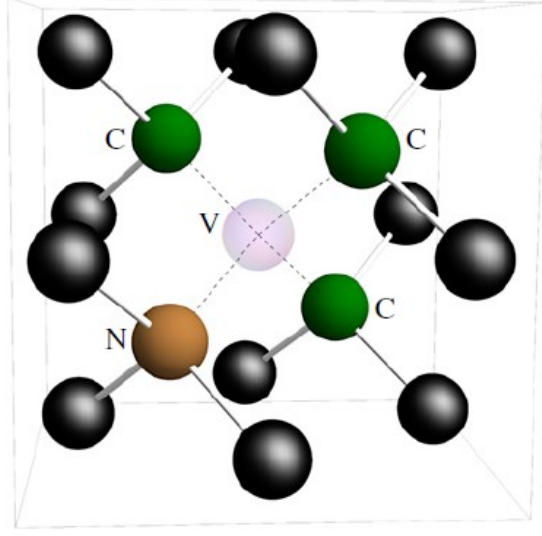


Figure 2.3: A graphic illustrating the NV centre from a review[5] shows the specified positions of carbon atoms, nitrogen, and vacancies. As shown in the graphic, the three green particles represent three carbon atoms adjacent to the vacancy, while the brown particle represents the nitrogen atom next to the vacancy.

rently, the well-known graphic for the electronic structure of the NV^- colour centre is shown in Figure 2.5. The graphic illustrates that the zero phonon line (ZPL) of the NV^- colour centre in diamond is 1.945 eV, which corresponds to the energy gap between the triplet states ^3E and $^3\text{A}_2$. Additionally, a meta-stable state, $^1\text{A}_1$ and ^1E , is shown with an energy gap of 1.190 eV. The following sections will mainly focus on the detailed review of electronic structure in experiments and simulation studies.

2.3.1 Experimental study on electronic structure of NV^- colour centre in diamond

In this project, since the main objective is to better understand how the presence of defects may potentially affect the electronic structure of NV^- , the first step is to provide a comprehensive review of the original electronic structure of the NV^- colour

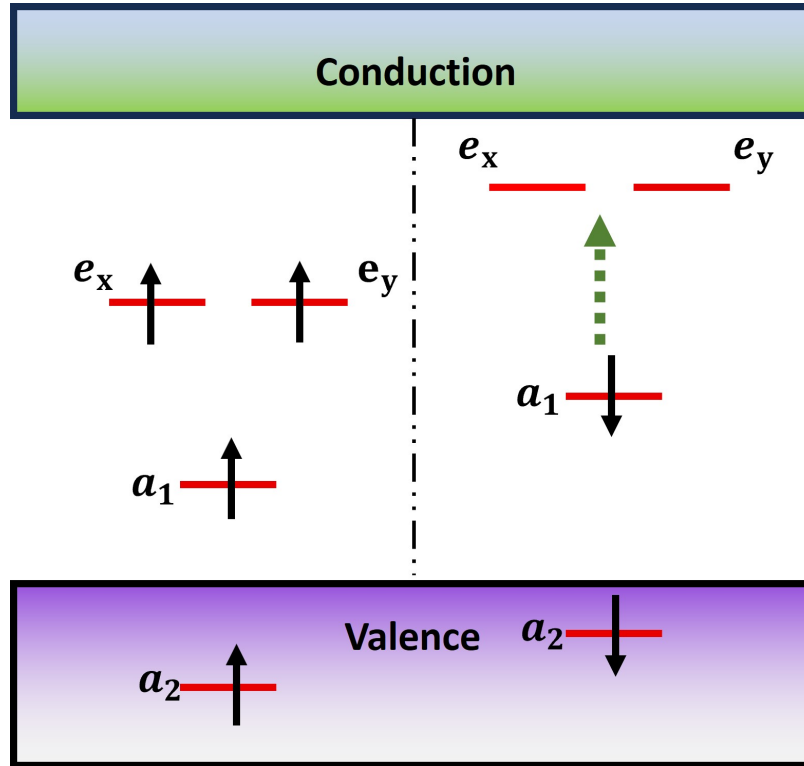


Figure 2.4: Graphic of the electron occupation of the NV^- colour centre at the ground state in diamond. In the 6-electron system of the NV^- colour centre, four electrons fully occupy the spin-up orbitals, as shown above, while two spin-down electrons occupy the a_1 and a_2 orbitals.

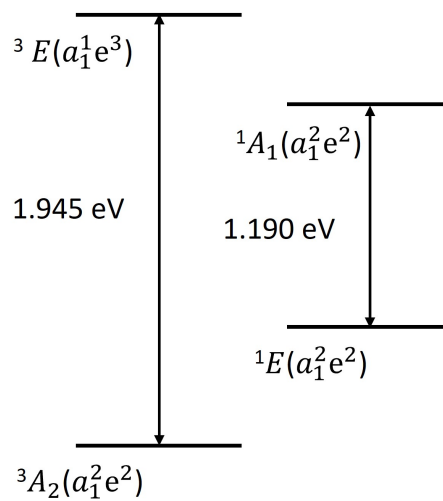


Figure 2.5: Graphic of the electronic structure of the NV^- colour centre in diamond [6]

centre. The following section will mainly focus on the research on the electronic structure of NV^- colour centre in diamond. First to mention is the triplet $^3\text{A}_2$ energy level. The ground state of this energy level was initially studied using EPR [54][50], revealing an energy splitting of 2.88 GHz. In the theoretical study of NV^- [55], this zero-field splitting is attributed to electron spin-spin interaction, while the hyperfine splitting arises from nuclear spin-electron spin interaction. Although the full details of the hyperfine structure are important, the influence of defects may not significantly affect this small energy level splitting. Therefore, the hyperfine structure will not be discussed in detail. When discussing the electronic structure of the triplet ^3E excited state, its energy level can be considered under two conditions: low temperature and room temperature. At low temperatures, the fine structure of the ^3E excited state was directly observed through photoexcitation spectroscopy, due to the exhibition of narrow optical linewidths[56][57]. However, the difficulty lies in the assignment of the split energy level which might be caused by the mixing effects of spectral diffusion, optical spin-polarization and spin mixing in the strain-split fine structure. According to recent studies, the zero-field splitting (ZFS) values in NV^- centres differ significantly between the ground and excited states due to changes in electronic structure and environmental conditions. The ground state $^3\text{A}_2$ has a ZFS of approximately 2.88 GHz, while the excited state ^3E exhibits a reduced ZFS near 1.4 GHz at room temperature. These variations reflect the impact of symmetry changes and electron distribution shifts in the defect configuration under different conditions, as discussed in the work of Gali et al.[58] and Rubinas et al[59].

2.3.2 Ab initio study on electronic structure of NV^- colour centre in diamond

When calculating the electronic structure of the NV^- colour centre in diamond, most research utilises density functional theory (DFT). The advantage of DFT is that it avoids solving the many-body electronic wave function and accurately determines the ground state of the system using the variational principle[60]. The idea of DFT is to apply a non-interacting system to estimate the real interacting system which is what we desire. To provide further detail, the expression of the ground state of the electronic energy in a system can be described as a component of four parts which are the kinetic energy of a non-interacting system, energy of electron-nuclei interaction, potential of electron-electron interaction and the exchange-correlation term. The last term which is called the exchange-correlation term, is unknown and varies from different systems. This term responds to collecting all the missing energy compared to a non-interacting system. As a result, the accuracy of the calculation is highly dependent on the approximation determined by the exchange-correlation term. Several approximations on exchange-correlation terms are widely applied in ground state simulation such as local density approximation(LDA)[61], generalised gradient approximation(GGA)[62] and some hybrid exchange-correlation approximation like B3LYP, HSE, B88, PBE0. Particularly, LDA and GGA perform well in calculating elastic and vibrational properties but are relatively limited in their ability to calculate the bandgap of solid materials. In contrast, hybrid functionals are better at addressing these issues, although they are computationally expensive.

Besides the ground state calculation, time-dependent density functional theory (TDDFT) is the method in excited state calculation. The difference between time-dependent DFT and DFT is that potentials should be set as the function of time. Also, currently, the exchange-correlation term in time-dependent density functional theory is still complex and not fully developed. Although TDDFT is well suited for certain excited states, studies have shown that DFT can extend beyond the global ground state to local minima corresponding to specific spin and spatial configurations. For example, the energy levels of the 1E , 1A_1 , and 3E states can be estimated using DFT, rather than solely the 3A_2 ground state[63]. However, since the exchange-correlation term should be symmetry dependent, code in DFT calculation usually sets symmetry-independent exchange-correlation term as implemented which might lead to unsatisfactory results[64]. This problem was explained by von Barth[64] that the symmetry independent exchange-correlation term also provides reasonable results for energy states which decrease in the non-interacting system to Kohn-Sham orbitals with single Slater determinants. Currently, in the simulation of NV centres, the triplet $^3A_2(m_s = \pm 1)$ and 3E energy level can be approximately described as single Slater determinants which provides a thought in the calculation of vertical energy of 3A_2 to 3E with the value of 1.77 eV in Goss's calculation[65][66]. Based on recent studies on NV centres, the 1E state in the NV^- colour centre can indeed be described by a single Slater determinant if complex orbitals are used, such as e^+ and e^- , rather than real orbitals (e_x , e_y). This approach simplifies the description of the wavefunction for the 1E state. This concept aligns with findings in the literature, where complex orbitals are often applied to accurately capture the electronic properties of NV centres in their

excited states. In contrast, real orbitals require a two-determinant description for more accurate results due to limitations in representing electron correlation and spin distribution. Papers, such as those by Lenef and Rand, discuss the role of complex orbitals and their effects on state symmetry and splitting under strain and magnetic perturbations, which further influence the NV centre’s optical and spin properties [67] [55]. This approach is particularly useful in density functional theory (DFT) studies where efficiency and accuracy are balanced by orbital selection, and it supports the modelling of NV centres’ electronic structures in both theoretical and experimental contexts.

A more rigorous method in excited states calculation than density functional theory(DFT) is the Configuration Interaction(CI). In configuration interaction calculations, the many-body wavefunction for each electronic state is approximated by expanding the state using multiple Slater determinants, which are constructed from a basis of single-electron orbitals. This method would be able to avoid the electron restriction problem in DFT. Also, this method can theoretically compute any excited state if computational resources permit. Because of the restriction of high computational demand, at this stage, configuration interaction is currently applied in a small cluster model. With the application of configuration interaction, error and disagreement in DFT simulation can be corrected, leading various different methods for calculation such as post-DFT method[68] and quantum chemical methods[69].

The above discussion focuses on the electronic structure of the NV^- colour centre, covering both experimental observations and *ab initio* computational studies. It is shown that the simulation results are in agreement with experimental data. For in-

stance, in A. Gali's calculation[70], the zero-phonon line (ZPL) value was determined to be 1.95 eV, which deviates by 0.01 eV from experimental data. Since experiments can be costly and challenging, combining experimental work with simulations can be a more effective approach for exploring and explaining new phenomena.

2.3.3 Spectroscopy of NV Centers: Simulation and Experimental Perspectives

The content of this thesis includes a comparison of optical spectra and an attempt to correlate the results with experimental data. This section will provide a brief overview of how simulation results are interpreted in terms of spectral data, as well as a review of research that compares experimental spectra with simulation outcomes. In a recent review by Ádám Gali, a comparison between simulated and experimental emission spectra for the NV centre is presented, as shown in Figure 2.6.[8] Although there may be some mislabeling on the x-axis of this graph, the ZPL is expected to be located at 1.945 eV. The emission spectrum of NV^- at 300 K consists of a ZPL along with a broad phonon sideband. In contrast, at low temperatures (around 4.2 K), due to reduced mobility of the diamond lattice, the phonon sideband observed at 300 K decouples into several distinct vibronic modes with reduced intensity. At low temperatures, the emission spectrum is less influenced by thermal effects, allowing for a more accurate comparison with simulation results. The simulation work by Gergő Thiering et al. combines ab initio wavefunctions with the adiabatic potential energy surface (APES) to construct the emission spectrum, which is depicted in red

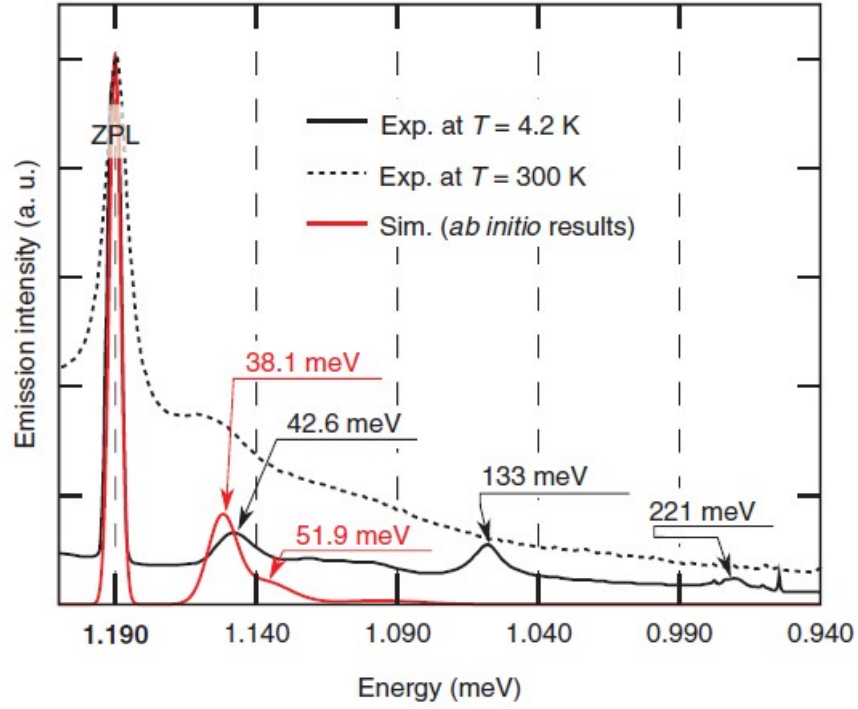


Figure 2.6: The experimental photoluminescence (PL) spectra of the singlet states at 4.2 K (solid black line) and at room temperature (dotted black line) are shown in comparison with the simulated spectrum obtained from the *ab initio* solution (red curve, from Ref. [7]).[8]

in Figure 2.6. The comparison shows that the ZPL aligns well with the experimental data, while there is a slight shift of approximately 4.5 meV observed in the first vibronic emissions.

2.4 Potential defects in diamond

In this section, we will review the potential defects that could be present in diamond. Specifically, defects will be divided into two categories: intrinsic defects and extrinsic defects. In this project, potential defects generated in diamond may affect the fluorescence signal and interfere with the stability of the desired NV^- colour centre. As a result, the review must focus on various defects that might form during laser annealing. The first category includes intrinsic defects, such as carbon interstitials, which have been studied for decades. Since it is challenging to directly observe these configurations (intrinsic defects can be explored using EPR based on their symmetry), most research on defects has been conducted through theory and simulation. More specifically, discussions on carbon interstitials were conducted using the expanded Hückel theory model, while extrinsic defects were investigated through Density Functional Theory (DFT), as will be fully elaborated in the following sections.

2.4.1 Carbon interstitial

In 1973, C. Weigel et al. explained that an interstitial carbon atom is likely to be in the configuration of either a split- $\langle 100 \rangle$ interstitial or a bond-centred interstitial, rather than being positioned in a tetrahedral or hexagonal site[9]. This conclusion is supported by the expanded Hückel method, which uses the linear combination of atomic orbitals (LCAO) basis set [71][72]. In the computations of C. Weigel et al., six types of interstitial configurations were considered for energy estimation. First, we introduce the tetrahedral and hexagonal sites, as depicted in Figure 2.7. As illus-

trated, this is the $(00\bar{1})$ plane in the diamond lattice, where T represents tetrahedral sites for interstitials, and H denotes hexagonal sites for interstitials. Moreover, the crystal indices are specified as $[100]$, $[111]$, and $[011]$ in Figure 2.7. When discussing split interstitials, a simple explanatory graph is depicted in Figure 2.8, which demonstrates the $\langle 110 \rangle$ plane. Split- $\langle 100 \rangle$ interstitial means one original carbon is split into two carbons along $\langle 100 \rangle$ direction. So split- $\langle 110 \rangle$ interstitial has the same meaning with different splitting directions. One special case to mention is that in the situation of split- $\langle 111 \rangle$, the $\langle 111 \rangle$ direction is also the direction of bonds in diamond lattice, which can be relaxed to bond-centred configuration. Among these all configurations, it was proved that split- $\langle 100 \rangle$ interstitial occupied the lowest energy while the second lowest energy situation was the relaxed bond-centred configuration with a value of 1.2 eV. In conclusion, the split-related situations are much lower energy compared to the tetrahedral and hexagonal sites while the split- $\langle 100 \rangle$ interstitial was regarded as the stablest situation[9]. As two potential defects with the lowest energy in diamond, later research[9] found out that the energy difference changed with the charge state of the defects. In a singly positive situation, the bond-centred configuration was only 0.32 eV higher in energy compared to the split- $\langle 110 \rangle$ configuration, whereas in the case of a doubly positive charge, the bond-centred configuration becomes the most stable configuration. This means that in NV^- colour centre in diamond, since NV^- is negatively charged, the defects of interstitial might be positively charged. As a result, both split- $\langle 100 \rangle$ interstitial and bond-centred would be taken into consideration in future of this project.

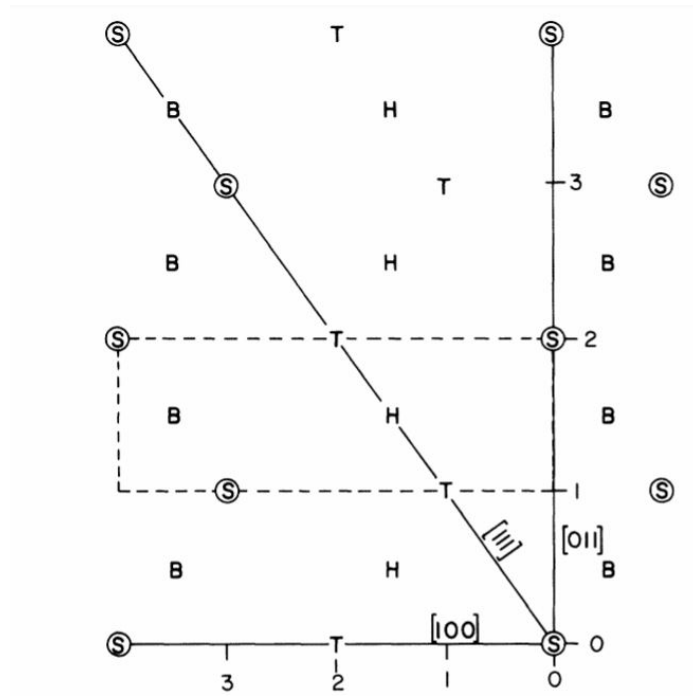


Figure 2.7: A graph on the explanation of tetrahedral and hexagonal site for interstitial carbon in diamond lattice[9].To be more in detail, this is the $(00\bar{1})$ plane in the lattice of diamond where T stands for tetrahedral sites for interstitial and H represents hexagonal sites for interstitial.

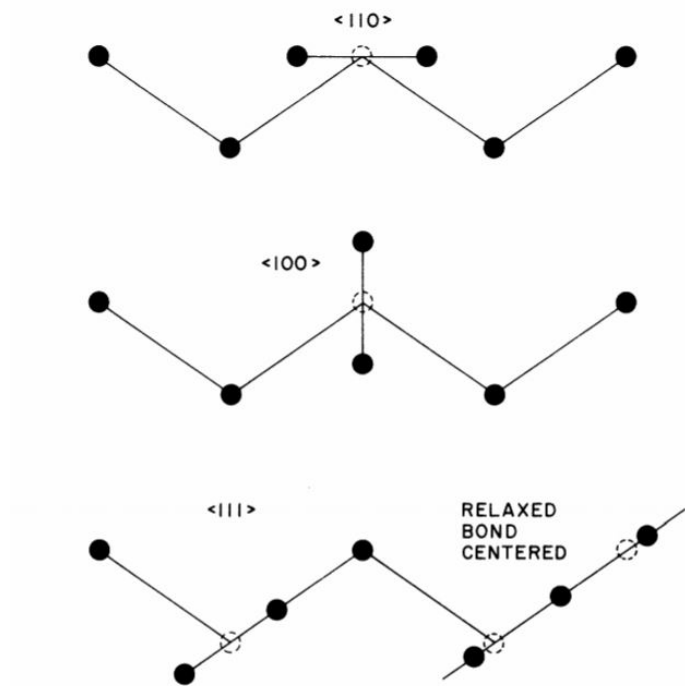


Figure 2.8: A graphic explaining the split-interstitial configurations is presented[9]. The top illustration depicts the split- $\langle 110 \rangle$ configuration, while the middle one shows the split- $\langle 100 \rangle$ configuration. The bottom illustration includes both the split- $\langle 111 \rangle$ configuration and the bond-centered configuration.

2.4.2 Extrinsic defects in diamond

In this section, non-carbon defects will be discussed in detail. To be more specific, the review will focus on nitrogen and vacancy-related defects through DFT calculation. The defects which will be studied in the following section are the substitutional nitrogen(N_s), the vacancy(V) and some related point defects(NV, N_2 , N_2V and V_2).

The first defect to discuss is substitutional nitrogen (N_s), which is the most prominent defect found in Type Ib natural diamond and in N-doped diamonds produced by the chemical vapour deposition (CVD) method. Experimental studies have been performed in substitutional nitrogen for a long time. It is experimentally proved that N_s can be stable in high temperatures, whose diffusion activation energy is around 5.0 eV[48]. This measurement was performed between the temperature degree of 1700 and 2100°C and at the pressure of 7 GPa. Compared to theoretical calculation, at 0 K temperature, activation energy of 6.3 eV was found for N_s to exchange with position to a neighbour carbon atom which means relatively high energy should be applied in migrating N_s . Also, in DFT simulation, the vertical transition and ZPL are also illustrated in Table 2.1. As demonstrated in Table 2.1, both vertical transition and its corresponding ZPL in DFT simulation are in good agreement with the experimental data. In terms of single vacancy(V), it was reported that the neutral vacancy in a diamond lattice is mobile between the temperature of 600 and 800°C with a diffusion activation energy of 2.3 eV. However, the negatively charged vacancy is immobile[45] which is shown in Table 2.2. When it comes to the NV centre, its vertical transition and corresponding ZPL can be produced well through HSE06 DFT calculation. How-

ever, its metastable state is still not able to be reproduced through DFT calculation because its excited state cannot be written as one particle configuration[73] which had been mentioned in the previous section. Also, its results of vertical transition and ZPL value are highly in agreement with experimental data which is illustrated in Table 2.1. When it comes to its diffusion property, according to the mechanism of generation of NV centre, it is reported that $N \rightarrow V$ is also an important step in its diffusion[74]. However, apart from this, a barrier of 4.5 eV diffusion energy indicated that NV can be treated as immobile. In terms of the defect of N_2 , it was identified as the A aggregate in Type IaA diamonds[75][76][77] and its vertical transitions and its corresponding ZPL are also in good agreement in Table 2.1. The next defect for discussion is the N_2V centre. As it is well known that the creation of NV centre is the combination of mobile $V(0)$ and N_s , this means the N_2 defect which is mentioned above will also have the ability to trap the vacancy. This trapping will produce an N_s -V- N_s structure with C_{2v} symmetry. In this situation, the vacancy neighbours two carbon atoms and two substitutional nitrogen atoms[75][78]. This kind of defect will be identified as an H3 optical centre which can be characterized by a value of ZPL at 2.463 eV because a singlet 1A_1 to 1B_1 state transition[79]. The final defect for review is the divacancy(V_2). As discussed before, the neutral vacancy is mobile at temperatures between 600 and 800°C, which means two mobile vacancies would have a possibility of binding together, forming a divacancy defect. In the research of Coomer et al.[80], the ground state of neutral divacancy was concluded as a triplet in C_{2h} symmetry rather than D_{3d} which was expected in D. J. Twitchen et al's research [81]. This finding was also confirmed by a later DFT calculation study with hybrid

Defect	Transition	Vertical		ZPL	
		HSE06 ^f	Experimental	HSE06 ^f	Experimental
N _s	¹ A ₁ → ¹ A ₁	4.6	4.6 ^a	4.1	4.1 ^a
V(-)	⁴ A ₂ → ⁴ T ₁			3.3	3.3 ^b
NV(-)	³ A ₂ → ³ E	2.3	2.2	2.0	2.0 ^c
N ₂	¹ A _{1g} → ¹ A _u	4.0		3.6	3.8 ^d
¹ N ₂ V(0)		2.8		2.7	2.5 ^e
³ N ₂ V(0)		2.7		2.6	2.5 ^e

^aReference[82][83] ^bReference[45] ^cReference[84] ^dReference[77] ^eReference[85]
^fReference[10]

Table 2.1: Comparison on DFT using functional of HSE06 and experimental results on the data of vertical transition and ZPL(unit: eV)

Defect	HSE06(LDA) ^a	HSE06+DFTB ^a	Experimental
V(0)	2.8(2.8)	2.6	2.3 ^b
V(-1)	3.5(2.5)		Immobile
NV(0)	4.7(4.8)	4.5	

^aReference[10] ^bReference[45]

Table 2.2: Comparison of energies of diffusion activation(unit:eV) in HSE06, HSE06+DFTB and experimental situation

functional which proved that the C_{2h} structure is 0.07 in energy lower than the D_{3d} symmetry structure.

After a review of the formation of each NV-related defect about their migration activation energy and energy-related transition, another important factor should also be taken into account which is their charge state. A comparison of all possible charge states in diamond lattice is illustrated in Figure 2.9. The conduction band and valance band were defined by diamond lattice using the DFT computational method. Then for each related defect, being located in a supercell of diamond lattice, different charges are attributed as an input for simulation using HSE06 hybrid functional DFT simulation. As illustrated in Figure 2.9, each defect theoretically has the possibility to be either neutral, single positive or single negative in a diamond lattice. Also, in

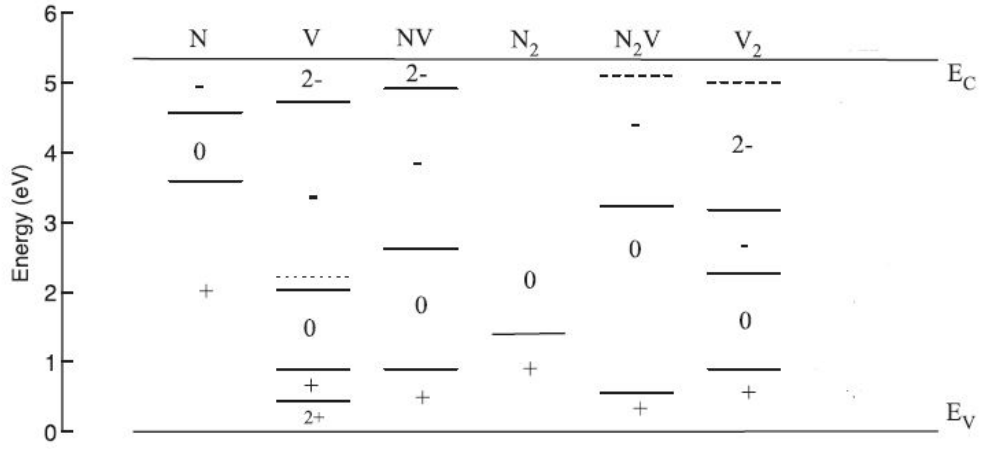


Figure 2.9: Comparison on the adiabatic charge energy level on different nitrogen-vacancy related defects[10].

the case of vacancies, NV centres, and divacancies, there might be a double negative defect, while in the case of vacancies, a double positive charge may also exist. Since the vacancy is mobile and substitutional nitrogen atoms exist in a diamond lattice in the experiment, all NV-related defects should be considered in the defect interaction study. The following section will focus on recent research on the interaction of defects in diamond.

2.5 Interactions between defects in diamond

In the previous section, a full picture was drawn of the list of potential defects in diamond in the process of laser annealing. Currently, few publications provide a comprehensive discussion on the mechanisms detailing how each related defect influences the stability of the NV^- colour centre in diamond during the process of laser annealing. However, some theoretical research has been conducted on how these NV-related defects influence the formation of NV centre. Also, some experimental studies on tracking NV colour centre through annealing will be discussed.

In the research by Peter Deák et al.[10], their simulation, which is based on neutrality equations, defect equations, and relevant DFT simulations, shows that NV colour centres are more likely to be created than vacancies through the process of irradiation. Also, in the process of postirradiation annealing, divacancies are preferred to be created rather than NV centres. Also, in this process, only a short range of diffusion for vacancies to substitutional nitrogen will increase the possibility of NV colour generation. Finally, this research also suggested that the presence of divacancies helps maintain the NV colour centres in a neutral charge state and influences the fluorescence properties of the NV^- centre in the diamond lattice. In recent research of tracking NV centre by repeating annealing[86], it is found that through the process of repeated annealing, formation, quenching and orientation changing of NV centre was discovered. In conclusion on this research, firstly, the density of NV^- colour centre was increased in the process of irradiation at the temperature between 950 and 980°C which is in agreement with the research of Peter Deák et al[10]. Another impor-

tant finding was that at 1050°C, observation showed that the orientation of NV had changed. The reason for orientation was believed to be the result of recombination with other nitrogen atoms.

2.6 Machine-Learning potential on large scale dynamics

2.6.1 Overview

Within the project’s scope, the utilization of machine learning force field potentials will be pivotal in simulating the diffusion behaviour of defects within sizable super-cell systems. However, achieving a balance between accuracy and computational efficiency presents a challenge. Traditional *ab initio* molecular simulations (AIMD) are computationally expensive, while classical force field (FF) simulations often exhibit limitations in efficiency. As a solution, Chapter 6 will focus on the development of a machine-learning potential to conduct molecular simulations with *ab initio*-like precision at a reduced computational cost. This section provides a concise overview of machine-learning methods, with particular emphasis on the Gaussian Approximation Potential (GAP) framework, which will be employed in this research.

Electronic structure calculations are computationally expensive due to their scaling behaviour with the number of atoms, N . For example, in density functional theory (DFT) calculations, the scaling is typically on the order of N^3 in the most common cases. As the system size and simulation duration increase in molecular simulations, computational resources become constrained, particularly for first-principle simulations. In recent decades, machine learning (ML) techniques have emerged as a compelling alternative, offering comparable accuracy to first-principle methods while demanding only a fraction of the computational resources. This method offers a

brand-new perspective on various complex systems, including disordered and amorphous phases. There are several methods available for generating machine learning potentials, including Gradient-domain machine learning (GDML) [87], Neural network potentials (NNPs) [88], and Gaussian Approximation Potentials (GAPs) [89]. Each of these approaches employs a unique mathematical regression technique to develop potentials tailored to describe and learn from specific systems. The following part will mainly review on the GAPs since they will be applied in the project.

2.6.2 Gaussian process regression

In this section, we will provide a brief introduction to Gaussian process regression. Following that, we will review some carbon-related potentials. A general overview of Gaussian process regression is depicted in Figure 2.10. The fundamental concept of the regression can be divided into three parts. Firstly, atomic descriptors (ξ) are constructed to represent complex environments, utilizing kernel functions to characterize the similarity between two distinct atomic environments, as shown in the first graph. Subsequently, Gaussian process regression is employed on the input dataset to generate a fit that closely resembles the true function. In cases where the number of observation data is limited, a relatively large uncertainty may arise. These generated functions can be further utilized in investigating various properties such as forces or tensors. For detailed procedures on each aspect, refer to Volker’s publication [11].

In 2017, a machine learning-based interatomic potential for amorphous carbon, referred to as GAP-17 [90], was formulated to explore the amorphous and liquid phases

of carbon. This potential was developed using density functional theory (DFT) with local-density approximation (LDA) reference data. With its ability to encompass various phases of carbon, GAP-17 possesses the capability to address numerous scientific challenges involving diverse structural environments. For example, it can potentially be applied in studying the growth mechanism of sp^3 hybridized amorphous carbon by ion deposition[91], crystal structure prediction[92], the characterization of 'porous' carbonaceous materials applicable in batteries and supercapacitors[93][94], and more. In 2020, an extended version of GAP-17 was introduced, named GAP-20. This updated version incorporated a larger ensemble of manually generated simulation structures, encompassing defects in graphene, nanotubes, and other intricate systems, which were added to augment the foundation of GAP-17's dataset.[12] A comparison of formation energies for various defects across different carbon structures is illustrated in Figure 2.11, with a particular focus on defects in diamond, which are of interest in this project. As shown in the graph, there is a difference of approximately 2-3 eV in the formation energy of the Diamond Monovacancy and a variance of 4-5 eV for the split-interstitial carbon in diamond between the results obtained from DFT calculation and those from GAP-20. This energy difference will be further investigated in Chapter 3, where the CN-GAP potential will be evaluated. Specifically, we will compare the formation energy of Frenkel defects and various nitrogen-involved defects in diamond with results obtained from DFT calculations.

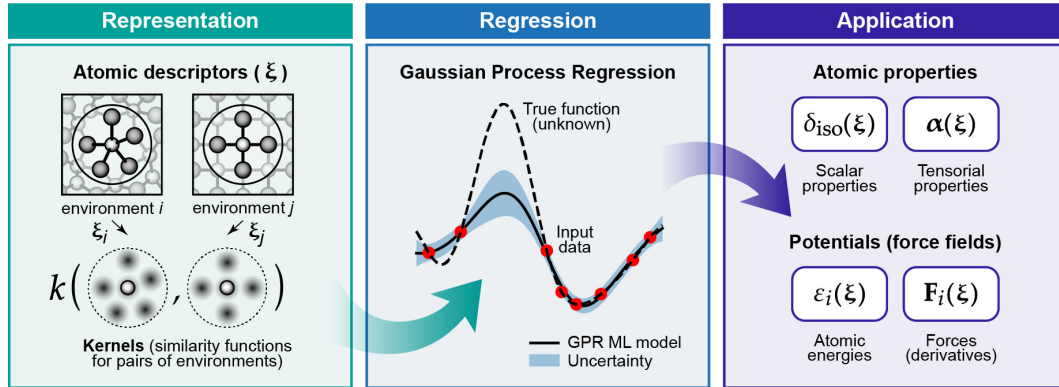


Figure 2.10: Overview of Key Concepts in Gaussian Process Regression (GPR) Machine-Learning Models for Atomistic Properties. The first graph illustrates the generation of atomic descriptors(ξ) to represent local atomic environments with kernel functions to describe the similarity of two different atomic environments. The second graph depicts the procedure in Gaussian process regression. The third part demonstrates how the generated descriptors can be applied in various investigations of properties, such as tensors or atomic energies.[11]

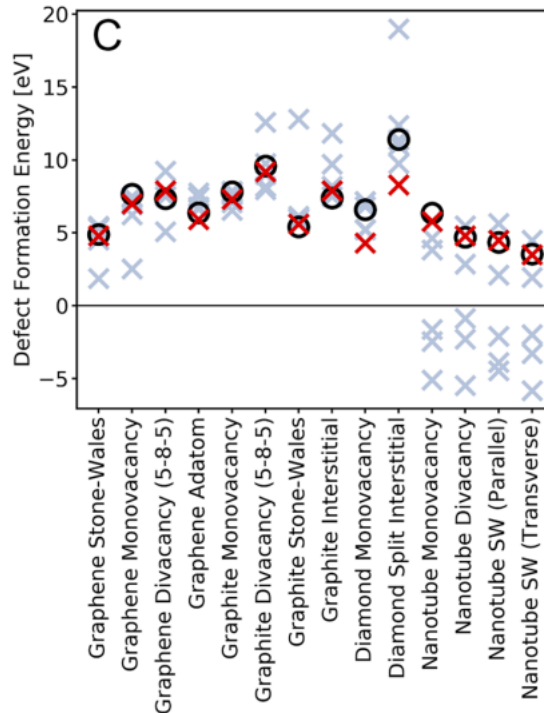


Figure 2.11: Comparison of formation energies for various defects with DFT (optB88-vdW) reference (black circles), GAP-20 (red crosses), and other models (blue crosses).[12]

Chapter 3

Theoretical background

3.1 Introduction

This chapter will introduce the relevant theoretical background of this research. As density functional theory (DFT) will be widely applied in this research project, the basic concepts of DFT will be presented, including the self-consistent field (SCF) calculation algorithms in solving the Schrödinger equation. Then some important elements from practical DFT calculation will be discussed such as plane wave, pseudopotential and exchange correlational functional.

The section is followed by time-dependent density functional theory (TDDFT) which will be applied in investigating the optical properties of different combinations of interstitial carbon and NV centre in diamond. Similarly, this section will start with some fundamental concepts of running TDDFT calculations. After this, a more recently developed method called linear scaling TDDFT will be introduced and this method will be involved in most of my excited states calculations.

The last part of the chapter will mainly focus on machine learning potential for large-scale molecular dynamics simulation. Specifically, it was applied in the molecular dynamics simulation of thermal annealing under various temperatures which will be presented in detail in chapter 6. This section will initialize with some basic concepts of machine-learning potential and then an illustration of its framework will be presented.

3.2 Density functional theory

Over the last three decades, density functional theory has stood as the predominant approach for the quantum mechanical simulation of periodic systems. It was widely applied in materials properties simulations. In this section, the fundamental principles underlying it will be introduced.

Density functional theory is an approach for solving the many-body Schrödinger equation where the various components are expressed as functional of electron density. The main idea of the theory is to reduce the number of degrees of freedom in the system, decreasing the computational cost when solving the many-body Schrödinger equation. To begin with, the many-body Schrödinger equation's Hamiltonian in atomic units can be expressed as follows

$$\hat{H} = \hat{V} + \hat{T} \tag{3.1}$$

In the equation of 3.1, $\hat{V}$ corresponds to the potential energy of the many-body system. The potential energy contributions are made up of interactions between electrons and nuclei. As a result, this will create three terms of interactions which are called nucleus-nucleus interaction, nucleus-electron interaction and electron-electron interaction. $\hat{T}$ is the kinetic energy term, donated by electrons and nuclei as well. Based on the fact that ions are much heavier than electrons, according to the Born-Oppenheimer approximation, their kinetic energies and nuclei-nuclei interaction potential can be considered as a constant and consequently can be neglected. Therefore,

the many-body Hamiltonian can be rephrased as:

$$\begin{aligned}\hat{H} &= -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_I^{N_n} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_i^{N_e} \sum_{i \neq j}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \\ &= \hat{T}_e + \hat{V}_{n-e} + \hat{V}_{e-e}\end{aligned}\tag{3.2}$$

The terms in equation 3.2 are the electron kinetic energy, the electron-nuclei potential and the electron-electron potential from left to right respectively. Here, $\mathbf{r}_i$ and $\mathbf{R}_I$ are the coordinates of the i^{th} electron the I^{th} nucleus. Z_I is the charge on the I^{th} nucleus. Although this Hamiltonian has been simplified, it is still complicated to solve due to the electron-electron potential term. The details of solving this complex term will be discussed in the subsection of the self-consistent field algorithm. An essential principle to highlight here is that when dealing with a Hamiltonian of a system, any given trial wavefunction ψ would result in higher energy compared to its ground state, which is called the variational principle[95].

$$E[\psi] \geq E_0\tag{3.3}$$

This principle is applied in DFT for ground state calculation.

The density functional theory was presented in the Hohenberg-Kohn theorems which conclude that there is a universal functional $E[n(r)]$, which does not depend on the external potential and only represents the particular system of interest, can be applied in obtaining the ground state energy and density.[96] (n corresponds to

the electron density). The energy functional can be written as:

$$E[n(r)] = T[n(r)] + V_{ext}[n(r)] + V_{ee}[n(r)] \quad (3.4)$$

In this equation, all the terms have the same meanings as the equation 3.2 while $V_{ext}[n(r)]$ is called external potential that contains electron-nuclei interaction. However, this theorem did not clarify the exact form of the density term. Kohn and Sham proposed a method to approximate those electron density functionals.[97] They applied a fictitious N non-interacting electron system to describe the real interacting system with the 'orbitals' ϕ_i and the constructed density was expressed as:

$$n(r) = \sum_i^{N_e} |\phi_i|^2 \quad (3.5)$$

A more clarified energy functional can be expressed as below:

$$E[n(r)] = T_s[n(r)] + V_{ext}[n(r)] + V_H[n(r)] + V_{xc}[n(r)] \quad (3.6)$$

As mentioned before, Kohn and Sham opposed a non-interacting system to approximate the real interacting system. In the equation 3.6, the non-interacting system includes the terms of $T_s[n(r)]$, $V_{ext}[n(r)]$ and $V_H[n(r)]$ while $V_{xc}[n(r)]$ means exchange-correlation term which contains all the errors produced through the non-interacting system. The specific form of the exchange-correlation term will be demonstrated later. The following part will have a demonstration of the algorithm for the solution Schrödinger equation in Kohn-Sham's theorem.

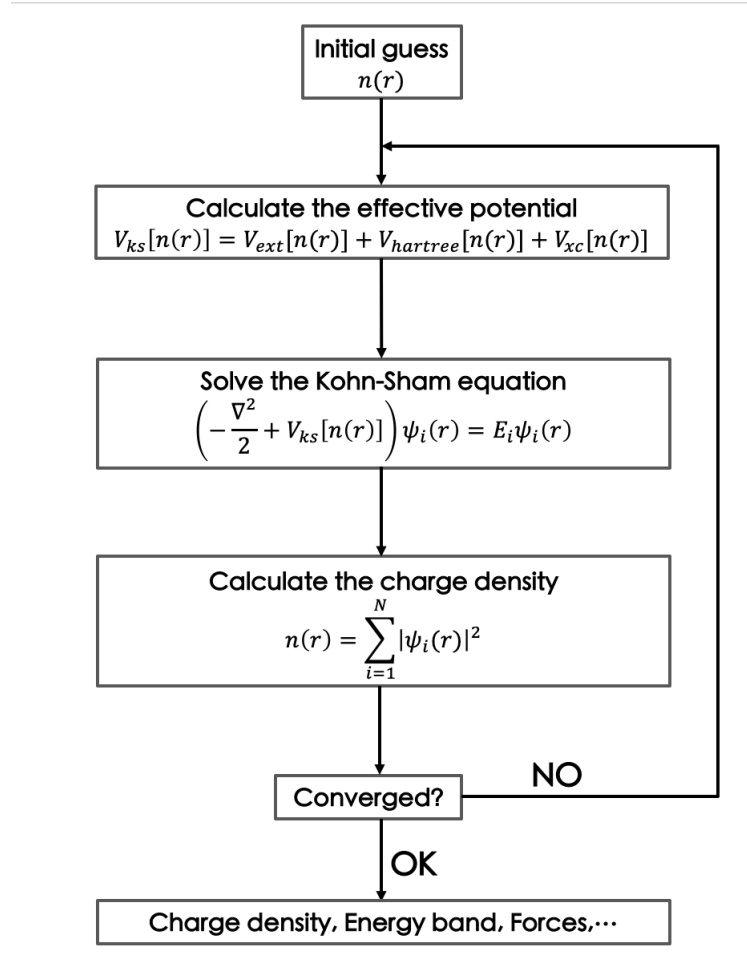


Figure 3.1: The workflow of solving Kohn-Shan equation self-consistently.

3.2.1 Solution of the Schrödinger equation

The Schrödinger equation in the Kohn-Sham Scheme can be rewritten as below:

$$\left(-\frac{\nabla^2}{2} + V_{ks}[n(r)]\right)\psi_i(r) = E_i\psi_i(r) \quad (3.7)$$

where $V_{ks}[n(r)] = V_{ext}[n(r)] + V_H[n(r)] + V_{xc}[n(r)]$. The self-consistent algorithm is shown in Figure 3.1. The process starts with an initial guess of the electron density $n(r)$. The effective potential can be obtained with the guess value of the electron

density. This potential form can be plugged into the Kohn-Sham equation, where the Kohn-Sham wavefunction for each electron ψ_i can be figured out. According to the equation 3.5, the charge density can be calculated which can compare to the previous guess of the electron density. Once the converged electron density is obtained, the self-consistent calculation is done.

3.2.2 Exchange correlational functionals

The research of exchange-correlational functionals is still a large and rapidly developing field since its real form has not been defined yet. Most of the computationally expensive exchange-correlation functionals are designed for particular systems, while two widely applied basic exchange-correlation approximations will be introduced below.

The first one is the simplest approximation among all called local density approximation(LDA) where the homogeneous gas model is applied to simulate the exchange-correlation energies of each infinitesimal density element:

$$E_{xc}^{LDA} = \int n(r)\varepsilon_{xc}(n(r))d\mathbf{r} \quad (3.8)$$

In the equation of 3.8, the term $\varepsilon_{xc}(n(r))$ is the exchange-correlational energy density of the uniform gas. The LDA approximation is a remarkable step in reducing the energy variety between the density functional theory and the real system. However, there still exist significant errors in different structure calculations using LDA. For example, the binding energy of most systems would have around 20-30% overestimation

and the calculated diffusion barrier is known as too small or absent.[98]

Generalised gradient approximation(GGA) is the second one to be introduced which is an improvement of LDA where both electron density and its gradient are taken into consideration:

$$E_{xc}^{GGA} = \int n(r) \varepsilon_{xc}(n(r), \nabla n(r)) d\mathbf{r} \quad (3.9)$$

The exchange-correlational functional applied in this thesis is one of GGA called PBE whose gradient term is constructed from experimental data. The PBE has significant improvement on the absolute error compared to LDA with the error in the range from 3% to 7%.[99]. To balance the computational cost and accuracy of results, PBE exchange-correlational functional is applied in most of this research.

3.2.3 Parameters on running DFT

After demonstrating some basic principles of DFT, this section will primarily discuss the convergence parameters when running DFT in practice. In this study, plane waves are applied as the basis set of wavefunctions in all of the DFT ground state calculations. In a periodic system, the wavefunction of an electron with plane wave basis sets can be expressed as:

$$\psi_k(r) = \frac{1}{\Omega} \sum_G c_{k,G} e^{i(k+G)r} \quad (3.10)$$

Where Ω corresponds to the volume of the lattice, $\mathbf{G}$ and $c_{k,G}$ are the reciprocal lattice vector and coefficients.

Here, two parameters need to be tested for convergence. The first one is k-point sampling. In principle, the more possible $\mathbf{k}$ samples, the more accuracy we could obtain. However, the calculated total energy will converge to a relatively small value when $\mathbf{k}$ points are sufficiently large which means it is significant to have an estimation of $\mathbf{k}$ points before running the calculation.

Similarly, the cutoff energy is another parameter that needs to be tested for convergence. There are an infinite number of allowed $\mathbf{G}$ in the reciprocal space but as the increasing of $|G + k|^2$, the corresponding coefficient $c_{k,G}$ will be less significant. As a result, a defined $E^{CUT} = \frac{\hbar^2}{2m}|G + k|^2$ is applied to truncate the plane wave expansion in equation 3.10.

3.3 Time dependent density functional theory

Time-dependent density functional theory (TDDFT) is an extension of the basic idea in ground state DFT. It is a theory to calculate the excited state of systems. This section will mainly illustrate the basic ideas of TDDFT including its analogy to ground state DFT calculation. Then, an advanced technique, which can reduce the computational cost of running TDDFT simulation, called linear-scaling density functional theory will be introduced. This technique will be applied in all of the TDDFT calculations.

In 1984, the Runge-Gross theorem demonstrated that for a many-body system evolving from a specified initial wavefunction, there exists a direct correspondence between the potential (or potentials) governing the system's evolution and the resulting density (or densities) of the system.[100] This implies that the many-body wavefunction, characterized by $3N$ variables, is equivalent to the electron density, which depends solely on 3 spatial coordinates. Consequently, all system properties can be calculated using the density functional. However, it's important to note that in time-dependent density functional theory (TDDFT), general minimization principles are absent, and a detailed discussion of the proof of the Runge-Gross theorem is beyond the scope of this discussion. Interested readers can find further evidence of the theorem's validity in the reference by Casida [101], which provides an illustrative overview of the progress in TDDFT.

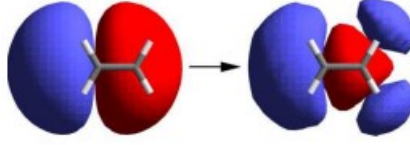


Figure 3.2: An example of NGWF optimization of an electronic orbital.

3.3.1 Linear-scaling density functional theory(ONETEP)

This section will delve into the theoretical framework behind linear scaling density functional theory (DFT) as implemented in the ONETEP software, elucidating key parameters pivotal to these calculations. The basic idea of the ONETEP theory is applying localized non-orthogonal generalised Wannier functions(NGWF) to reproduce the original plane-wave basis orbitals. Specifically, in the traditional Kohn-Sham DFT, the density matrix $n(r, r')$ can be written as :

$$n(r, r') = \sum_i f_i \psi_i(r) \psi_i^*(r') \quad (3.11)$$

where $\psi_i(r)$ represents the eigenstate and f_i denote the occupation state. In terms of the localized non-orthogonal functions, it can be rewritten as:

$$n(r, r') = \sum_{\alpha\beta} \phi_\alpha(r) K^{\alpha\beta} \phi_\beta(r') \quad (3.12)$$

where the matrix $K^{\alpha\beta}$ is the density kernel presenting the occupation of the non-orthogonal basis. Optimizing the form of the basis set allows the elimination of the scale of the DFT simulation from $\mathcal{O}(N^3)$ to $\mathcal{O}(N)$, where N corresponds to the number of atoms. An example of NGWF optimized orbitals can be found in Figure

3.2. Further details on the elimination of scaling can be found in the reference [102]. It's noteworthy that achieving 'plane-wave' accuracy necessitates thorough testing to ensure convergence of the defined non-orthogonal function radius. This aspect will be further explored in Chapter 7, where TDDFT calculations will be conducted to investigate the absorption spectrum of the NV centre and interstitial carbon ensemble in diamond.

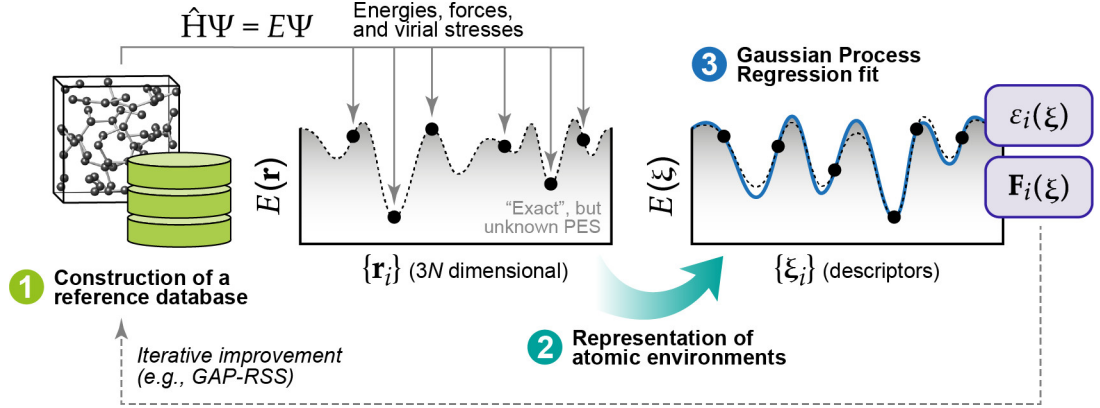


Figure 3.3: Three main steps in GAP generation are as follows: (1) Creating a reference database of quantum-mechanical data for appropriately selected structural models, (2) Representing atomic environments, often using combinations of 2-body and SOAP descriptors, and (3) Performing Gaussian process regression.[11]

3.4 Gaussian Approximation Potential(GAP)

As outlined in the literature review, GAP-20 potentials have versatile applications in investigating the properties of defects across various crystalline carbon structures. This section will elucidate key concepts and provide a brief overview of the framework for training GAP potentials.

3.4.1 Framework of Gaussian Approximation Potential

The framework for training a GAP potential can be found in Figure 3.3 where three main steps are contained. The initial step involves generating a reference database. Typically, this database is computed using *ab initio* methods and comprises information such as total energy, forces, and stresses. These reference data construct the precise yet unknown potential energy surface (PES), which awaits further fitting. Concurrently, the selection of reference data is also significant. After the construction of the database, suitable structural descriptors should be chosen to represent

the database structures. The descriptors commonly applied are distances and angles between atoms together with a Gaussian kernel and many-body Smooth Overlap of Atomic Positions (SOAP) representation with a polynomial kernel. The kernels and representations in GAP have distance cut off, usually around 5-6 Å. In this study, 2-body, 3-body, and many-body SOAP descriptors are utilized to train the carbon-nitrogen (CN) Gaussian Approximation Potential (GAP). Upon completion of the fitting process using these descriptors, the atomic energy can be expressed as a summation of a fixed number and type of kernel basis functions. Subsequently, the obtained energy and force outcomes can be cross-checked against the reference database for validation. Further optimized parameters can be found in the reference of Volker’s review[11] which will not be discussed further here.

Chapter 4

Perturbation of a neutral vacancy with a nearby interstitial carbon

4.1 Introduction

GR1 is a common signal of indication of the presence of neutral vacancy in diamond. However, the perturbation of interstitial carbon and neutral vacancy is unknown. This chapter aims to investigate the interaction between a neutral vacancy and a nearby interstitial carbon.

4.2 Computational details

In this section, the simulation details will be demonstrated. The whole calculation is performed using the method of DFT with PBE as the exchange-correlational functional. This model is progressed in the CASTEP code[103] and the c2x program is used in extracting the volumetric orbital data. As mentioned in the chapter on the theoretical background, two main parameters need to be tested converged, which are the cut-off energy and the k-points grid. This will be discussed in the following section.

The supercell model is generated by Crystallmaker software where two types of configurations are created. The simulation is initialized with a size of $3 \times 3 \times 3$ (216 atoms) but it is optimized to $3 \times 3 \times 6$ (432 atoms) to eliminate the effect of boundary condition from the z direction of a split- $\langle 100 \rangle$ interstitial carbon. To begin with, one monovacancy and one split- $\langle 100 \rangle$ interstitial carbon are individually created for comparison with relative literature to ensure the validation of this simulation. Then, different ensembles of neutral vacancy and split- $\langle 100 \rangle$ interstitial carbon are generated where the separation of two defects is within a distance of less than 5 Å. Specifically, one combination of these defects is shown as an example in Figure 4.1. In this graph, a split- $\langle 100 \rangle$ interstitial carbon defect is accommodated at the centre of a $3 \times 3 \times 6$ supercell whose length is 10.679 Å, 10.679 Å, 21.358 Å. A vacancy is then created around this interstitial carbon within a distance of less than 5 Å by removing an existing carbon in the diamond lattice. With the condition of symmetric locations for the vacancy, there are 6 different symmetric reduced situations in total. These con-

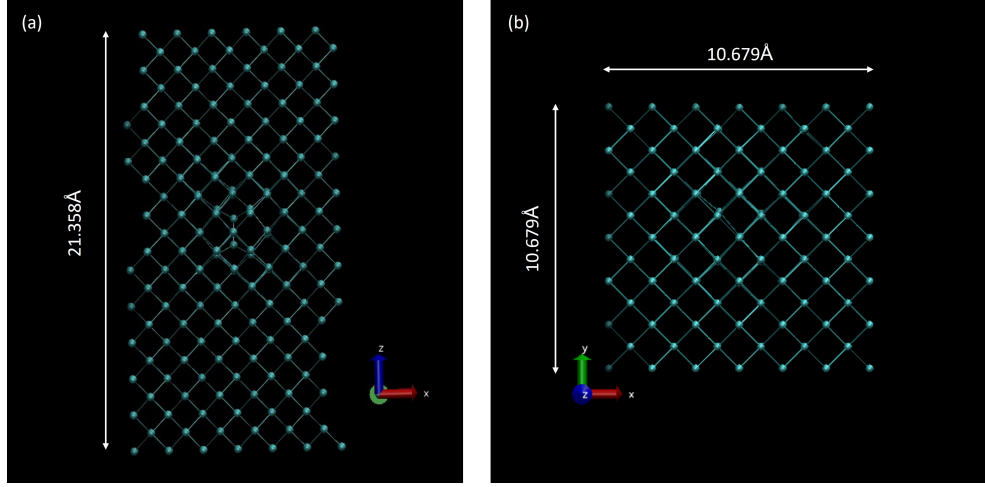


Figure 4.1: An illustration of a combination of one vacancy and one split- $\langle 100 \rangle$ interstitial carbon in (a) x-z view and (b) x-y view.

structured models are applied in geometry optimization and bandstructure calculation. The algorithm of Broyden–Fletcher–Goldfarb–Shanno(BFGS)[104] is used in finding the local minimum when the geometry optimization task is operated, resulting in a convergence of residual tolerance within 5×10^{-6} eV/Å. In the calculation of bandstructure, the k-point selection goes through the highly symmetric path of $\mathbf{W}(0.50, 0.25, 0.00) \rightarrow \mathbf{G}(0.00, 0.00, 0.00) \rightarrow \mathbf{X}(0.50, 0.00, 0.00) \rightarrow \mathbf{W}(0.50, 0.25, 0.00) \rightarrow \mathbf{L}(0.25, 0.25, 0.25) \rightarrow \mathbf{G}(0.00, 0.00, 0.00)$. These settings will be the same for the chapter on the interaction between negatively charged nitrogen-vacancy centre and interstitial carbon on geometry optimization and bandstructure calculation.

4.2.1 Convergence test

As mentioned before, cutoff energy and k-point sampling, which is described as Monkhorst-Pack(MP) spacing[105] here, should be tested for convergence. In addition to examining the convergence of their total energy, the formation energy is

a more common aspect of the parameter testing. The formula for computing the formation energy of a defect can be described as follows:

$$E_f = E_{tot} - \sum_i n_i E_i \quad (4.1)$$

where n_i is the number of atoms of element i in the system and E_i is the chemical potential of an atom of element i . In this case, the chemical potential of an individual carbon atom is computed by the total energy of a pure diamond lattice divided by the number of carbon atoms.

The outcome of formation convergence is shown in Figure 4.2. The graph **(a)** corresponds to the converge test on the formation energy of neutral vacancy in diamond. Various combinations of energy cutoff and MP spacing are applied in formation energy computation. It is observed that when MP spacing is less than 0.04, there is an obvious dropping from 6.95 to around 6.90 eV while the formation energy converges within 0.01 eV when cutoff energy is above 800 eV. The value of its formation energy is around 6.9 eV which is acceptable compared to some relative DFT literature where Slepetz *et al.* reported the value of 6.07 eV and Bernholc *et al.*[13] stated the result of 7.2 eV[106]. Similarly, in terms of the formation energy of split- $\langle 100 \rangle$ interstitial carbon, which is shown in graph **(b)**, there are few differences in the choice of MP spacing but the cutoff energy should be larger than 800 eV to ensure the convergence criteria the same as that of neutral vacancy. The converged formation energy of split- $\langle 100 \rangle$ interstitial carbon is around 11.71 eV, which agrees with the experimental research where 12 eV is reported.[14] To ensure the accuracy of results in the simu-

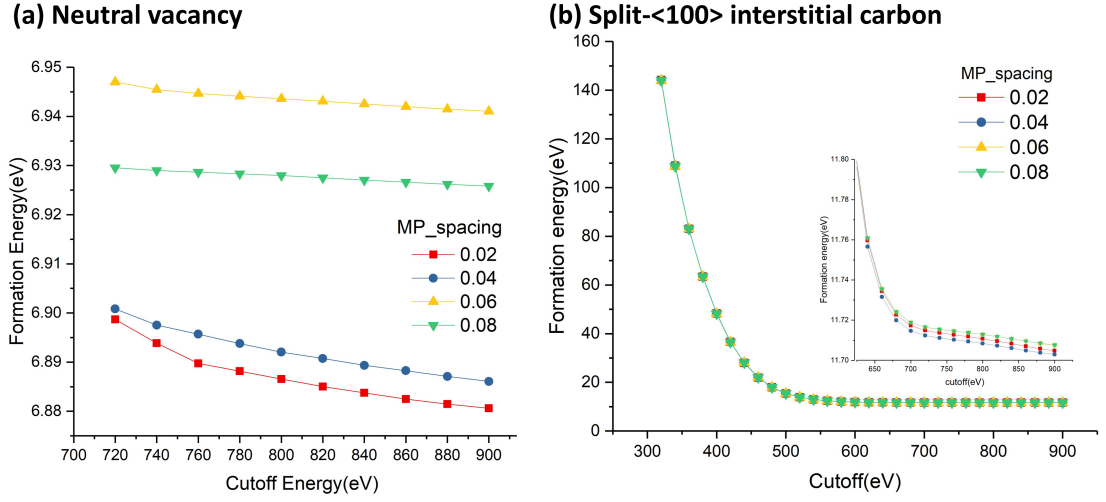


Figure 4.2: Converge test on the formation energy of **(a)** neutral vacancy and **(b)** split- $\langle 100 \rangle$ interstitial carbon

lation of the interaction between these two defects, 900 eV of cutoff energy and 0.02 MP spacing are chosen for further investigation.

4.3 Results

This section will start with a discussion of the results of individual defects which are neutral split- $\langle 100 \rangle$ interstitial carbon and vacancy. The interaction between them will then be illustrated in terms of electronic orbitals and band structure. Finally, the relationship between their relative positions and electronic structures will be analyzed.

4.3.1 Individual defects analysis

The results of split- $\langle 100 \rangle$ interstitial carbon can be found in Figure 4.3. As shown in Figure 4.3, each of the interstitial carbon is sp^2 bonded with 2 nearby carbon atoms. At the same time, one spare electron constructs the π orbital, perpendicular to $[100]$ direction, which can be observed in graph **(a)**. The two formed π orbitals are orthogonal to each other, as shown in both **(a)** and **(b)**, with an energetic orbital occupying the Fermi level, as illustrated in the band structure in **(c)**. This is in good agreement with the reported literature.[47]

In terms of the relaxation of a neutral vacancy in diamond, two types of relaxed structures were identified, and their comparison is shown in Figure 4.4. The first found configuration is a tetrahedral model where the distance between the four adjacent carbon atoms to the vacancy is the same, occupying a symmetry of T_d configuration. As can be seen from graph **(a)**, the edge length of this regular tetrahedron, made of four carbon atoms, is 2.7 Å. A more stable optimized configuration of neutral vacancy with observed and shown in graph **(b)** with a symmetry of D_{2d} . This is a consequence of Jahn-Teller distortion where a structure of tetragonal configuration is formed[107].

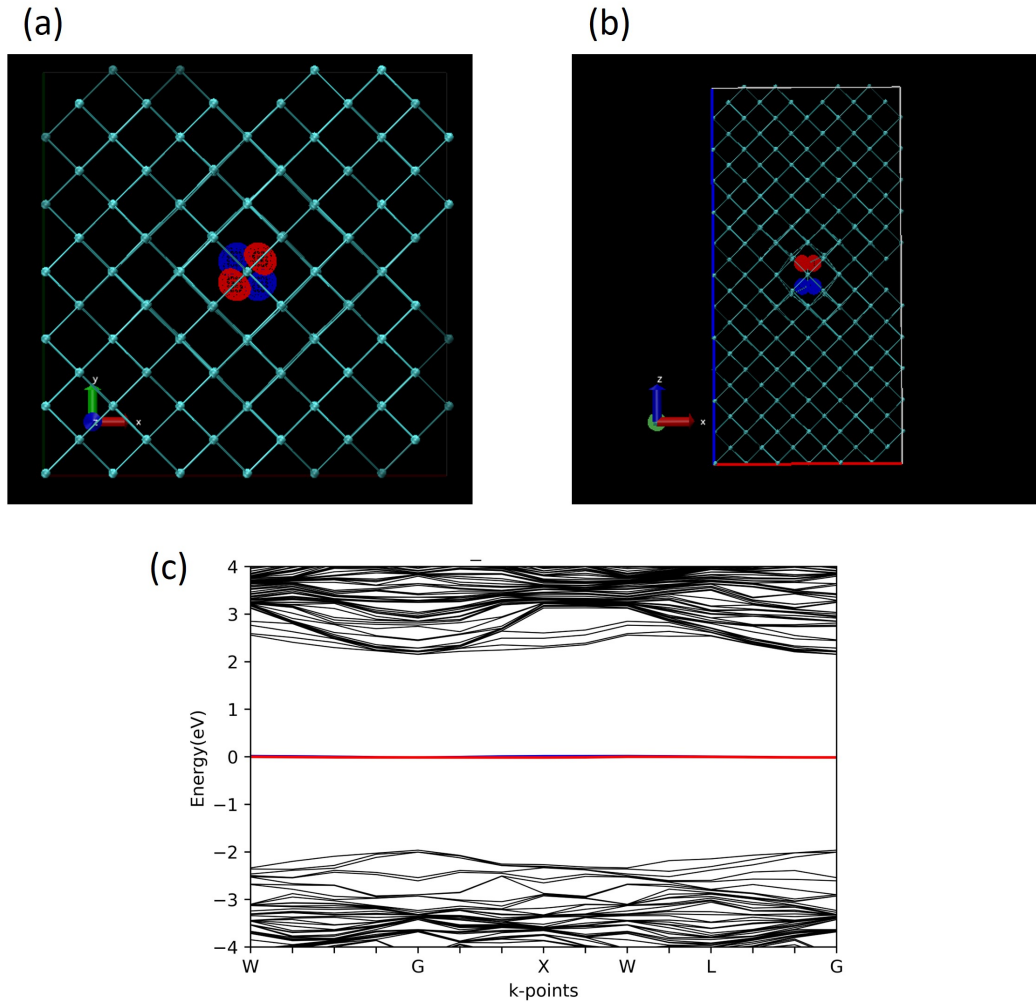


Figure 4.3: Electronic orbitals of split- $\langle 100 \rangle$ interstitial carbon of **(a)** x-y view and **(b)** x-z view. An isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen. Graph **(c)** is the corresponding band structure.

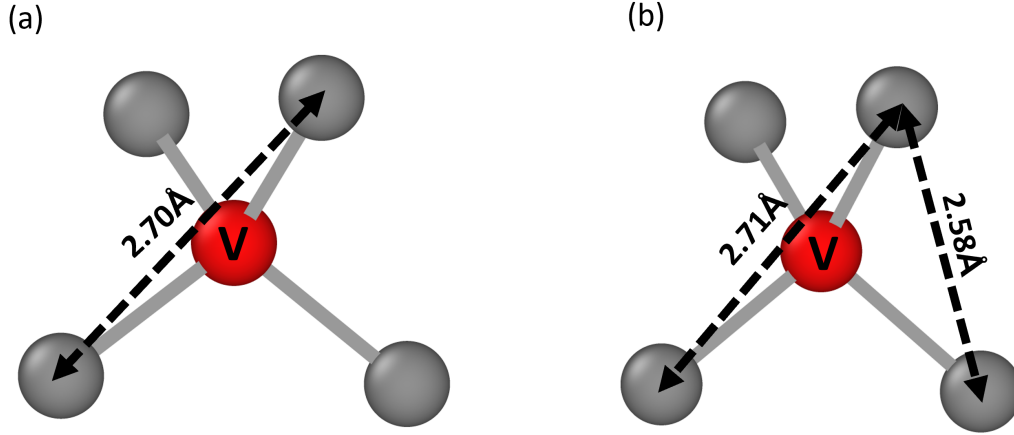


Figure 4.4: Optimized geometry comparison on neutral vacancy in **(a)** T_d symmetry and **(b)** D_{2d} symmetry

A further comparison of electronic configuration and bandstructure can be discovered in Figure 4.5. The T_d type symmetry displays four identical spare electrons, filling those similar energetic bands which can be inspected through the bandstructure plot in graph **(b)**. Concerning the D_{2d} situation, although it appears to present some similarities in electronic orbitals, a significant energy splitting can be observed in the band structure, as shown in the comparison between **(a)** and **(c)** in Figure 4.5. This splitting would potentially allow the transition of electrons between different bands, producing desirable photoluminescence signals like GR1. The following part will discuss the interaction between a split- $\langle 100 \rangle$ interstitial carbon and a neutral vacancy in diamond.

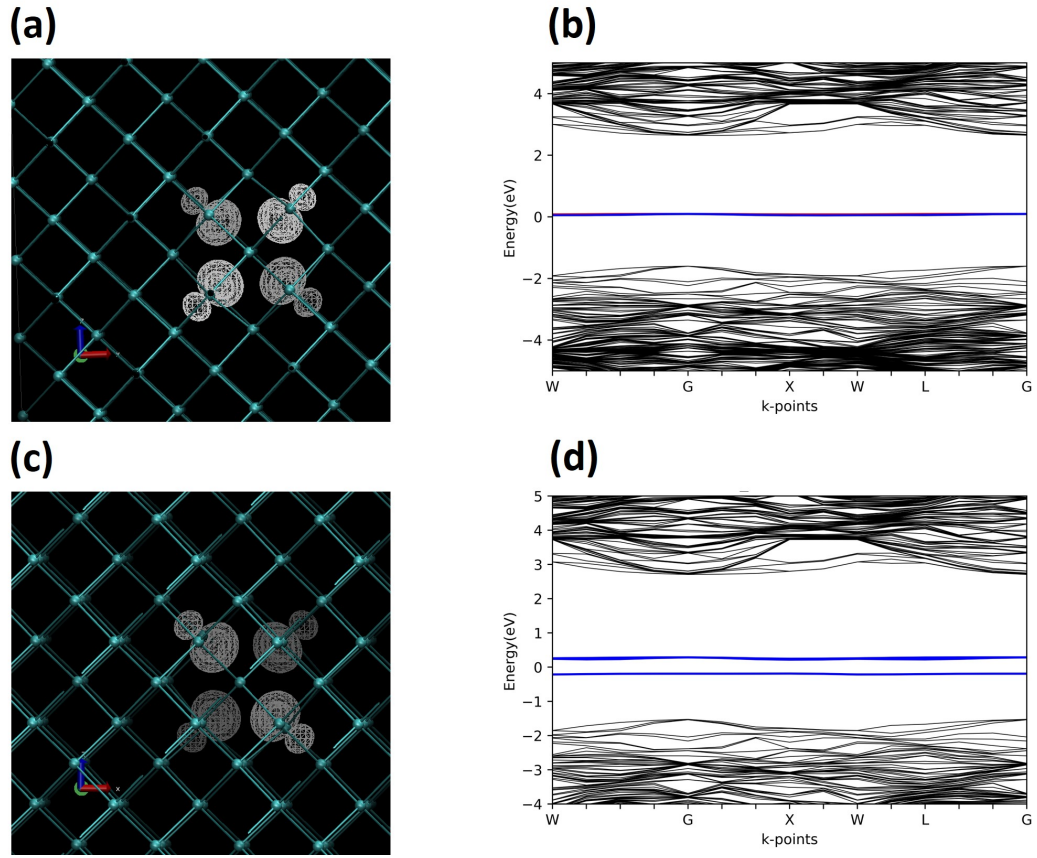


Figure 4.5: Visualization of electronic orbitals for a neutral vacancy in (a) T_d symmetry and (c) D_{2d} symmetry. Band structure analysis of the neutral vacancy in (b) T_d symmetry and (d) D_{2d} symmetry. For the electronic orbitals, n isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

4.3.2 Interaction between neutral vacancy and interstitial carbon

The previous section exhibited the atomic positions and electronic properties of individual studied defects (neutral vacancy and split- $\langle 100 \rangle$ interstitial carbon). This part will mainly focus on the interaction between these two defects. After proper analysis of the optimized results among all of the tested simulations, three types of situations can be concluded, namely recombination, non-hybridization and hybridization which are demonstrated in Figure 4.6.

In the situation of recombination, the interstitial carbon is not allowed to accommodate itself at its original position. As the procedure of geometry optimization progresses, the interstitial carbon diffuses into the initial site of the vacancy, causing recombination. This can be discovered in Figure 4.6(**a**) where no obvious defects are found. Its interrelated bandstructure, shown in the graph (**b**) of Figure 4.6, illustrates that no internal bands are lying between the conduction and valence band.

The situation of hybridization and non-hybridization are classified by whether the electronic orbitals from different defects are hybridized or not. For instance, in non-hybridization, which can be found in graphs (**c**) and (**d**), the electronic structure of the neutral vacancy and split- $\langle 100 \rangle$ interstitial carbon can be characterized separately. Specifically, the elements in red describe the corresponding electronic manifolds and bands of the interstitial carbon while the colour blue labels the defect of neutral vacancy. It can be distinguished from either electronic orbitals or bandstructure plots. Compared to the previous isolated defect results, a distortion occurs on the split- $\langle 100 \rangle$

interstitial carbon, causing energy splitting on the corresponding π bonds. However, since it would not affect the electronic properties of neutral vacancy, the GR1 luminescence signal is considered to remain, depending on the electronic configuration of the neutral vacancy. When it comes to the neutral vacancy in the situation of non-hybridization, no significant changes can be found compared to its isolated structure, confirming its 'bright' capability on the GR1 signal.

In contrast to non-hybridization, those hybridization types mean the electron manifolds are hybridized to each other, forming a brand-new defect complex that can not be analyzed separately. Graphs (e) and (f) in Figure 4.6 demonstrate an example of a result of hybridization. The remarkable hybridized band is coloured in yellow. It is demonstrated that the electronic orbitals from interstitial carbon and neutral vacancy are hybridized, forming an energy band around the Fermi level. This implies the GR1 signal might quench due to the disappearance of the featured neutral vacancy in the bandstructure. The following section will have a further investigation of the relationship between their interactions and relative positions.

4.3.3 Relative Locations analysis

The earlier part mainly focuses on several specific situations related to recombination, non-hybridization, and hybridization. In this subsection, further research will be carried out to explore the relative positions between defects and their interaction toward each other.

The identical positions of these simulated vacancy sites can be reproduced based

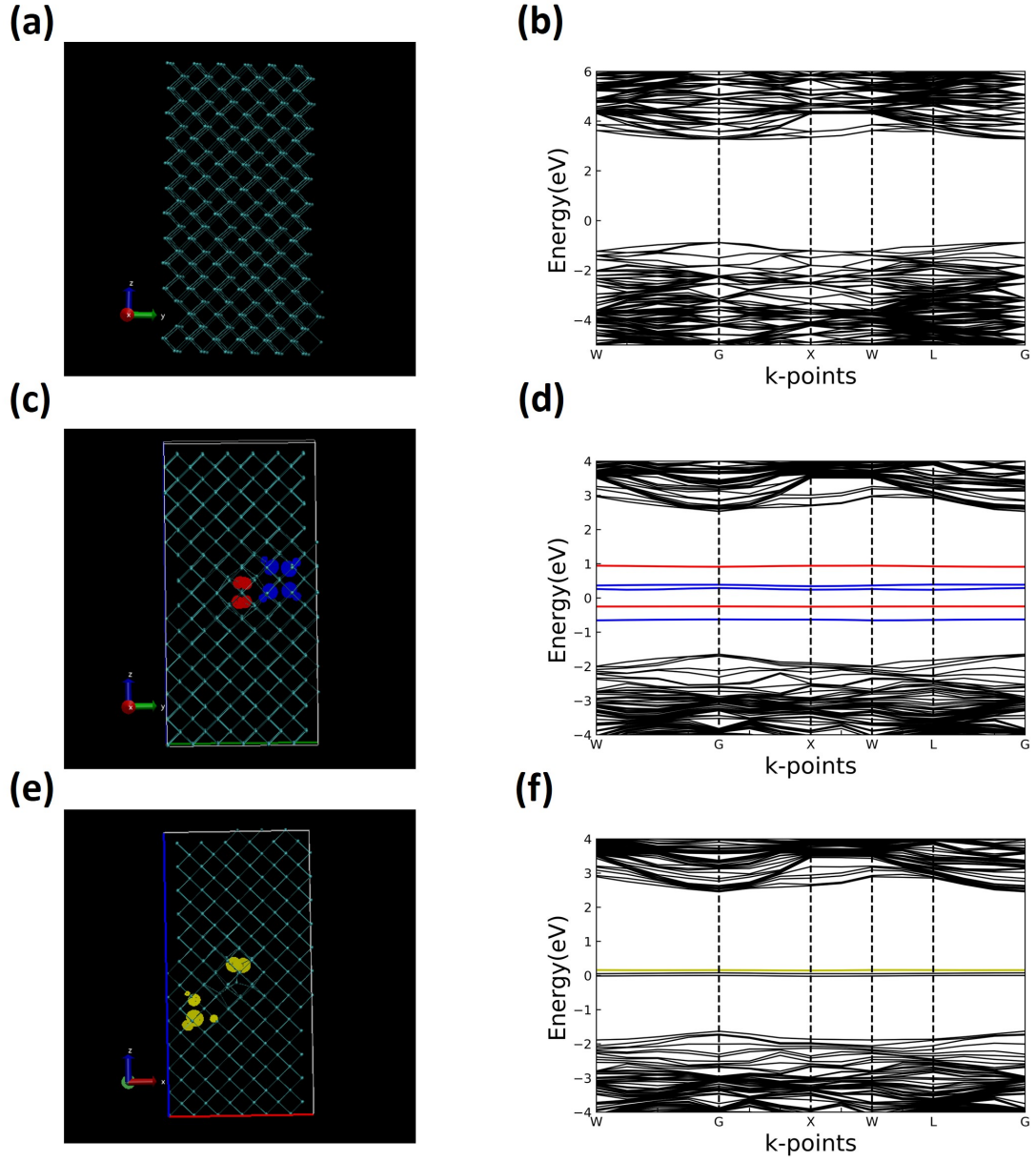


Figure 4.6: (a) and (b) correspond to optimized geometry and bandstructure of the recombination situation while (c) and (d), (e) and (f) present the relaxed atomic configuration with electronic manifold and corresponding bandstructure of non-hybridization and hybridization type. For the electronic orbitals, an isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

on the diamond's symmetry, and their projection in 3-dimensional space is presented in Figure 4.7, graph **(a)**. These vacancy sites are determined by their initial positions before optimization for better visualisation. As is shown in this graph, a split- $\langle 100 \rangle$ interstitial carbon pair is marked in the middle. At the same time, three types of vacancy sites, identified as recombination, non-hybridization and hybridization, are illustrated in three different colours. It is shown in the graph that when a vacancy is dropped at the first nearest possible site, it will cause recombination where the interstitial carbon will relax to the vacancy site. As the increase of the distance between two defects, both non-hybridization and hybridization would occur where more precise relative parameters should be applied for better understanding. In 4.7 **(b)**, the distance and angle between two defects are employed to represent their relative positions. The distance is simply the length between the vacancy site and the middle of the split- $\langle 100 \rangle$ interstitial carbon pair while the angle is computed based on a vector $[100]$ and a vector pointing from the middle of the interstitial carbon pair to a vacancy. It can be concluded from the plot that when the angle between the 2 mentioned vectors is in a range of around 65° to 115° , non-hybridization would happen. Otherwise, the photoluminescence signal will disappear due to recombination or hybridization. This phenomenon might be the consequence of a strain produced by an interstitial carbon which will be discussed in the next chapter. In conclusion, when the interstitial carbon and neutral vacancy are placed within a distance of less than $5 \text{ \AA}$, based on the results of the graph **(a)** in Figure 4.7, a possibility of 50%(20 out of 40) on the quench of fluorescence signal from neutral vacancy.

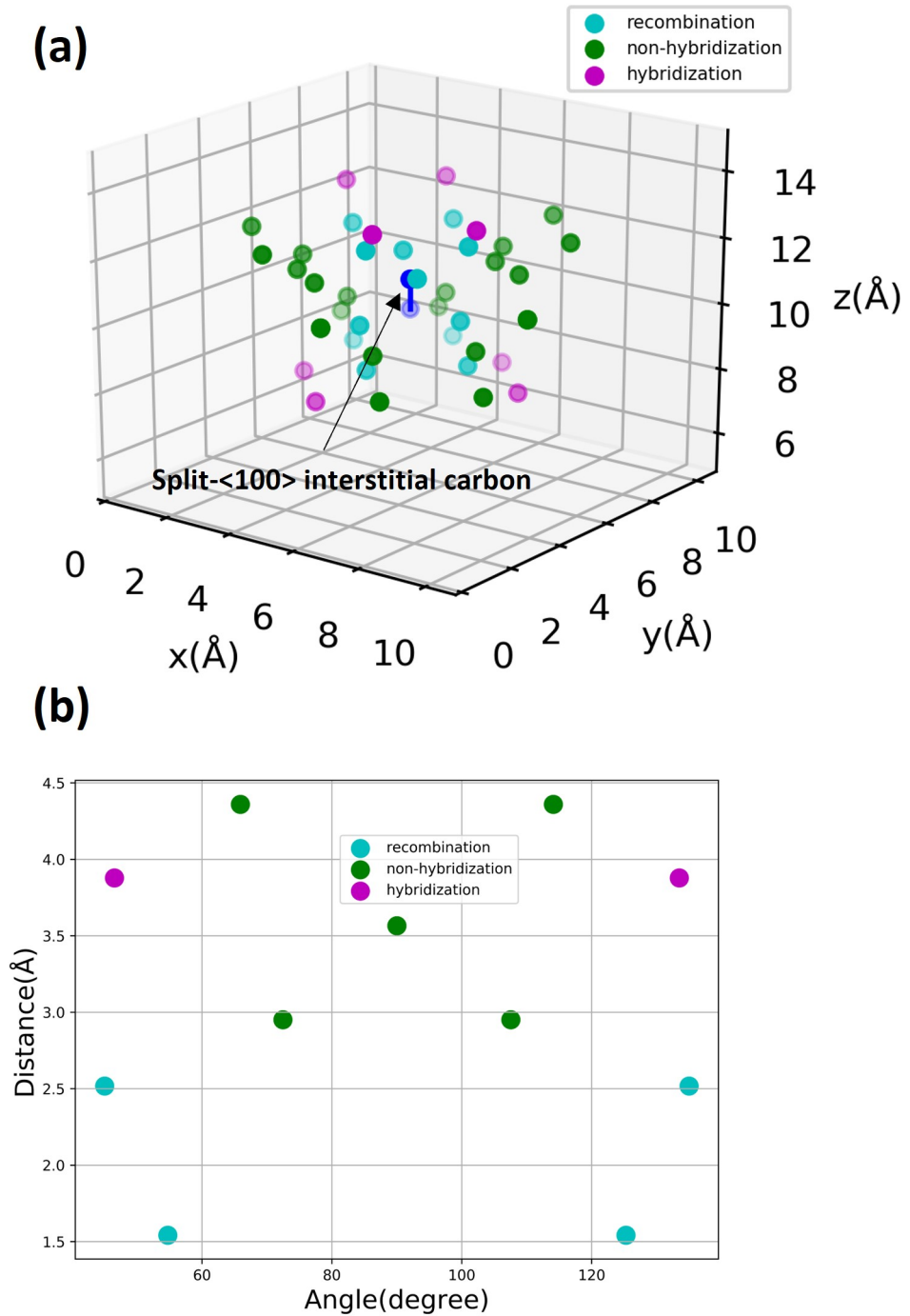


Figure 4.7: **(a)** A 3-dimensional graph on all possible sites for the neutral vacancy while the split- $\langle 100 \rangle$ interstitial carbon is shown at the centre. **(b)** A demonstration of relative positions between the vacancy and interstitial carbon in terms of their angles and distances.

4.4 Conclusion

This chapter chiefly discusses the interaction between a neutral vacancy and a self-interstitial carbon in diamond. Specifically, qualitative research is performed in perturbation of a neutral vacancy, regarded as the source of GR1, with a nearby self-interstitial carbon based on the changes in their electronic structure.

To begin with, two defects are calculated individually through geometry optimization and band structure calculation. It can be drawn from the results that the split- $\langle 100 \rangle$ interstitial carbon pair agrees with the literature well with its two perpendicular identical π -bonds localized on each interstitial carbon atom. Simultaneously, the neutral vacancy firstly results in the T_d symmetry structure and then finalizes a more stable configuration in the D_{2d} symmetry. Various ensembles of these two defects are constructed in a supercell for further investigation of their interaction study where three types of situations occur namely recombination, non-hybridization and hybridization. Recombination is a type of configuration where a self-interstitial carbon recombines to the position of a vacancy while the other two situations define the existence of hybrid orbitals between these two defects. The results of their bandstructure calculation imply that the GR1 might not quench in the situation of non-hybridization since the electronic structure of the neutral vacancy is unchanged. On the contrary, as a consequence of a significant influence on the initial electronic structure of neutral vacancy, the situations of recombination and hybridization are considered as 'off' in the GR1 signal.

In terms of the localization analysis, it turns out that when the angle between a

vector formed by the vacancy site and the middle of the self-interstitial carbon pair and a vector determined by the split- $\langle 100 \rangle$ interstitial carbon is in a range of 65° to 115° with a distance of less than $5 \text{ \AA}$, non-hybridization would happen where the GR1 signal remains. This phenomenon is hypothesised as the strain effect produced by the interstitial carbon which will be discussed in the next chapter. Finally, taking all the possible symmetric ensembles into account, there is a possibility of 50% that the GR1 would disappear when one split- $\langle 100 \rangle$ self-interstitial carbon is placed around a neutral vacancy within $5 \text{ \AA}$.

Chapter 5

Perturbation of a negatively-charged NV with a nearby interstitial carbon

5.1 Introduction

As mentioned, the negatively charged nitrogen vacancy centre(NV^-) plays an important role in quantum technology. During the generation of NV centres via laser writing, we sometimes observe blinking in the real-time photoluminescence (PL) signal. This phenomenon may result from several factors. For instance, it could arise from variations in the absorption process, where fewer electrons are excited to higher energy states. Consequently, different emitted photons with varying energies are observed in the real-time PL data. The associated calculations, including TDDFT analysis, will be discussed in detail in Chapter 7. Alternatively, this blinking could

also be related to the emission process itself. If the NV centre is in an excited state, changes in the electronic structure may alter the energy of emitted photons. Emission can occur via either radiative or nonradiative pathways, depending on photon-phonon coupling. This chapter will particularly investigate the interaction between an NV⁻ and a split- $\langle 100 \rangle$ self-interstitial carbon (C_i) at the aspect of strain effects and electronic structure. Changes in the electronic structure suggest that the emission process could be affected when an interstitial carbon is present near an NV centre in a diamond.

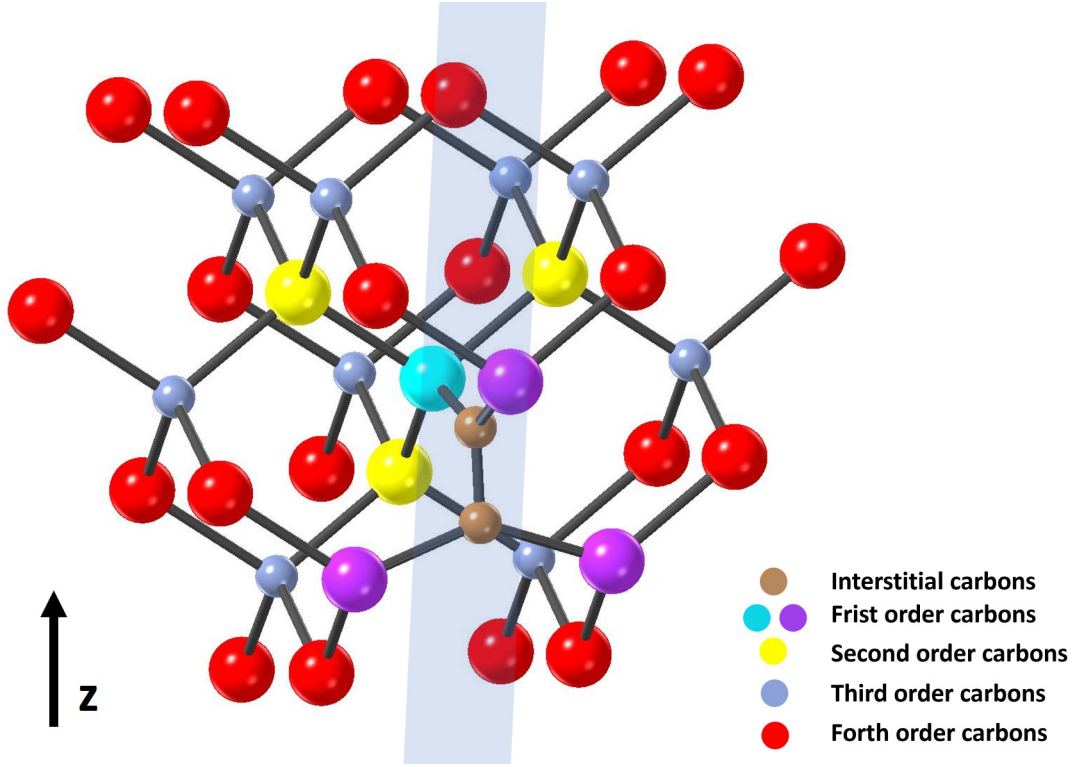


Figure 5.1: A demonstration on all calculated ensembles of one NV^- and one C_i in diamond. A split- $\langle 100 \rangle$ self-interstitial carbon pair is placed at the centre, and any of the first, second, or third nearest carbon atoms are potential sites for a nitrogen atom to substitute, accompanied by a neighbouring vacancy, forming an NV^- centre.

5.2 Computational details

In this section, the whole computational details will be presented. The simulation is performed using DFT with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Similar to the previous chapter, the geometry optimization and electronic properties calculation are performed using CASTEP code[103] and the c2x module is applied in orbital data extraction. Additionally, an *ab initio* molecular dynamic(AIMD) simulation, aiming at understanding the diffusion behaviour of a C_i and a NV^- , is held in the software of CP2K.[108].

All the simulations run in this chapter are performed in a supercell in a size of 3

$\times 3 \times 6$, the same as the previous chapter to reduce the influence of the boundary condition in the z-direction from the split- $\langle 100 \rangle$ C_i . This supercell is first generated by *Crystalmaker* and then modified manually for different expected combinations of defects.

To begin with, this simulation will focus on individual defects (NV^- and C_i) in diamond. Since the C_i had been studied in the previous chapter, it will not be discussed again here. A converged test will be illustrated in the aspect of the cutoff energy and MP spacing to ensure the accuracy of the simulation. With the optimized isolated defects constructed (NV^- , C_i and V where C_i and V were finished in the previous part), their strain interactions can be investigated through the results of their optimized structure. This simulation will be followed by a calculation on geometry optimization and bandstructure computation on different ensembles of one NV^- and one C_i in diamond. The computational details of geometry optimization and bandstructure calculation are the same as the previous simulation on the C_i and V interaction which will not be illustrated again here. The construction rules of creating various combinations NV^- and split- $\langle 100 \rangle$ C_i are displaced in Figure 5.1. From the figure, one split- $\langle 100 \rangle$ C_i is located at the centre and its first, second, third and fourth nearest neighbour carbons are marked as different levels of 'order'. For example, the first nearest neighbour carbon is called First order carbon. All of the first, second and third-order carbons can be replaced by a nitrogen atom at a time, forming one type of configuration that contains one NV^- and one C_i by removing an adjacent carbon atom of nitrogen. To ensure the boundary conditions do not affect the results in either the x or y direction, all the ensembles, symmetric with a plane

constructed by two interstitial carbons and one first-order carbon(coloured in cyan), are taken into consideration for comparison.

Two of the representative ensembles of one NV^- and one C_i are transferred to a $6 \times 6 \times 6$ supercell for an NVT-MD simulation in CP2K. To guarantee the quality of transformation from CASTEP to CP2K, three aspects called relative total energy, forces and positions, are compared which will be discussed in the section on convergence test.

5.2.1 Convergence test

As discussed in the previous chapter, the convergence test of individual neutral vacancy and split- $\langle 100 \rangle$ C_i have been calculated. The convergence test of the remaining NV^- defect will be analysed here. The result of formation energy convergence is presented in Figure 5.2 where different combinations of cutoff energy and MP-spacing are applied. As illustrated in Figure 5.2, as the size of the Monkhorst-Pack (MP) spacing decreases and more k-points are collected, there is no significant drop observed in the formation energy of an NV centre. In terms of the cutoff energy, it can be observed from the graph that it converges smoothly within 0.01 eV with a value above 700 eV. Meanwhile, the formation energy around 6 eV is in agreement with Ádám Gali's finding[8] with an error of lower than 1%. A conserved parameter of 0.02 in MP spacing and 900 eV as the cutoff energy is chosen for the rest of the calculations in this chapter since the following DFT calculations will involve two defects in a supercell.

As mentioned in the computational details, a trial AIMD simulation is performed

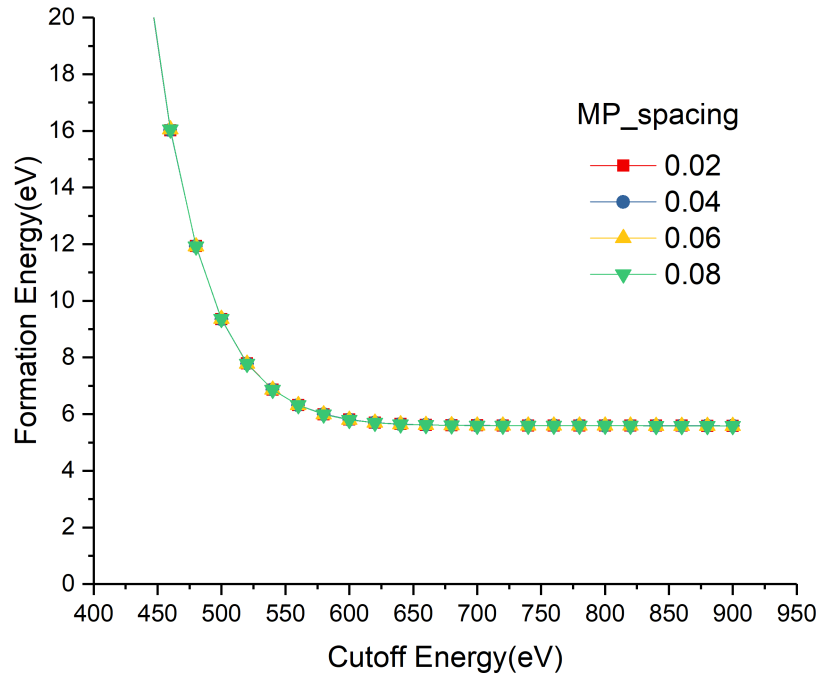


Figure 5.2: The convergence test of formation energy on NV^- colour centre in diamond concerning cutoff energy and k points

in CP2K for a better understanding of the diffusion mechanism on the interaction between NV^- and C_i under thermal environments. Therefore, a transferable converged test is required to ensure the accuracy of the result performed in CP2K. The comparison results between CASTEP and CP2K are illustrated in Figure 5.3 at the aspect of difference on total energy, forces and positions.

Figure 5.3 (a) shows the comparison of total energy between CASTEP and CP2K. Due to differences in the software, the total energies of their system cannot be directly compared. In this case, ten random atomic configurations are selected to perform single point calculation using CASTEP and CP2K separately. By setting the first configuration as the reference, the following configurations' total energies can be represented as 'delta energy' which means the total energy difference between the current configuration and the reference one. It can be observed from Figure 5.3 (a) that the energy difference is relatively small and the energy difference is computed as less than 0.0007 eV. Similarly, the corresponding forces and positions comparison is illustrated in (b) and (c) where the force difference is less than 0.007 eV/Å and the position difference is no more than 0.00014 Å. The outcome of these comparisons is acceptable and can present the accurate consistency from CASTEP to CP2K.

5.3 Results

In this section, the results mentioned above will be discussed. This will start with the analysis of relaxed geometry and bandstructure of an NV^- colour centre in diamond. Then strain interaction between NV^- and split- $\langle 100 \rangle$ C_i would taken into consideration where the strain effect produced by a split- $\langle 100 \rangle$ C_i toward an NV^- in a distance above 6 Å will be presented. After this, the main attention will zone into the area that the distance between two defects within 6 Å. Finally, the results of migration behaviour will be illustrated through AIMD simulation.

5.3.1 Individual defects analysis

As discussed in the previous chapter, the analysis of individual defects shows that the neutral vacancy (V^0) and the split- $\langle 100 \rangle$ interstitial carbon (C_i) align well with the relevant literature, particularly regarding their atomic configuration and electronic structure. As depicted in Figure 5.4, the molecular orbitals of an NV^- with C_{3v} symmetry can be observed in graphs (a) and (b). In graph (a), the a orbital localizes around the nitrogen atom marked in red, while in graph (b), the corresponding e_x and e_y orbitals, coloured in blue, symmetrically accommodate themselves around the adjacent three carbon atoms to the vacancy. This agrees with A Lenef's theory published in 1995.[55]. Details of the energetic level on relative electronic orbitals are displayed in the same colour as it is shown in the band structure plot in graph (c). It indicates that the a_2 orbital around the nitrogen atoms occupies the energy around 1.5 eV below the Fermi level while two degenerate orbitals of e_x and e_y fill

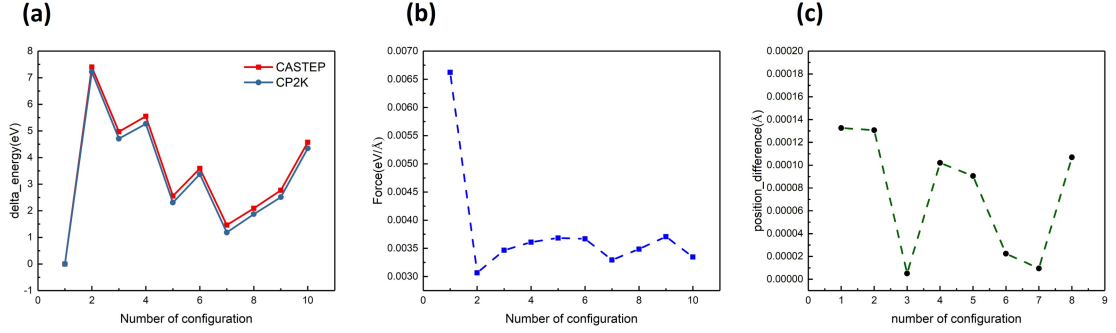


Figure 5.3: A transferable converge test from CASTEP to CP2K with respect to (a) energies, (b) forces and (c) positions

out equivalent energy band near Fermi level.

5.3.2 Strain interaction

In this part, the strain interaction between an interstitial carbon(C_i) and a negatively charged nitrogen vacancy centre(NV^-) will be discussed. As mentioned previously the electronic structure might be influenced by the presence of generated Frenkel defects(Vacancy and interstitial carbon). Therefore, the investigation initializes with the strain produced by isolated individual defects, shown in Figure 5.5 (a). In this chart, the magnitude of strain on both split- $\langle 100 \rangle$ self-interstitial carbon and vacancy are illustrated where the vacancy shows a small localised negative strain field with the decrease of displacement. In terms of the split- $\langle 100 \rangle$ self-interstitial carbon, the strain field demonstrated a larger magnitude and longer range. This can be found in more detail in the graph (c) where the magnitude of strain alongside with $\langle 100 \rangle$ direction would produce a larger strain effect compared to its perpendicular axis. This strain distribution of a split- $\langle 100 \rangle$ interstitial carbon to some extent explains the unfinished question that arose in the previous chapter about the relationship between the relative

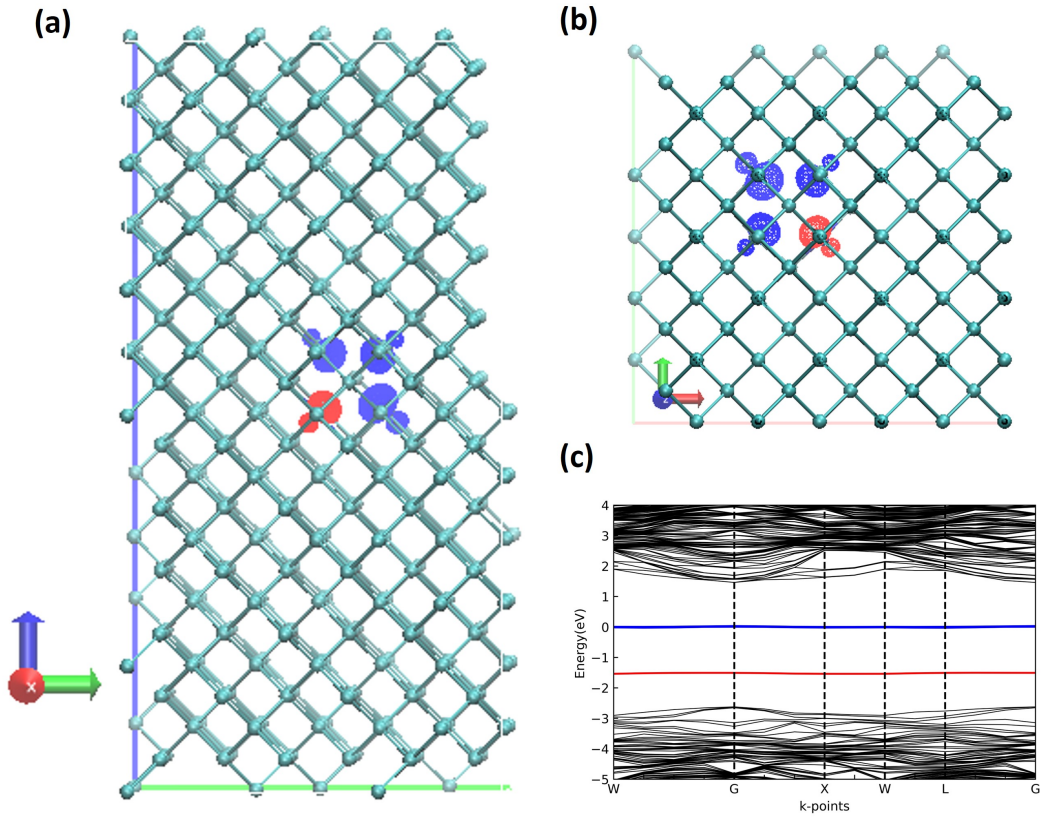


Figure 5.4: The graph (a) and (b) are the optimized structure of NV⁻ with the featured electronic manifold of e_x , e_y and a_2 in y-z view and x-y view respectively while graph (c) represents its corresponding bandstructure plot. For the electronic orbitals, an isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

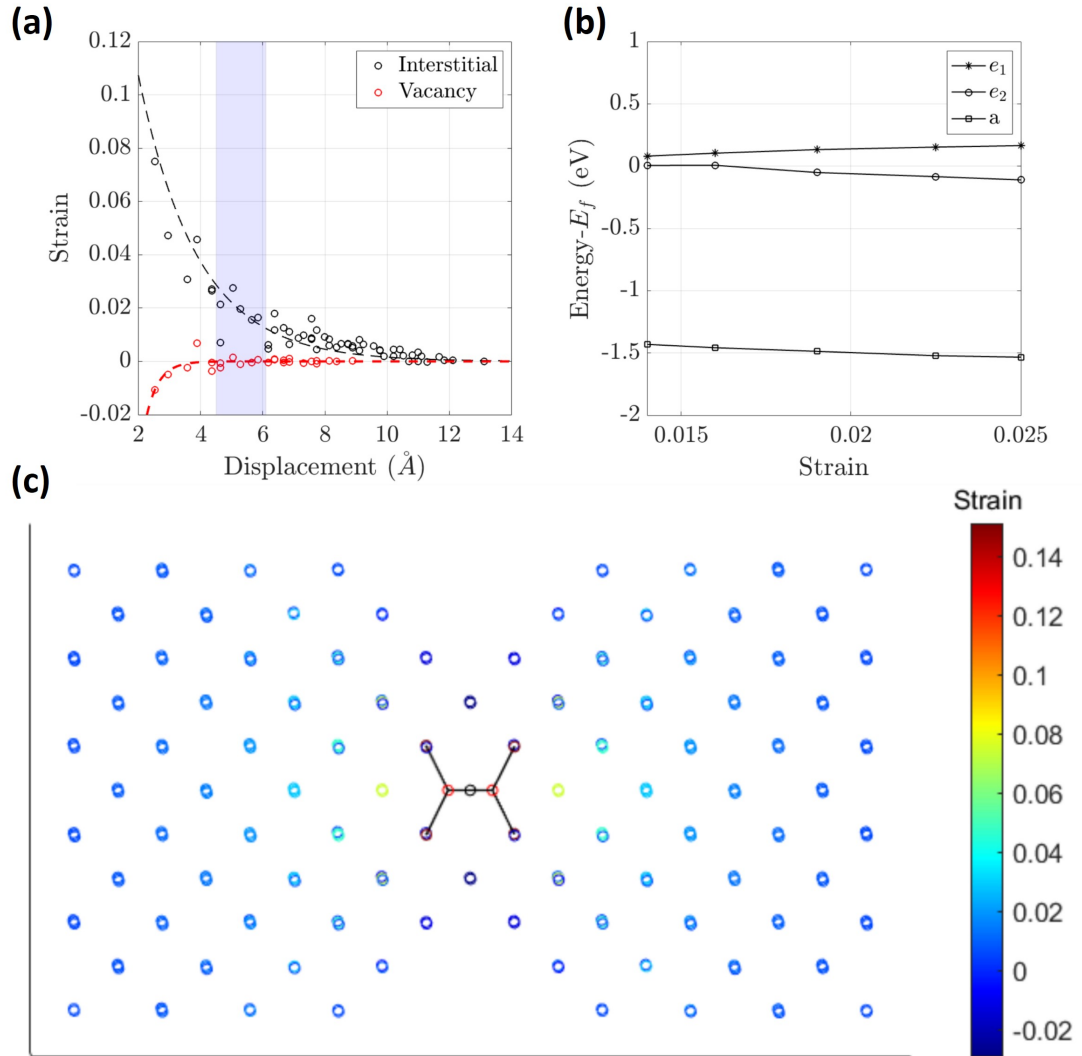


Figure 5.5: **(a)**: Strain magnitude versus the distance toward the defect of vacancy and interstitial carbon. **(b)**: Band splitting on NV^- with the application of various strain. **(c)**: An overview of strain distribution induced by a split- $\langle 100 \rangle$ self-interstitial carbon.

positions of a neutral vacancy and a split- $\langle 100 \rangle$ interstitial carbon and their hybridized situations. The hybridization can be interpreted as the consequence of the strain field produced by the interstitial carbon. When a neutral vacancy happens to be located at a site perpendicular to the $\langle 100 \rangle$ direction, the corresponding strain is considered small and therefore, non-hybridization would occur. On the contrary, if the vacancy is placed alongside the $\langle 100 \rangle$ axis closed to the C_i defect, typically with a displacement less than 4 Å, strong strain magnitude would affect the electronic structure, causing hybridization of orbitals between two defects.

The influence of the produced strain from interstitial carbon on the electronic structure of NV^- can be found in Figure 5.5 **(b)**. The selected strain range in the graph **(a)** is applied to an NV^- perpendicularly since if the strain is effected on an NV^- in parallel, it will not break its symmetry. The degenerated symmetric orbitals e_x and e_y would experience a splitting of 280 meV with a separation of 4.5 Å and 75 meV with a displacement of 6.1 Å. This is consistent with Davies *et al*'s theory on uniaxial stress applied to the NV centre.[84] The strain magnitude from interstitial with a separation of 4.5 Å to 6.1 Å is applied to an NV^- centre in diamond above. However, in a closer range, the interaction would be more complicated since more factors should be taken into account such as electrons, atomic positions *etc.* The following part will focus on a closer range, focusing on the interaction between defects on their electronic structure properties.

5.3.3 Electronic interaction

This section will mainly present the results of ground-state DFT simulations on various optimized ensembles of a NV^- centre and a split- $\langle 100 \rangle$ self-interstitial carbon in diamond. The generation rules of these ensembles are mentioned in the part of computational details previously. Among all of the 48 situations in total, including 12 second nearest and 36 third nearest, it can be categorised as one of four cases: reconstruction type-1, reconstruction type-2, non-hybridization and hybridization.

5.3.3.1 Reconstruction

Reconstruction is a type of situation where new defect complexes are formed after the procedure of geometry optimization. Here, two main representative configurations are demonstrated below, marked as type-1 and type-2.

One of the results from type-1 can be found in Figure 5.6 where (a), (b), and (c) shows its atomic configuration and corresponding molecular orbitals, and (d) represents its bandstructure plot. The reconstruction type-1 is featured with the equilateral triangle structure generated by the initial two interstitial split- $\langle 100 \rangle$ self-interstitial carbons and one adjacent carbon with a side length of 1.31 Å, slightly less than the bond length of the diamond lattice, 1.54 Å. The mentioned triangle constructs a symmetric plane for this defect complex despite the presence of a nitrogen atom on one side. The molecular orbitals are denoted in different colours for better visualization. Specifically, those in blue represent manifolds around carbon atoms while the red one demonstrates orbitals from the nitrogen atom. From the bandstructure, we can

observe that the energy level of the original a_2 orbital from NV^- centre shifts closer to the conduction band with the value of around 1.1 eV while the rest of the bands exhibit a potential of emission due to a proper energy gap between them. Here, we only discuss one typical case of reconstruction type-1. The rest will differ slightly, and their emission properties will not be individually investigated in detail. Also, to the best of my knowledge, these reconstruction type-1 structures have not been observed, and their emission properties are considered to be different from those of the desired NV^- defect in diamond. In this case, the photoluminescence signal of an NV^- is considered to be destroyed.

Considering the situation of reconstruction type-2, which can be found in Figure 5.7, a more distorted atomic configuration is illustrated. The construction type-2 can be seen as an intermediate stable stage of the recombination of an interstitial carbon atom to the site of vacancy. An insight into this atomic structure from Figure 5.7 (a) indicates that the second interstitial carbon, noted as C_i2 , tends to squeeze away its adjacent carbon and the adjacent carbon is in the position of moving toward the vacancy site. This tendency will ultimately generate a substitutional nitrogen in diamond. The corresponding bandstructure of the type-2 configuration expresses a relatively large bandgap compared to type-1, which implies there might be no detected photoluminescence.

5.3.3.2 Non-hybridization and hybridization

The previous part illustrates those situations where the configurations of NV^- and C_i are broken down, forming new types of defect complexes. In this section, attention

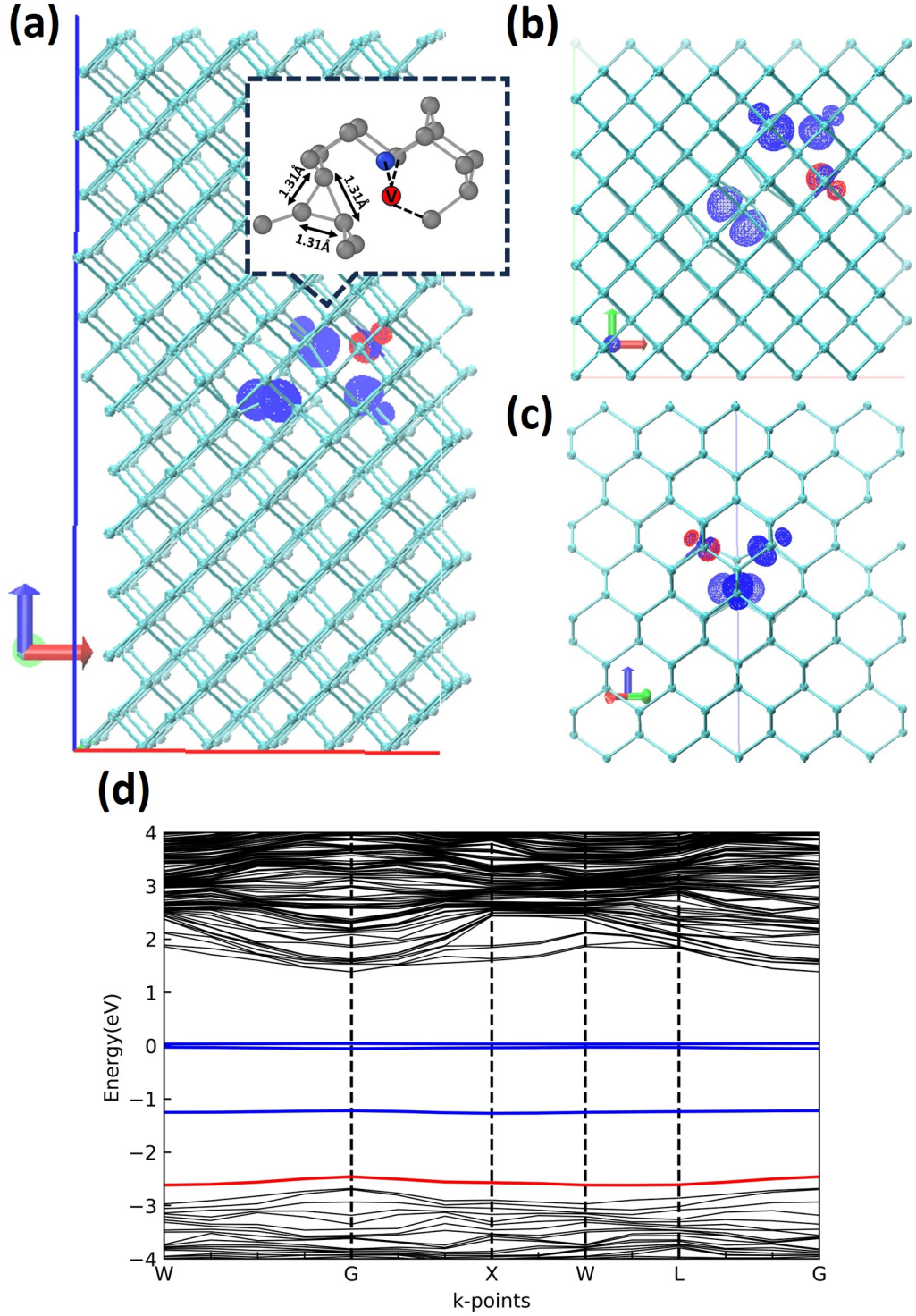


Figure 5.6: (a), (b), and (c) show the atomic configuration and electronic orbitals of reconstruction type-1 from various perspectives, while (d) illustrates its corresponding bandstructure. For the electronic orbitals, an isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

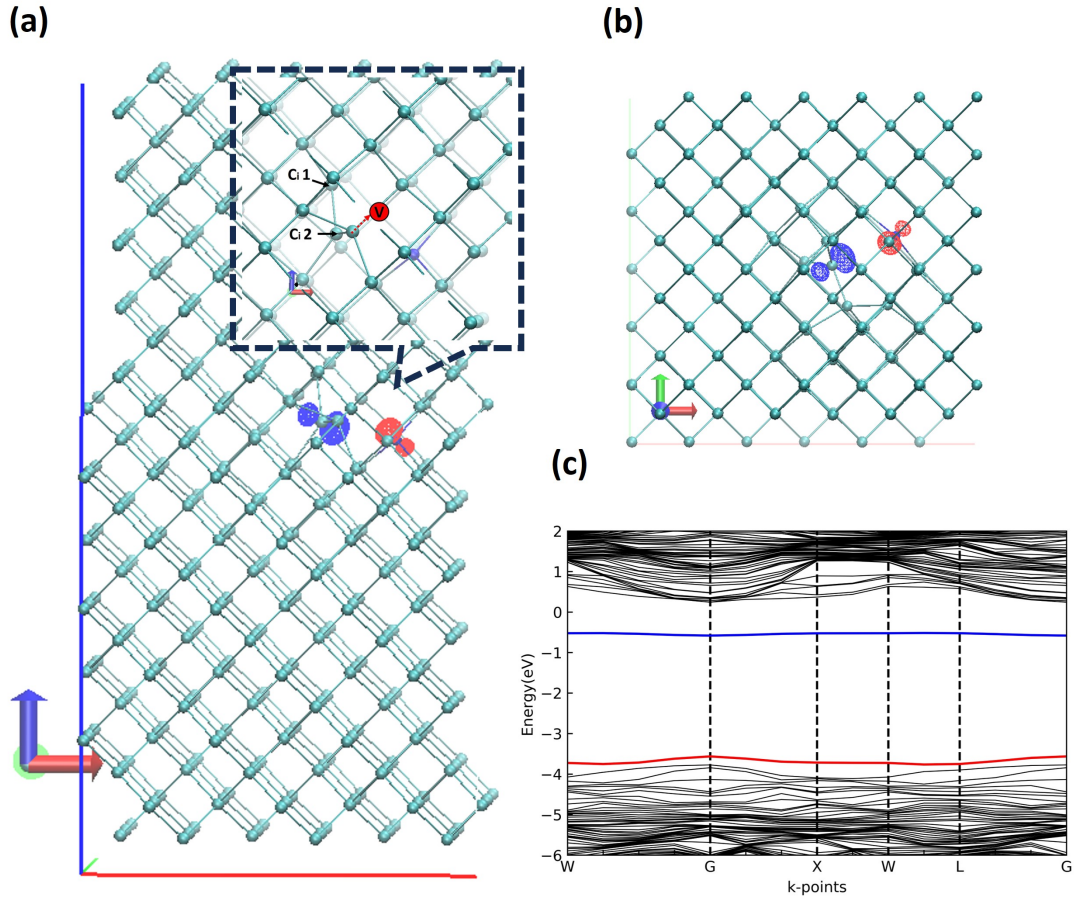


Figure 5.7: A illustration of the atomic configuration and electronic orbitals of reconstruction type-2 in (a) x-z view and (b) x-y view while (c) represents its corresponding bandstructure. For the electronic orbitals, an isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

will be paid to those situations where their distortions are relatively small compared to those in 'reconstruction'. Among all of these less distorted structures, it can mainly be divided into two parts, namely non-hybridization, and hybridization, as shown in 5.8.

Similar to the discussion in the previous chapter on the electronic interaction between an interstitial carbon and a neutral vacancy, non-hybridization means the electronic structure of the split- $\langle 100 \rangle$ self-interstitial carbons and NV^- can be individually analyzed whereas, in hybridization, hybridized orbitals between two defects can be found.

The relaxed structure of non-hybridization is shown in Figure 5.8 **(a)** with its bandstructure plot in **(b)**. It can be extracted from the graphs that the electronic structure of the NV^- colour centre closely resembles its individual counterparts, exhibiting similar molecular orbital shapes, symmetries, and corresponding occupied band energy levels. However, the split- $\langle 100 \rangle$ self-interstitial carbons demonstrate an energy-splitting on bandstructure and no obvious distortion observed on the π bond compared to its isolated results. Since the electronic structure of NV^- remains and there is no reported literature on the capability of emission on C_i , the photoluminescence signal is considered the same as the isolated NV^- .

For the situations of hybridization, one of their configurations is shown in Figure 5.8 **(c)** and **(d)**. Specifically, the orbitals in orange correspond to one of π orbitals from the split- $\langle 100 \rangle$ C_i hybridized with one of the degenerated e_x or e_y orbitals from the NV^- colour centre while the orbitals in green show hybridization of π bond from C_i and a_2 orbitals in the NV^- . Since the electronic structure of the NV^- is destroyed,

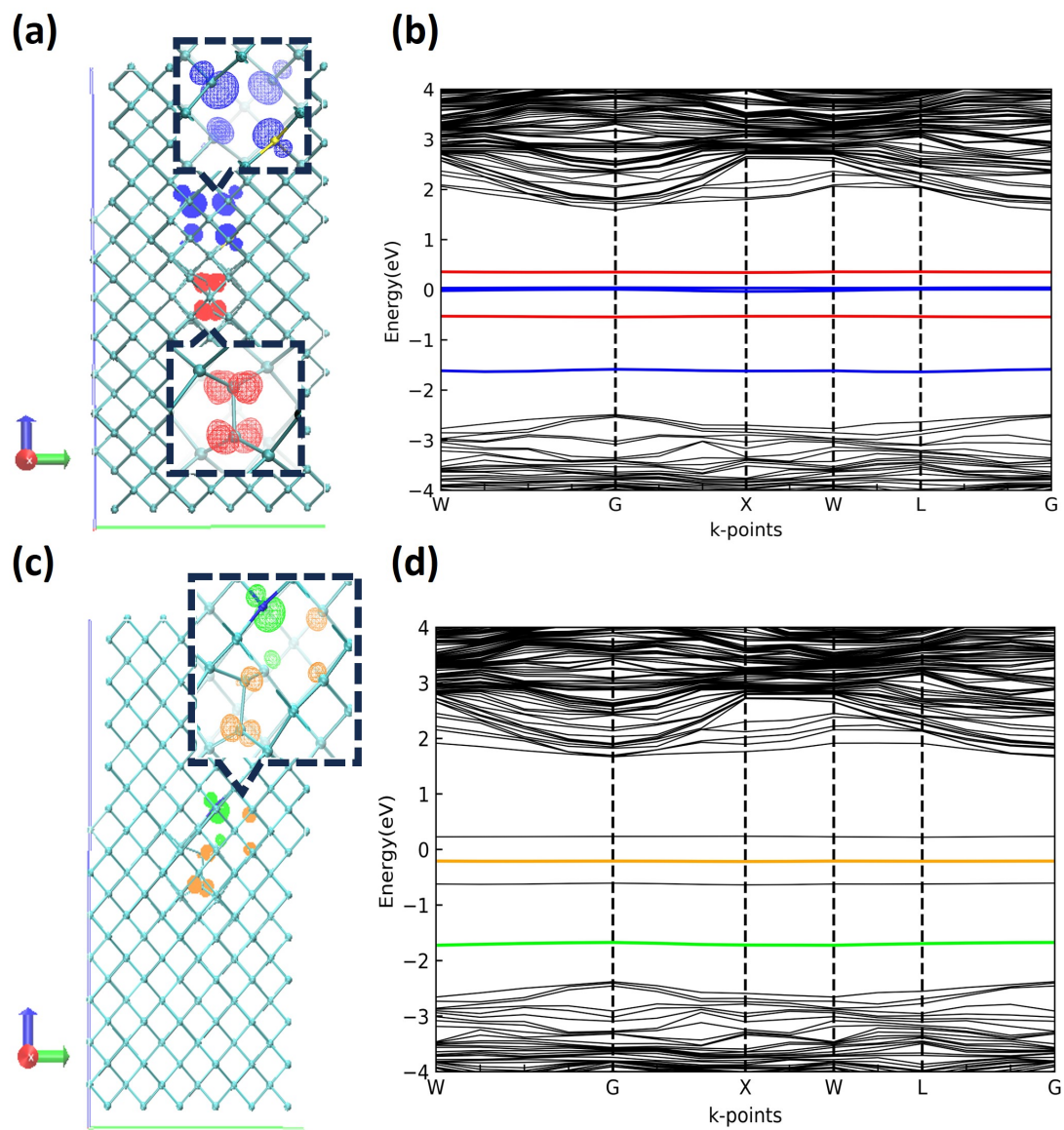


Figure 5.8: A illustration of atomic configuration and bandstructure in the situation of (a),(b) non-hybridization and (c),(d) hybridization. For the electronic orbitals, an isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

the transition from the a_2 band to the degenerated e_x or e_y orbitals in the NV^- cannot be performed. The hybridization would have two types of consequences presented in the photoluminescence signal detector. The first is that through the observation from the bandstructure, potential transitions might happen in these hybridized bands in the bandgap, producing photons with lower energy compared to pure NV^- . These relatively weak signals would change as the migration of the split- $\langle 100 \rangle$ C_i , resulting in a blinking of the photoluminescence signal. Another possible outcome is that those hybridized electronic bands might cause non-radiative pathways for electrons to relax from their excited state to the ground state. In this situation, the photoluminescence signal will quench, since no photon will be emitted.

5.3.4 Energy and location differences

In the previous section, we have shown several featured examples of the situations in reconstruction, non-hybridization, and hybridization together with their corresponding potential consequences on the photoluminescence detector. In this part, a further discussion will focus on the total energy differences for each simulated configuration and the location distributions on all the simulated split- $\langle 100 \rangle$ C_i concerning an NV^- colour centre. Figure 5.9 presents a plot exhibiting the total energy differences among various configuration types. In general, configurations resulting in non-hybridization demonstrate the highest relative total energy which is set as zero according to the plot. In the second-nearest region, non-hybridization exhibits the lowest stability due to its highest total energy, whereas hybridization and reconstruction type-2 dis-

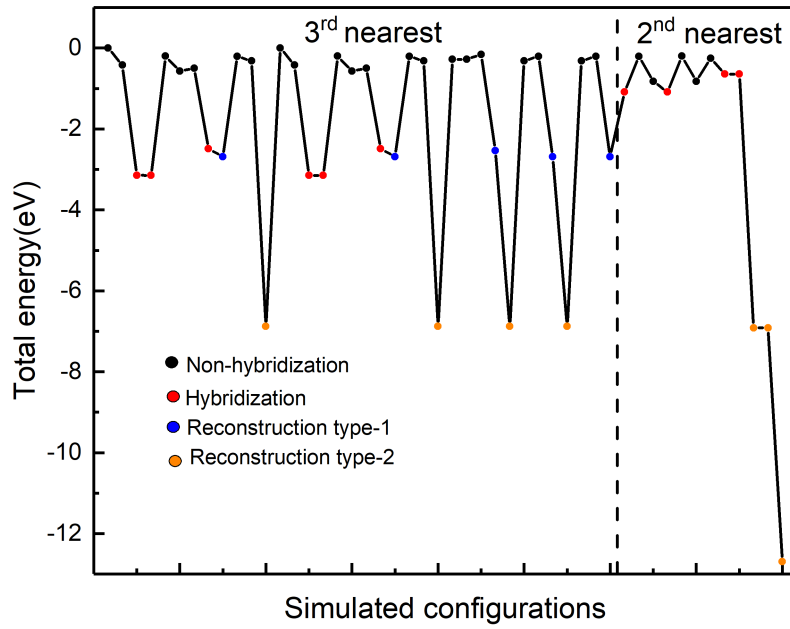


Figure 5.9: A plot of the total energy difference between each simulated configuration of the ensembles, where reconstruction and hybridization occur with a distinct drop in the energy compared to non-hybridized configurations

play more stable configurations. In the third-nearest region, where reconstruction type-1 is observed, the configurations are arranged by total energy in descending order as follows: non-hybridization, hybridization, reconstruction type-1, and reconstruction type-2. It is notable that the energy difference between each simulated configuration is approximately 3 eV, ranging from non-hybridization to hybridization or reconstruction type-1, and about 4 eV from hybridization or reconstruction type-1 to reconstruction type-2. Since the laser annealing process demonstrates the ability to migrate interstitial carbons in diamond, it is possible that the photoluminescence signal may change due to the hopping of interstitial carbon, forming different types of defect ensembles.

The mentioned hypothesis can be further explained by taking a glance at the relative locations of each C_i and NV^- , present in Figure 5.10. In the figure, an NV^- is placed at the centre (an arrow from nitrogen to vacancy) of the diagram while each interstitial carbon shows one combination situation of two defects. Meanwhile, the different situations are distinguished by different colours such as cyan for reconstruction, green for non-hybridization, and purple for hybridization. Overall, when split- $\langle 100 \rangle$ self-interstitial carbons localize on the nitrogen site of the NV^- centre, the non-hybridization phenomenon tends to dominate. This means that the electronic structure of NV^- remains largely unaffected. On the contrary, if one interstitial carbon pair is placed on the vacancy site, both situations, including hybridization and reconstruction, would occur. This means the blinking and quenching phenomenon in the photoluminescence signal might probably be present since the electronic structure of both defects is significantly changed. Here arises a possible explanation for the

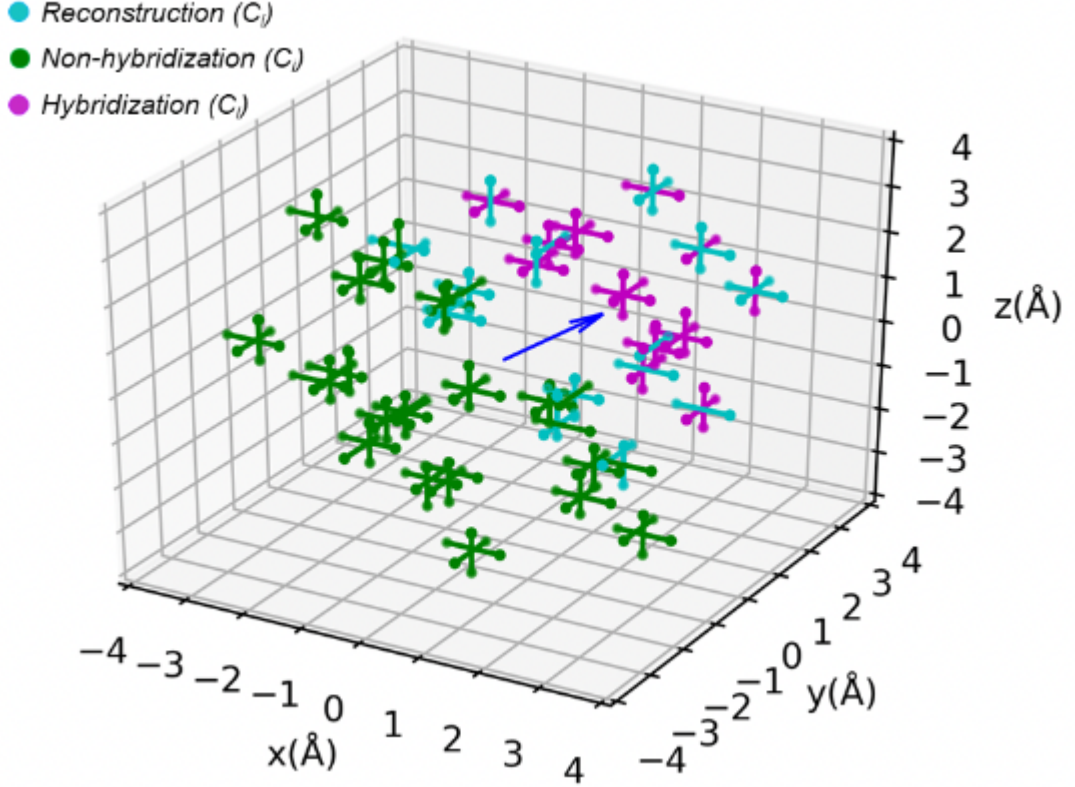


Figure 5.10: Diagram illustrating the positions of split- $\langle 100 \rangle$ carbon self-interstitials around the NV centre. Each interstitial is colour-coded to indicate whether its presence leads to hybridization(purple), non-hybridization(green), or reconstruction(cyan) with the NV centre. The nitrogen atom and vacancy of the NV centre are marked as an arrow from nitrogen to vacancy.

changes in the photoluminescence signal, which can be stated as follows, as the diffusion of split- $\langle 100 \rangle$ self-interstitial carbons, their configurations might go through situations of hybridization, non-hybridization, or reconstruction, potentially ending up with hopping between blinking, quenching and stabilizing in the photoluminescence plot. However, the diffusion procedure is yet to be known and an AIMD simulation will be performed in the following section.

5.3.5 *Ab initio* molecular dynamic results

This part will mainly show some key results on *ab initio* molecular dynamic simulations. Considering the balance of simulated time scale limitations and computational costs, calculations are performed in a $6\times 6\times 6$ supercell system for 1 ps with a time step of 1 fs. However, this simulated time is not large enough compared to real experiments on thermal annealing where the annealing time is in the unit of hours or days. An AIMD (Ab Initio Molecular Dynamics) simulation is designed here to investigate the potential migration of defects within a thermal environment. Specifically, an interstitial carbon is accommodated at the vacancy or nitrogen site of a NV^- colour centre at the temperature of both 300K and 1300K. Since there are no obvious movements at 300K, the following discussion will mainly focus on the results of 1300K.

In Figure 5.11 (a), the molecular dynamics results of one interstitial carbon localized on the vacancy site of an NV^- colour centre are shown. The line marked in green represents the migration path of the interstitial carbon. The graph illustrates that the highlighted interstitial carbon undergoes an intermediate phase halfway through before ultimately settling at the vacancy site. This suggests that the interstitial carbon may recombine at the vacancy site of the NV^- centre, potentially destroying the generated NV^- . When it is located on the nitrogen site of an NV^- centre, shown in (b), the interstitial carbons illustrated oscillate around their original site, presenting no migration behaviours. Due to the limitation of the timescale and size of the supercell in AIMD simulations, an alternative should be developed for further

investigations. A method of machine learning potential will be generated in the next chapter to overcome this obstacle.

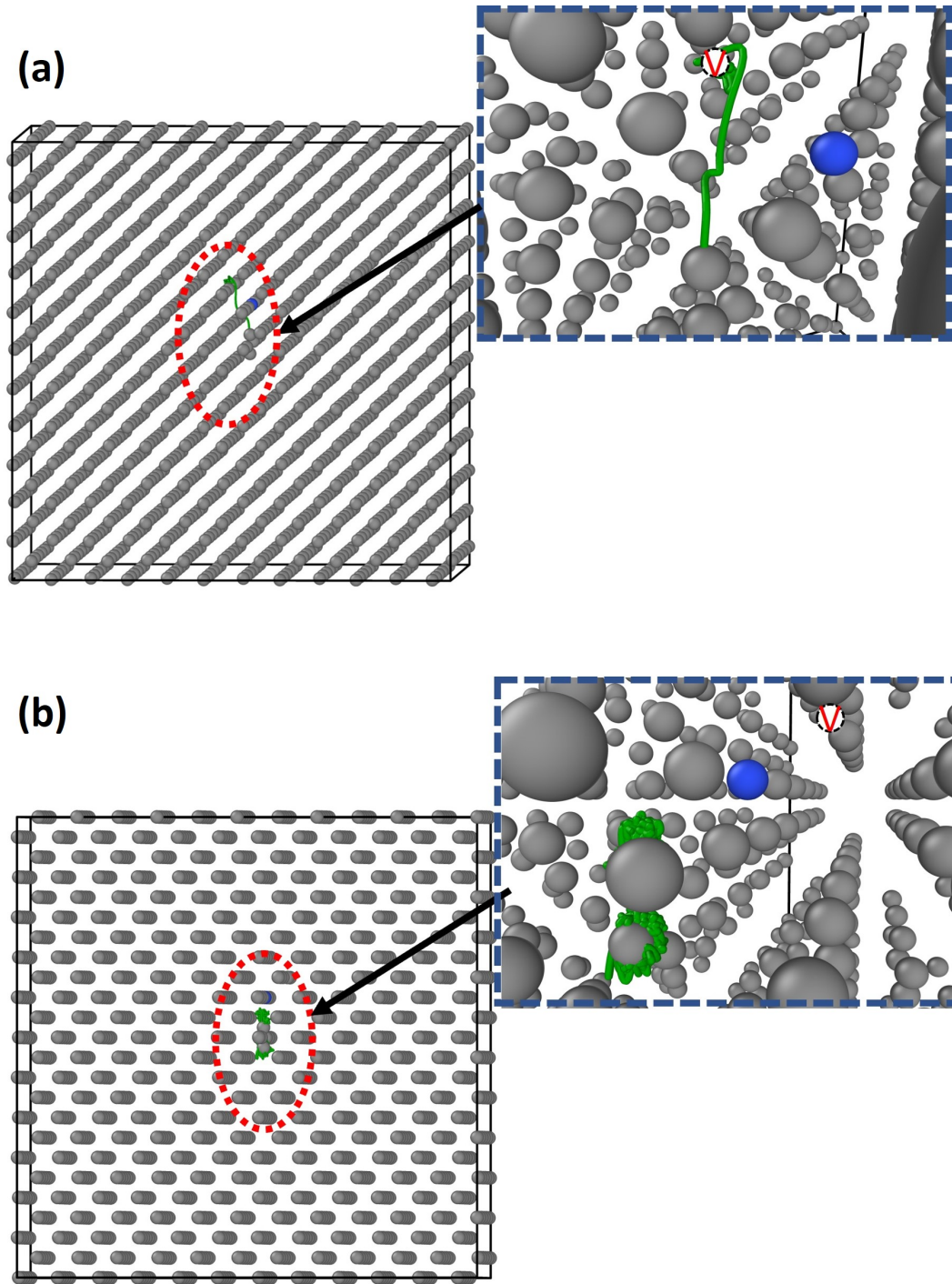


Figure 5.11: An illustration of the diffusion path track (marked in green) under NVT molecular dynamics simulation on one split- $\langle 100 \rangle$ carbon self-interstitials localized on (a) the vacancy site of NV^- centre and (b) the nitrogen site of NV^- centre.

5.4 Conclusions

In this chapter, the perturbation of a negatively charged NV centre and a nearby interstitial carbon is taken into consideration. The study starts with geometry optimization and electronic properties calculation on the individual isolated defects where both split- $\langle 100 \rangle$ carbon self-interstitials and NV^- are in agreement with the reported literature.

The research on the interaction between a split- $\langle 100 \rangle$ self-interstitial carbon and an NV^- is carried out in two parts. The first part focuses on the strain interaction within a distance range of 4.5 to 6.1 Å. A strain produced by a split- $\langle 100 \rangle$ C_i is applied on the NV^- , causing energy splitting from 75 to 280 meV on the degenerated electronic orbitals e_x and e_y . A further study focuses on a shorter distance range in the aspect of the changes in their electronic structures where three main situations can be found, called hybridization, non-hybridization and reconstruction respectively. It is suggested that the photoluminescence experiment would produce a stable signal the same as a formed NV^- colour centre in the non-hybridization situation whereas blinking and quenching might occur in the situation of hybridization and reconstruction due to the destruction of the electronic structure of NV^- colour centre. The uncertainty of blinking or quenching depends on whether there is a non-radiative pathway for electrons to relax. According to the total energies and relative position distribution in all the simulated situations, the interstitial carbon can potentially diffuse between the nitrogen site or vacancy site of the NV^- centre, where most non-hybridization situations occur when interstitial carbon is placed at the nitrogen site

while hybridization and reconstruction would happen at the other site.

Finally, a trial AIMD simulation is performed to investigate the diffusion mechanism of the interstitial carbon around a NV^- colour centre. The result shows that if the interstitial carbon occupies the vacancy site of the NV^- centre, it will eventually recombine at the vacancy position. Meanwhile, at the nitrogen site, no obvious movement is detected due to the limitation of the simulated time scale and computational cost, where a more powerful tool is required to balance this gap which will be present in the next chapter.

Chapter 6

CN(Carbon-nitrogen)-GAP

potential and its applications

6.1 Introduction

This chapter will mainly focus on the generation of CN(Carbon-nitrogen)-GAP(Gaussian approximation potential) and its performance in running NVT-MD simulation. As mentioned in the previous chapter, AIMD is done to investigate the dynamic behaviours of interaction between one interstitial carbon(C_i) and one nitrogen vacancy (NV) centre. However, due to the computational expense and time limitations, the results of AIMD do not present sufficient data to study the interstitial carbon with an NV centre nearby. For example, no obvious diffusion is detected when an interstitial carbon is localized at the nitrogen side of an NV. Therefore, a machine-learning potential called GAP is developed to strike a balance between accuracy and efficiency. Its purpose is to enhance the understanding of the interaction between these two

defects across diverse environmental conditions. This chapter will begin with the whole details of potential generation including database construction, DFT calculation, training procedure and validation of formed potential. Then, some validation tests such as the formation energy and diffusion barriers of each defect are performed. Finally, a large-scale molecular dynamics simulation, containing one interstitial carbon and one NV centre with different relative positions, is held in the NVT ensemble.

6.2 Method

This section elaborates on every computational procedure involved in this chapter, including data generation from a sample dataset, main training parameters on the GAP and DFT calculation and so forth.

6.2.1 Training of the CN-GAP potential

6.2.1.1 Sample construction

This CN-GAP potential aims at designing a diamond lattice that is on a much larger scale, with nitrogen-doped and carbon-related defects, and a combination of them simultaneously. The dataset of this potential is made up of three parts. The first part is created based on the selected structures out of the GAP20[12] dataset to represent the accurate data created by the transferable machine-learning potential of carbon.

The first part of the GAP-CN training dataset involves structures of 'Dimer', 'SACADA'(database of exotic carbon allotropes) [109], 'Fullerenes', 'Nanotubes', 'Crystalline Bulk', 'Defects', 'Graphite', 'Surfaces', 'Crystalline RSS'(random structure search from GAP17 potential) [92], 'Graphene', 'Diamond', 'Single Atom', and 'Graphite Layer Sep'. These structures have been carefully selected to serve as the foundational samples for the CN-GAP dataset. Next, to increase the accuracy of the 'defective' structures, a variety of nitrogen-doped and carbon-related defects, and their combinations, are generated. Here, a corresponding idea of 'defective' needs to be initialised in the form of a variety of defects including nitrogen-vacancy (NV),

substitutional nitrogen (N_s), interstitial nitrogen (N_i), divacancy (VV), monovacancy (V) and interstitial carbon (C_i). Specifically, we first build a $3 \times 3 \times 3$ perfect diamond supercell. Next, we randomly create the different defects under consideration in the diamond lattice. Finally, we perform a random perturbation on the atoms' position and the lattice parameters ranging from 10 % to 30 %. An example of 'defective' structure construction is shown in Figure 6.1, in the form of a N_s plus N_i embedded in a deformed $3 \times 3 \times 3$ diamond supercell lattice. In Figure 6.1, single substitutional nitrogen plus one interstitial nitrogen are created in a $3 \times 3 \times 3$ diamond supercell. A perturbation is then applied to the supercell. The third part of our dataset is from the iteration loop in Figure 6.2 to improve the accuracy of the force and energy error. The details can be explained in the section on 'Training the CN-GAP potential'.

6.2.1.2 DFT calculation

The synthetic samples are then applied to DFT (Density Functional Theory) calculations based on the CASTEP code. The PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional is utilised with ultrasoft pseudopotentials. The cutoff energy is set to 600 eV and the MP (Monkhorst-Pack) grid spacing is specified to 0.02. Constraints are set to eliminate the displacement in the cell during the calculation.

6.2.1.3 Training the CN-GAP potential

After the construction of the dataset through the first principle calculation, the training sets are then converted into a Gaussian Approximation Potential (GAP) using the Quippy code (<https://libatoms.github.io/GAP/index.html>). The fitting pro-

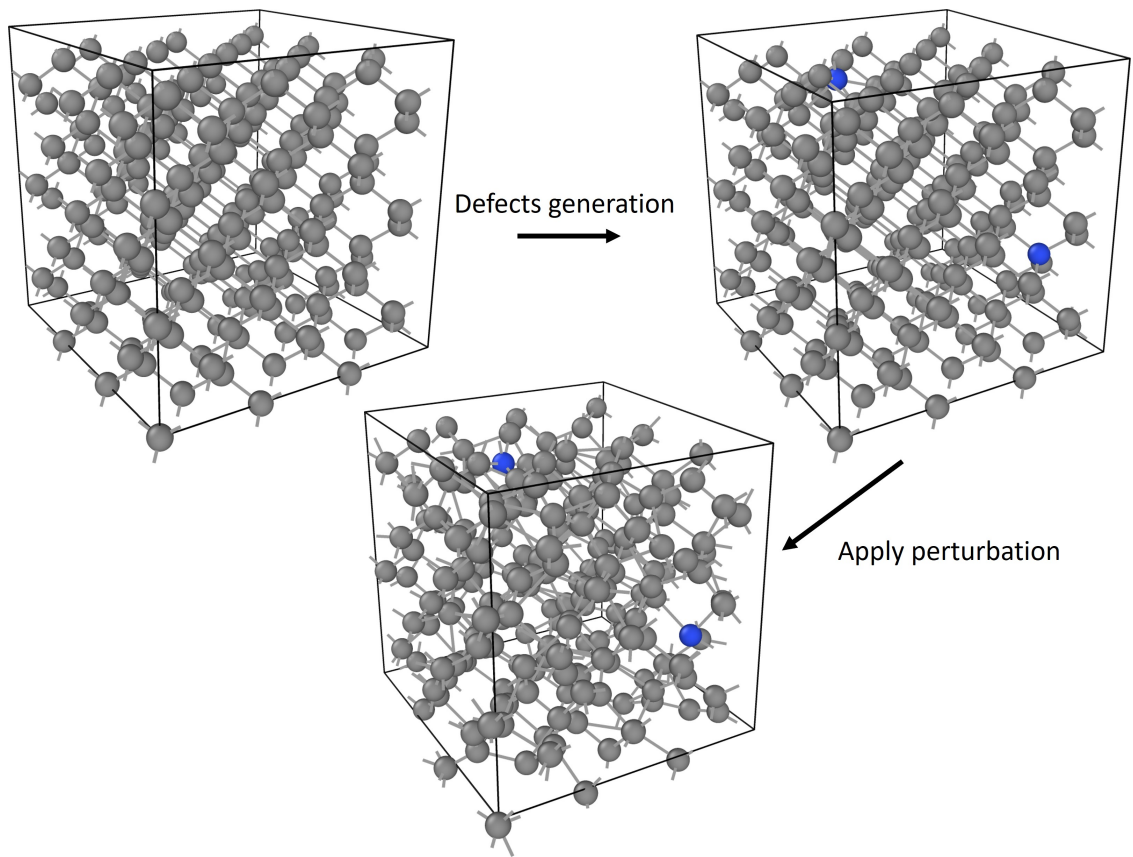


Figure 6.1: An illustration of the construction of one sample containing a substitutional nitrogen(N_s) and an interstitial nitrogen(N_i) in a $3 \times 3 \times 3$ supercell.

gram is parallelised over many nodes using ScaLAPACK with MPI and OpenMP on a high-performance computing (HPC) machine[110]. Table 6.1 summarises the CN-GAP training parameters and the three classes of descriptors used (up to 2-body, 3-body and SOAP). Most of the parameters were taken from the GAP20 carbon fit[12] since the majority of the crystal structure comes from there. Meanings of the parameters are explained in the reference[90]. Besides, it sets the regularisation parameters for the expected errors on energies and forces as 0.001 eV/atom and 0.02 eV/Å.

	2-body	3-body	SOAP
$\delta(\text{eV})$	2	0.5	0.2
$r_{cut}(\text{\AA})$	3.7	3	3.7
r_{Δ}			0.4
$\sigma(\text{\AA})$			0.5
n_{max}			12
l_{max}			4
Sparsification	Uniform	Uniform	CUR

Table 6.1: Key parameters used in the CN-GAP potential training.

6.2.1.4 Molecular dynamics simulations

After the first trial of GAP fitting, the constructed potential is applied to perform molecular dynamics using the QUIP[89] pair style implemented in LAMMPS[111]. In particular, the molecular dynamics simulation is conducted in the environment of a constant-volume, constant-temperature(NVT) ensemble using a Nose-Hover thermostat at a temperature of 3000 K for 10 ps with the time step of 2 fs. This enables the generation of sufficient snapshots for the iteration procedure and provides adequate perturbation on the constructed defective structure.

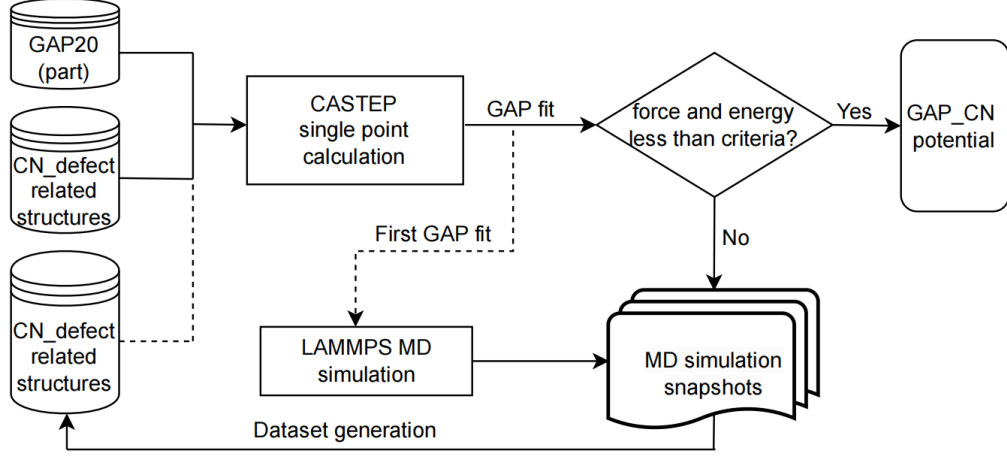


Figure 6.2: A flowchart illustrating the process for generating the CN-GAP potential.

6.2.1.5 Training procedure of CN-GAP

Figure 6.2 shows the training procedure of the CN-GAP construction. The GAP20 and CN defect-related structures, both designed structures, serve as the input geometries for DFT calculation by CASTEP, respectively. In particular, the CN defect-related structures are made of a diamond supercell composed of $3 \times 3 \times 3$ primitive cells, which contains single defects such as nitrogen-vacancy (NV), substitutional nitrogen (N_s), interstitial nitrogen (N_i), divacancy (VV), monovacancy (V) interstitial carbon (C_i) and combinations of any two of the above single defects. Then, their total energy and atomic force data are used to fit the parameters of the CN-GAP potential in the GAP fitting program, thus generating the first iteration of CN-GAP potential. The first iteration of the CN-GAP potential is used for molecular dynamics simulations in LAMMPS. To improve the precision of force and energy calculations enabled by the CN-GAP potential, frames taken from the MD simulations are used as extra CN defect-related structures to reiterate the best-fit potential.

6.2.1.6 Validation of the CN-GAP potential

The quality of the developed CN-GAP potential that should be used for subsequent modelling of nitrogen-doped diamond samples is checked against DFT-based energies per atom and forces. This comparison is shown in Figure 6.3(a) and (b). Root Mean Square Error (RMSE) and Mean Absolute Error (MAE) are taken as the measure of the difference between the result from CN-GAP and the result from DFT. It is observed in the scatter plot that energy data demonstrated a good fit as the value of the MAE is less than 20 meV/atom and RMSE is in the region of 51 meV/atom, whereas, Force data showed a very strong fit as the MAE is less than 0.15 eV/Å and RMSE is in the region of less than 0.3 eV/Å. We emphasise that the discontinuity in the energy comparison arises from the differences in the crystalline structure from the GAP20 database, with the data in the middle from the aforementioned structures related to the CN structural defects constructed.

Further validation of the force and energy for each defective carbon-nitrogen-related structure, along with the distribution of each configuration, is illustrated in Figure 6.3(c), (d) and (e). From the graph, it is shown that both the RMSE and MAE for force errors are below 0.3 eV/Å, while for energy errors, they are all below 0.01 eV/atom. It is notable that the defective structure containing one interstitial nitrogen and one substitutional nitrogen, marked as 'Ni_Ns', occupies the largest number of configurations to maintain consistent force and energy accuracy with other types of defective structures.

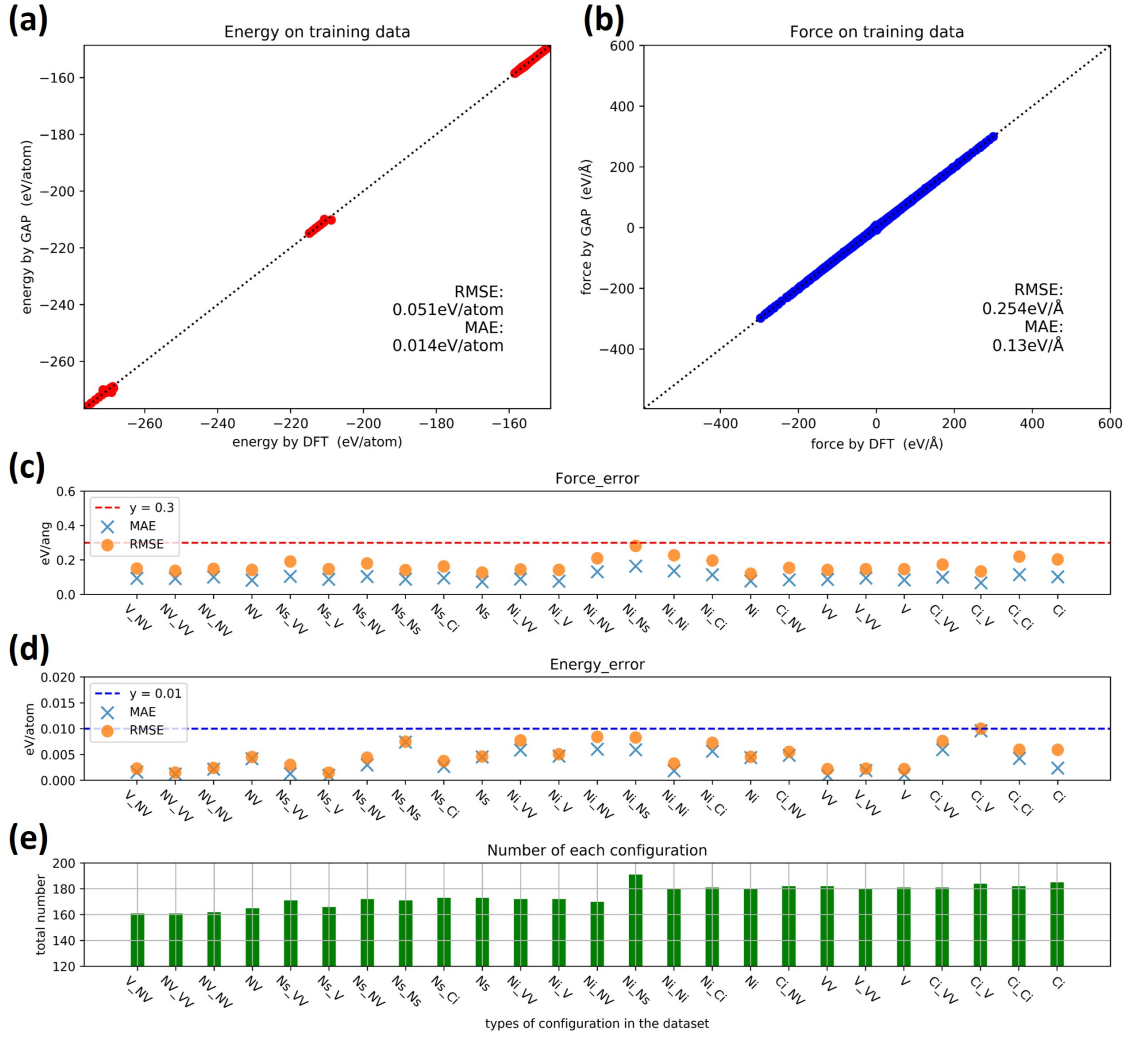


Figure 6.3: (a) A scatter plot comparing the energy results obtained from DFT and GAP. (b) A scatter plot comparing the force results between DFT and GAP. An illustration of the Root Mean Square Error (RMSE) and Mean Absolute Error (MAE) for various defective structures concerning (c) force and (d) energy. Plot (e) demonstrates the distribution of each defective structure within the data samples.

6.2.2 Testing of the CN-GAP potential

To further evaluate the quality of the generated CN-GAP potential, particularly regarding defect migration, two types of simulation tests are conducted: diffusion barrier investigation and formation energy calculation.

6.2.2.1 Diffusion barrier

This generated potential will be used primarily to study the diffusion of defects in diamond, so we recalculate the energies of the diffusion barriers of vacancy, nitrogen-vacancy and interstitial carbon defects for comparison. The diffusion barrier of the two defects mentioned above is calculated by the Python library atomic simulation environment(ASE)[112] with the nudged elastic band(NEB) method. To investigate the vacancy diffusion, we optimise the initial and final states as shown in Figure 6.4(a). Figure 6.4(a) is designed to display a single layer of diamond in the $\langle 111 \rangle$ direction. This is followed by an elastic band that ties together the states, creating a string of imagined replicas lined up along the route. These replicas are then nudged to relax to the minimum energy pathway using the Nudged Elastic Band (NEB) technique. This iterative process involves applying forces to each image perpendicular to the band direction, leveraging the energy gradient along the pathway. Upon completion of the NEB calculation, the energy profile along the minimum energy pathway is scrutinized to identify the diffusion barrier, corresponding to the maximum energy point along the pathway. The calculated diffusion barrier is 2.1 eV (Figure 6.4(a)) and the experimental value is 2.3 eV [84], which is an 8% difference. Likewise, the

exchange of NV reveals a hopping barrier of 5.11 eV with an error of 6 % to *A. Gali* whose work[10] demonstrates a barrier of 4.8 eV.

In terms of the investigation of the diffusion barrier of interstitial carbon, a thermal dynamics method is applied. This method is based on the Arrhenius equation, stated as follows:

$$r = r_0 \times e^{(-\frac{E_{diffusion}}{k_b T})} \quad (6.1)$$

Here, r represents the diffusion frequency, r_0 corresponds to the frequency factor, which remains constant, while k_b and T represent the corresponding temperature. To initiate the simulation, the same sample containing one interstitial carbon in a $6 \times 6 \times 6$ diamond supercell is subjected to NVT molecular dynamics simulations at temperatures of 2000, 2300, 2500, 2700, and 3000 Kelvin. The simulation employs the Nose-Hover thermostat for 10 ps with the time step of 2 fs. For each temperature simulation, we record the hopping frequency of interstitial carbon. Using Equation 6.1, we can simplify the relationship between the diffusion frequency r and the temperature $1/T$ as follows:

$$\ln(r) = -\frac{E_{diffusion}}{k_b} \times \frac{1}{T} + \ln(r_0) \quad (6.2)$$

In this case, the diffusion barrier of interstitial carbon in diamond can be determined through the slope of the linear plot between $\ln(r)$ and $1/T$. As present in Figure 6.4 (c), a linear fitting is illustrated and the diffusion barrier energy is calculated as 1.8 eV. This result aligns with the experimental findings in Ref.[46], where an activation energy of 1.68 eV is reported.

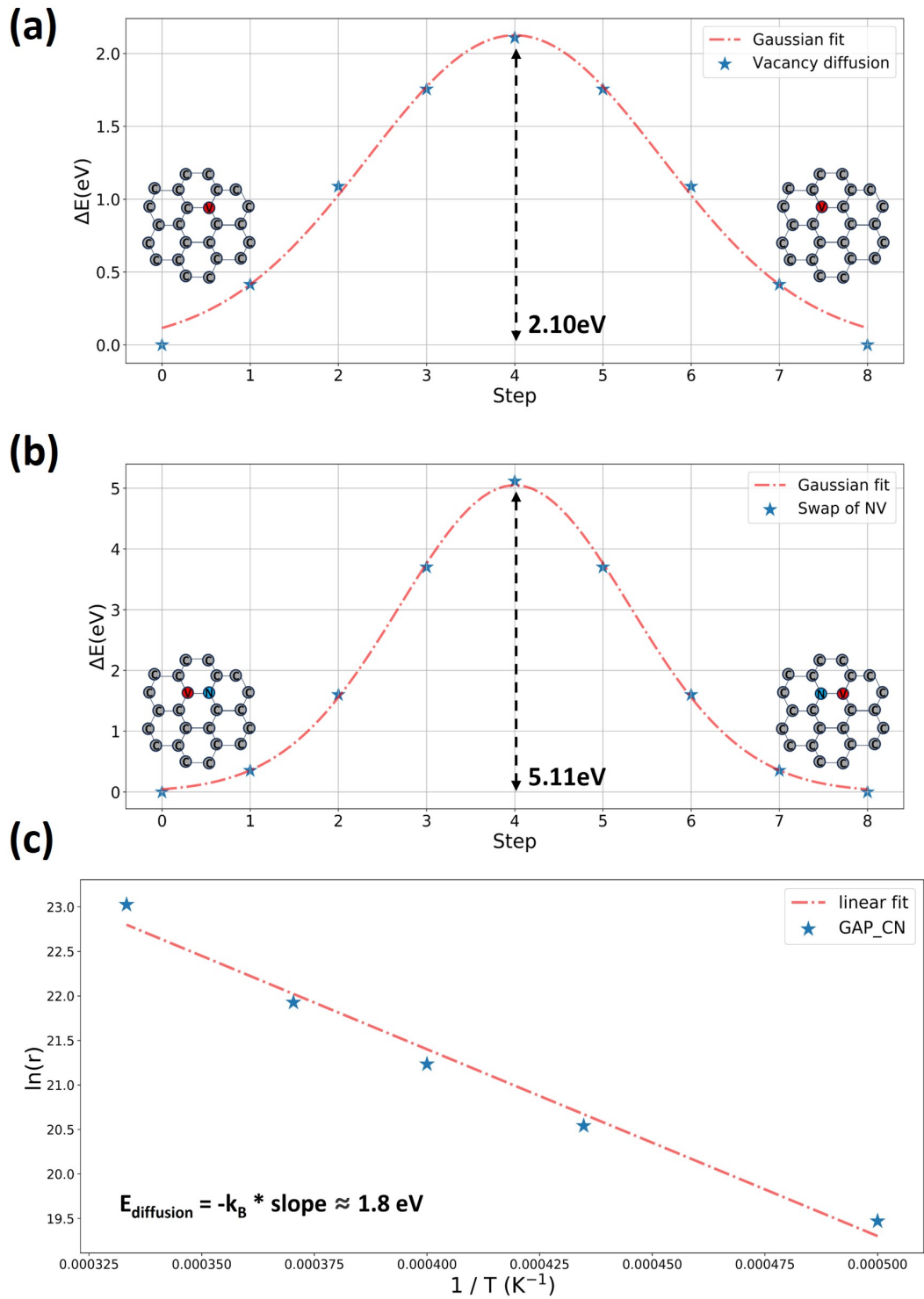


Figure 6.4: Applied the Nudged Elastic Band (NEB) method to investigate (a) the diffusion barrier of vacancies in diamond, and (b) the barrier of NV swapping. Graph (c) illustrates an analysis of the diffusion barrier of interstitial carbon using a thermodynamic approach.

6.2.2.2 Formation energy

This section will further investigate the stability of each individual studied defect, including nitrogen-vacancy (NV), vacancy (V), interstitial carbon (C_i), substitutional nitrogen (N_s), and interstitial nitrogen (N_i). The procedure of computing the formation energy follows the equation 6.3 as below:

$$E_f = E_{tot} - \sum_i n_i E_i \quad (6.3)$$

where n_i is the number of atoms of element i in the system and E_i is the chemical potential of an atom of an element i . For an individual carbon atom, it is calculated by the total energy of a diamond lattice structure divided by the number of carbon atoms, whereas for a single nitrogen atom, the chemical potential is determined by half the total energy of N_2 in a sufficiently large box with 10 Å as its length. The calculated formation energy for each defect obtained using the GAP potential as well as using CASTEP with the PBE exchange-correlation functional is presented in Figure. 6.5. It is worth mentioning that the reference demonstrated in the graph applies DFT with different exchange-correlation functionals like HSE06, which is a hybrid functional and potentially yields more accurate results. As shown in the figure these nitrogen-related defects such as NV, N_s and N_i display a small formation-energy error (the absolute error is within 0.5 eV), but the absolute formation-energy error is 1 eV for vacancy and is approximately 2 eV for C_i .

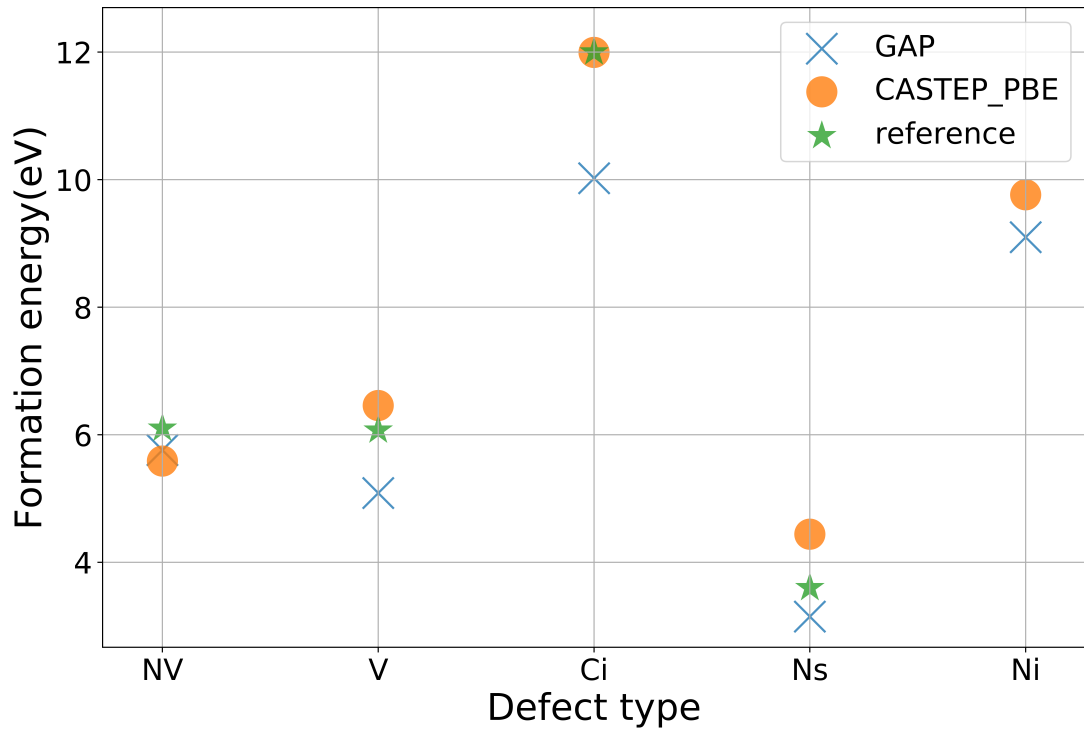


Figure 6.5: An illustration of comparison on formation energy computed by CN-GAP CASTEP and related reference on nitrogen-vacancy (NV)[8], vacancy (V)[13], interstitial carbon (C_i)[14], substitutional nitrogen (N_s)[15], and interstitial nitrogen (N_i)[16].

6.3 Application of CN-GAP

In the section, the generated CN-GAP potential will be applied in molecular dynamics simulation to investigate the diffusion behaviour under the annealing procedure. Thanks to the potential, it becomes feasible to conduct molecular dynamics simulations with larger systems, extending up to the nanometer scale, and time scales up to the picosecond range. Such simulations would be computationally expensive using *ab initio* molecular dynamics methods alone. A molecular dynamics simulation will initially be performed to study the diffusion mechanism when interstitial carbon is placed on either the vacancy side or the nitrogen side of the NV centre. Then, further investigation will focus on the approximate distance for interstitial carbon to recombine with the vacancy if it is firstly located at the position between nitrogen and vacancy.

6.3.1 Computational details

The molecular dynamics simulations are conducted using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [113]. The initial input file was created with CrystalMaker [114], and the generation of defects as well as the input file creation are done from scratch by using the python package ASE (atomic simulation environment) [112]. To achieve a compromise between simulation time and computational resources, all simulations are run at 2600 Kelvin with a Nose-Hoover thermostat within the NVT (constant Number of particles, Volume, and Temperature) ensemble. Atomic velocities are initialised according to a user-defined temperature with a

random seed, and the simulation timestep is set to 1 femtosecond.

There are three kinds of simulation models, each having one interstitial carbon and one NV centre in a diamond, which are done from different initial positions of the interstitial carbon. Specifically, the "vacancy side" model refers to the scenario where the initial interstitial carbon is placed at the vacancy side of the NV centre, while the "nitrogen side" model corresponds to the interstitial carbon being initially located at the nitrogen side. These two types of simulations are performed in a diamond supercell of $6 \times 6 \times 6$ lattice with a dimension of about 20 Å. In the "middle side" model where the size of the supercell is $15 \times 15 \times 15$ containing about 27000 atoms, the interstitial carbon is initially positioned along the extension line passing through the midpoint of the NV centre and aligned with the $[1\bar{1}0]$ direction with the distance ranging from 2 to 14 Å.

6.3.2 Results

6.3.2.1 Vacancy side model

In this simulation, the interstitial carbon is hosted on the vacancy side of the NV centre with a distance of about 6 Å between them. An overview of the simulation procedure can be found in Figure 6.6.

In graph (a), there are layers of snapshots taken at particular time steps. It is understood that the carbon atoms of the substrate lattice of the diamond have been moved away using Wigner-Seitz defect analysis [115]. Distances of interstitial carbons towards the vacancy position are illustrated in graph (b) over simulation time. Based upon the combined information provided by graph (a) and graph (b), we see that, beginning at the start, the interstitial carbon relaxes into the split- $\langle 100 \rangle$ interstitial carbon configuration which remains dominant until around 3200 fs when one the interstitial carbon's strikes the vacancy position and the NV centre has disappeared. This is evident in the graph (b) where the distance between interstitial carbon 1 and the vacancy site is suddenly reduced to zero when combined with the vacancy site. The observed behaviour is consistent with the results of the previous Chapter, where we found that, if the interstitial carbon is at a vacancy site of the NV centre, there is a possibility of hybridisation between the electronic orbitals of the NV centre and the interstitial carbon pair. This hybridization leads to blinking behaviour in terms of the photoluminescence signal. Consequently, the diffusion phenomenon observed here could be interpreted as the real-time fluorescence signal transitioning from blinking to quenching as the interstitial carbon merges with the vacancy site, altering the

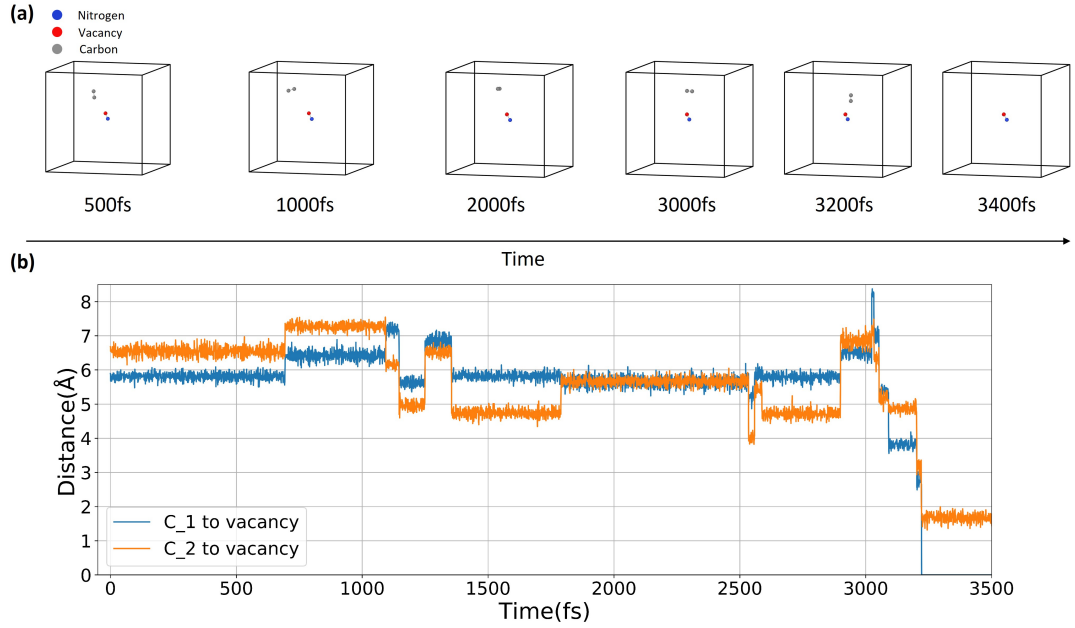


Figure 6.6: An overview of NVT molecular dynamics simulation illustrates the recombination process of interstitial carbon and vacancy, particularly when the interstitial carbon is initially located at the vacancy site of the NV centre.

electronic properties of the NV centre.

6.3.2.2 Nitrogen side model

The same kind of simulation is repeated when the initial condition of the interstitial carbon is at the nitrogen side of the NV centre as shown in Figure 6.7. The displacement between these two defects is approximately 6 Å. From the figure, we can see that the interstitial carbons mainly diffuse out from the NV centre under the times scale of 2000 fs. However, after 2000 fs, the interstitial carbon diffuses around the boundary of the supercell with no tendency to diffuse back towards the NV centre.

Based on the previous chapter, when the interstitial carbon is on the nitrogen side of the NV centre, recombination or non-hybridisation takes place. In the context of this diffusion simulation, this suggests that the fluorescence signal may initially

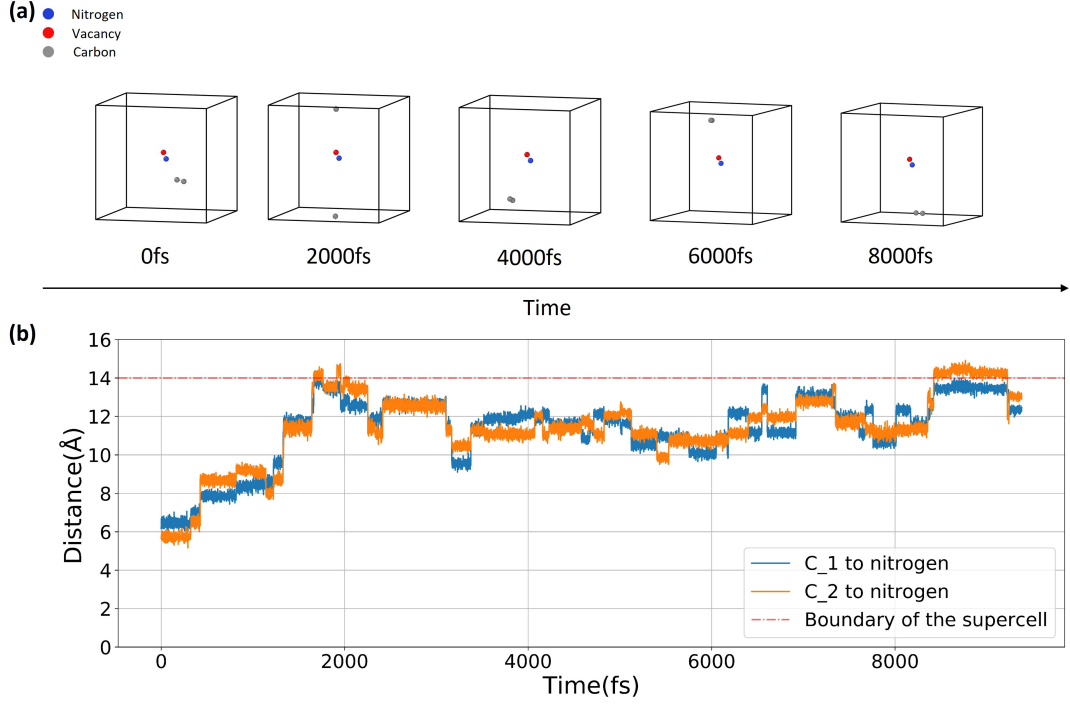


Figure 6.7: A general graph illustrating the initial placement of an interstitial at the nitrogen site of the NV centre indicates that it will tend to diffuse away over time.

exhibit characteristics between blinking and quenching, eventually culminating in a clear, stable, and strong signal. This behaviour indicates the generation of NV centres without any nearby interstitial carbon, leading to a stable fluorescence signal.

6.3.2.3 Middle side model

This section will concentrate on testing the threshold distance for the interstitial carbon to recombine with the vacancy of the NV centre as the displacement increases along the $[1\bar{1}0]$ direction, while the NV direction is $[111]$. The threshold, approximately 6 Å, is determined from Figure 6.8. Specifically, Figure 6.8(a) illustrates the trajectory of the interstitial carbon throughout the MD simulation, with its displacement profile referenced in Figure 6.9(a). Additionally, Figure 6.8(b) depicts the

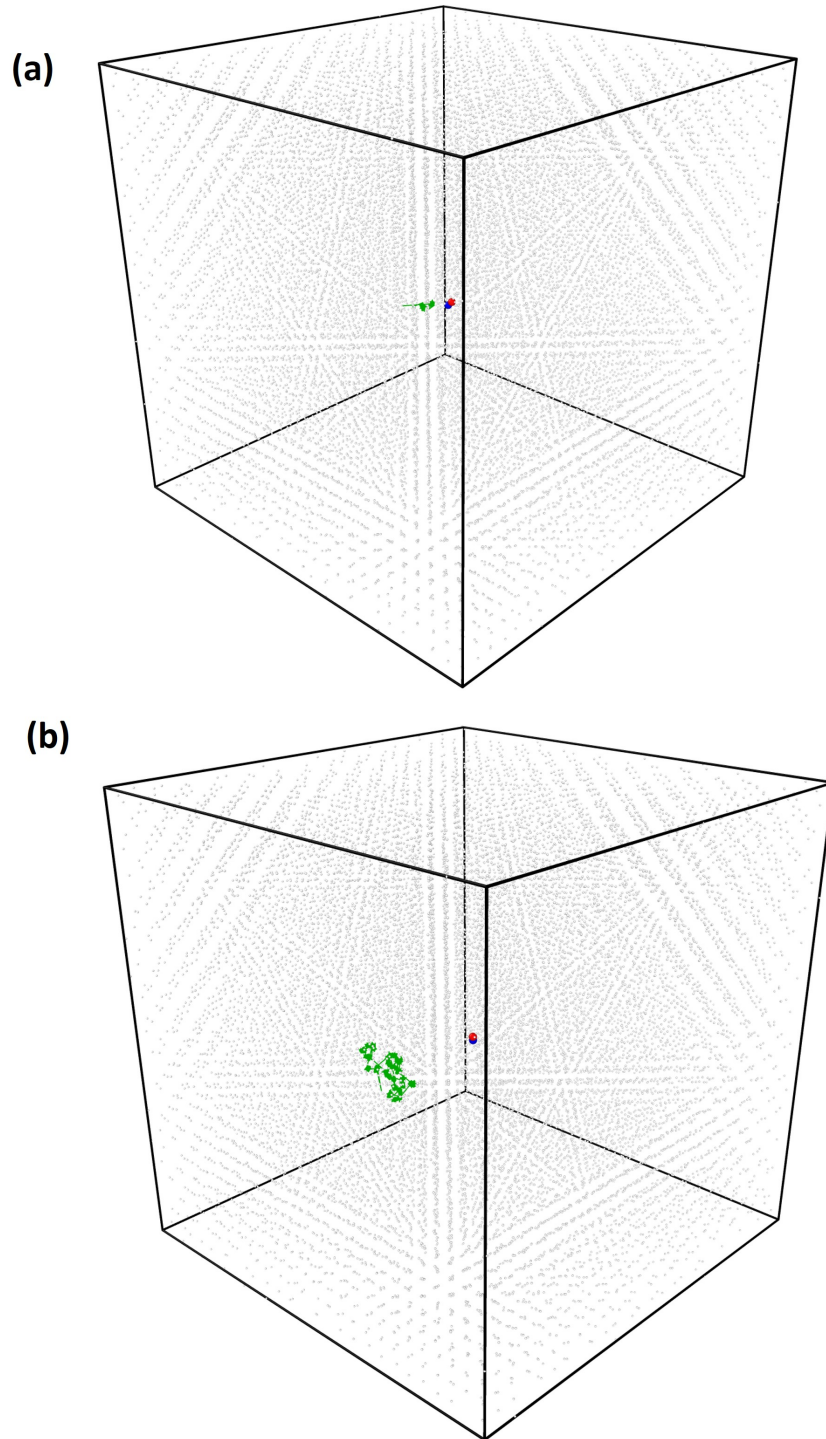


Figure 6.8: Threshold distances between the NV centre and interstitial carbon in scenarios (a) involving recombination and (b) without recombination. The green lines show the trajectory of the diffusing interstitial carbon.

minimum distance between the interstitial carbon and the NV centre, indicating instances where recombination does not occur. This information correlates with the displacement plot referenced in Figure 6.10(d). The thermal annealing molecular dynamics results indicate that when the interstitial carbon is separated along the $[1\bar{1}0]$ direction from 6 Å to 7 Å, it tends to diffuse around the NV centre instead of merging with the vacancy side of the NV centre.

Detailed information on the displacement profile can be found in Figure 6.9, which illustrates displacements ranging from 2 to 6 Å, and in Figure 6.10, which covers separations from 6 to 14 Å. From Figure 6.9, it can be concluded that for displacement lengths less than 6 Å, all simulations ultimately result in diffusion towards the vacancy position of the NV centre, leading to the disruption of the formed NV centre. Furthermore, the recombination time for displacements of 2-3 Å is approximately 250 fs, for 4-5 Å it is about 320 fs, and for 5-6 Å it is approximately 580 fs, indicating no tendency to migrate away from the NV centre. For displacements of 2-3 Å, no intermediate steps are observed before the recombination of the interstitial carbon and vacancy. For displacements of 4-5 Å, an intermediate step is evident with a duration of around 40 fs. However, for displacements of 5-6 Å, there should be two intermediate steps preceding the recombination, but the duration of the second step is extremely short and barely observable. This suggests the presence of an attractive force from the vacancy towards the interstitial carbon, effectively accelerating the recombination mechanism for displacements within around 6 Å in the diamond lattice.

In Figure 6.10, simulations with displacement lengths exceeding 6 Å are depicted,

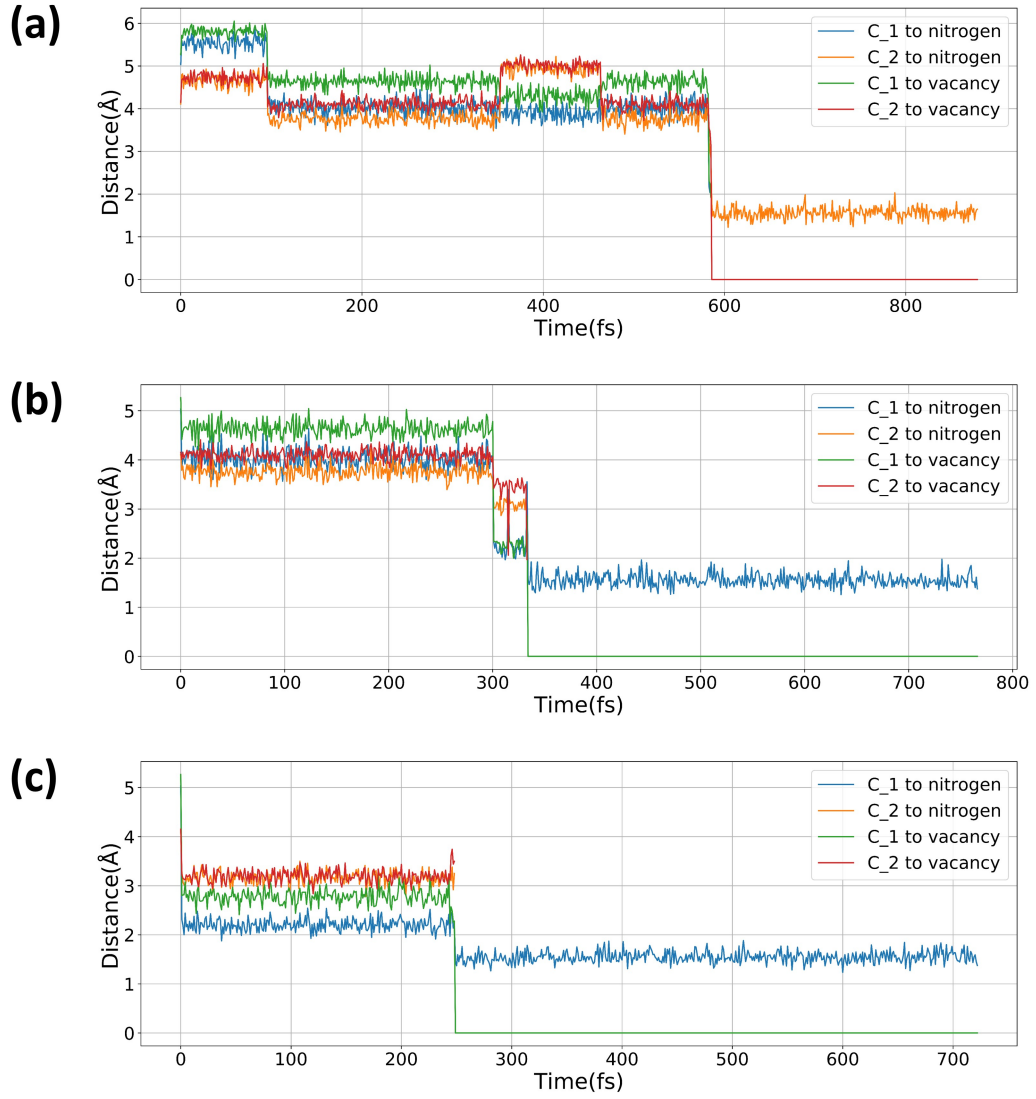


Figure 6.9: A demonstration illustrating how the interstitial carbon ultimately recombines with the vacancy position as the displacement between the two defects increases (from around 2 to 6 Å).

all exhibiting duration times above 2500 fs. Among these displacements, no clear behaviours indicating a tendency for the interstitial to recombine with the vacancy are observed. Some simulations show an attempt to diffuse away from the NV centre, as depicted in Figure 6.10(d), while others attempt to move back towards it, as shown in Figure 6.10(a). Additionally, graphs (b) and (c) illustrate that the interstitial carbon is diffusing around the NV centre without exhibiting a tendency to diffuse away or recombine. This phenomenon suggests that the attractive force exerted by the vacancy of the NV centre is weaker in regions where the displacement exceeds 6 Å, and consequently, it is not sufficient to attract the interstitial carbon quickly.

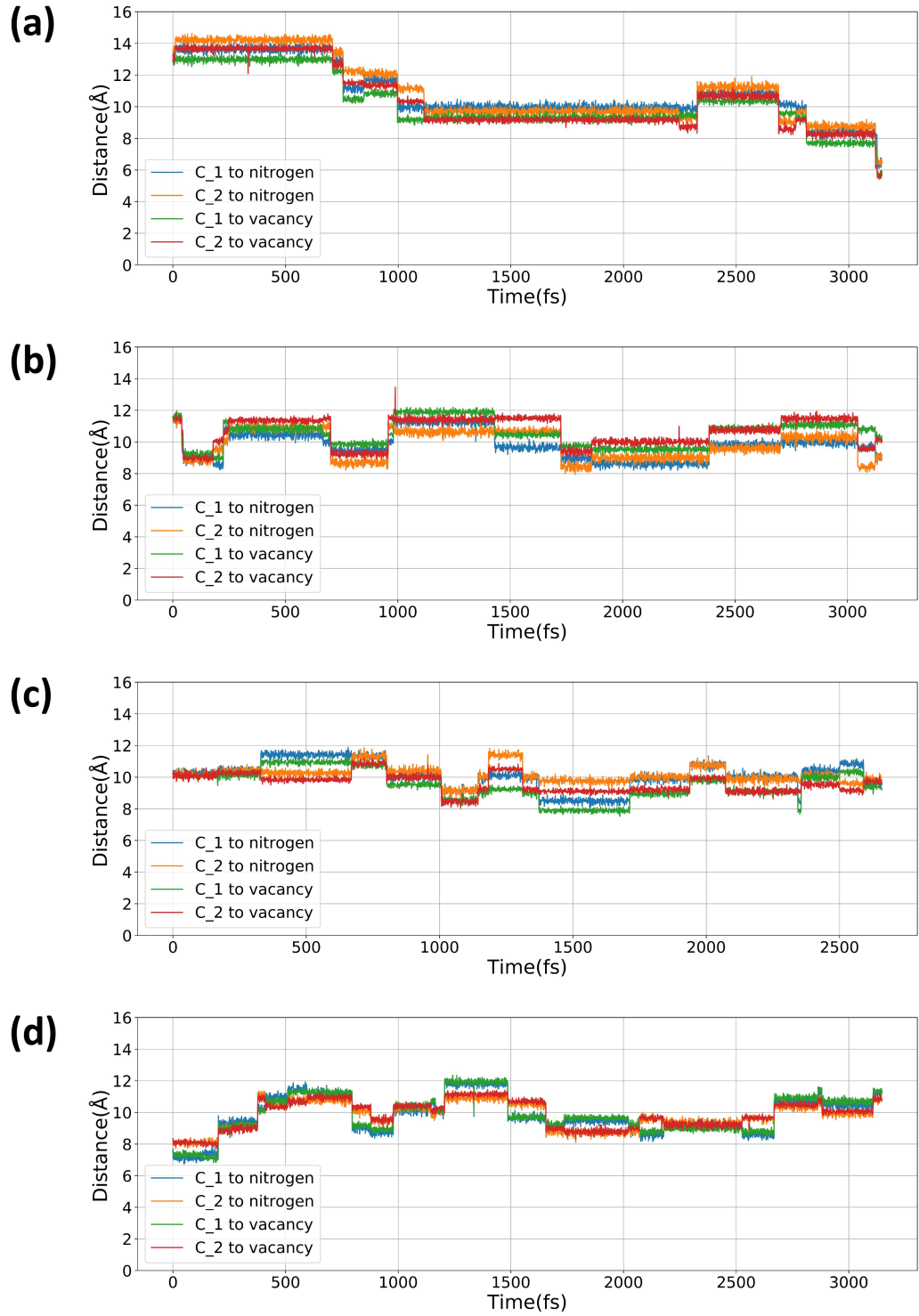


Figure 6.10: An overview of all situations where the interstitial carbon does not combine with the vacancy when the displacement exceeds 6 Å.

6.4 Conclusion

In this chapter, a machine-learning potential, namely CN-GAP, is constructed for large-scale molecular simulations on nitrogen-doped and relative defects in diamond. The construction begins with the generation of the database, which comprises the crystalline portion of GAP20 and nitrogen-doped structures along with their respective defect configurations. Afterwards, an algorithm is designed to optimise the accuracy of CN-GAP potential at the aspects of forces and energies by self-iteration. The optimized potential is further validated by calculating the diffusion barrier of interstitial carbon, vacancy and NV centre as well as formation energy on the defect of NV, vacancy, carbon interstitial(C_i), substitutional nitrogen(N_s) and interstitial nitrogen(N_i). After the construction of CN-GAP potential, it is applied in studying the diffusion mechanism on NV and C_i under a thermal environment. The results indicate that the interstitial carbon can either recombine to the vacancy site of the NV centre or diffuse away. A further molecular simulation performed in a sufficiently large supercell suggests that at 2600 K the maximum distance for an interstitial carbon to recombine within 3000 fs is around 6Å.

Chapter 7

Absorption properties of negatively-charged NV and interstitial carbon

7.1 Introduction

So far, through the previous study, we know that the blinking fluorescence might come from the hybridization of electronic structure on the ground state. Also, according to the molecular dynamics simulation, interstitial would trend to either diffuse away or recombine, leaving NV^- remained or destroyed. However, rather than deriving from the emission process, the absorption procedure would potentially affect the fluorescence signal. In particular, the wavelength of the photoluminescence laser is 532 nm. This implies that any obvious shifts or changes in absorption would significantly influence the transition from the ground state to the excited state. This

chapter aims to investigate the changes in the absorption properties in diamond that contain a random combination of one NV^- and one interstitial carbon by applying the method of linear scaling TDDFT simulation.

A general workflow is demonstrated in Figure 7.1. Considering the computational resource and time, the simulation initializes with a pure NV structure in a $4 \times 4 \times 4$ diamond lattice containing 510 carbon atoms and 1 nitrogen atom. Then two main tasks will be performed afterwards. The first one targets investigating the excited state differences on NV^- at 0 K and 300 K. The 0 K structure is generated by geometry optimization with the acceleration of CN-GAP potential through the ASE package. On the other hand, the 300 K pure NV^- sample experiences one further step where an NVT ensemble molecular dynamics simulation is performed. All these constructed samples are then applied in linear scaling TDDFT simulation through ONETEP[102] for further absorption properties calculations. The second task refers to the comparison of excited states on various ensembles of NV^- and C_i . The random ensemble samples are constructed by dropping one carbon atom into the pure NV sample with CN-GAP potential accelerated geometry optimization afterwards. Analogously, these optimized configurations will be applied in TDDFT simulations for absorption spectrum comparison.

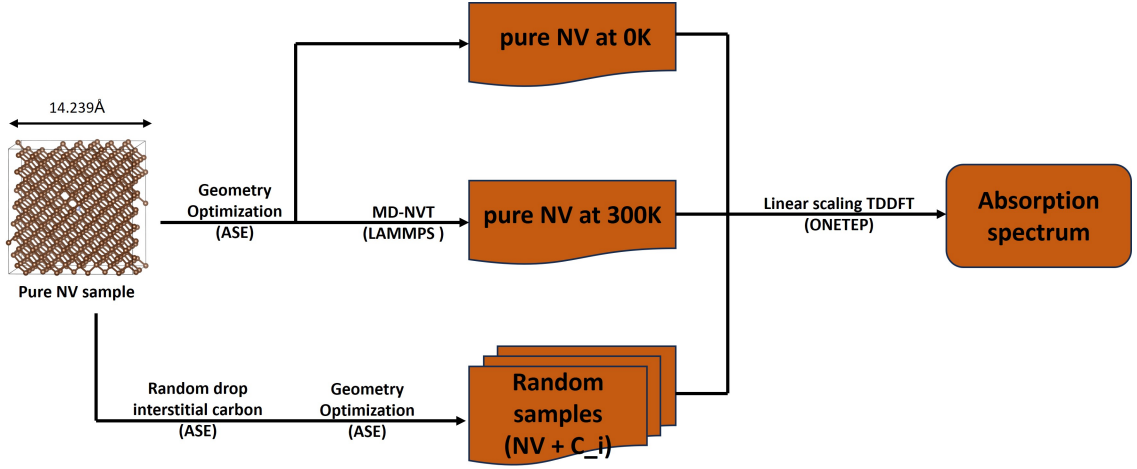


Figure 7.1: A details of workflow for absorption spectrum investigation

7.2 Computational details

7.2.1 Structure construction

The input NV sample in a $4 \times 4 \times 4$ supercell diamond structure is constructed by *CrystalMaker* for further process. The atomic simulation environment(ASE) is employed to process geometry optimization with the constructed CN-GAP potential. During the procedure of geometry optimization, the optimizer of BFGS[104] is applied with the converged criterion force on all individual atoms less than $0.001 \text{ eV/\AA}$.

7.2.2 Molecular dynamics

The molecular dynamics simulation for NV^- at 300 K is conducted using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) with the CN-GAP potential is implemented with QUIP. The MD simulations are executed at 300 Kelvin using a Nose-Hoover thermostat in the NVT (constant Number of particles, Volume, and Temperature) ensemble. Atomic velocities are initialized based on a specified

temperature using a random seed, and the simulation timestep is set to 1 femtosecond and the duration time for the simulation is 2000 fs. The temperature profile is checked to stabilize at around 300K with a less than 20 K fluctuation. The final snapshot is extracted for further linear scaling TDDFT calculation.

7.2.3 Linear scaling DFT

The mentioned structures are then applied in ONETEP[102] for a single point, conduction and TDDFT calculation. In particular, Perdew–Burke–Ernzerhof(PBE) [116] are set as the exchange-correlational functional for all the simulations while pseudopotential is employed in treating the interaction between core and valance electrons. To explicitly model the real electronic structure of NV^- , one extra charge is added into the system and the spin-polarized feature is turned on. The cutoff energy and the Non-orthogonal Generalized Wannier Functions (NGWFs) are tested converged with the value of 1000 eV and 9 Bohr radius, shown in Figure 7.2. To better describe the conduction band converged, the radius of NGWFs increases to 10 Bohr. Twelve conduction bands are optimized and ten TDDFT states are calculated. An isosurface value of $0.015 \text{ e}/\text{\AA}^3$ is applied for molecular orbitals visualization in VESTA throughout this chapter.

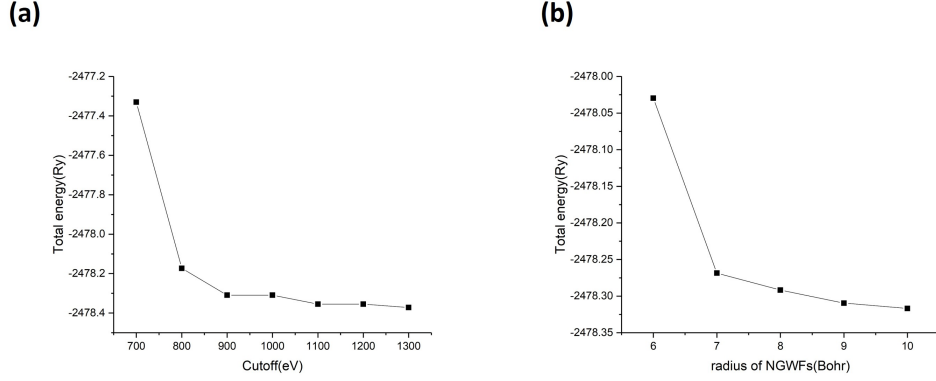


Figure 7.2: Convergence test of linear scaling DFT simulation.

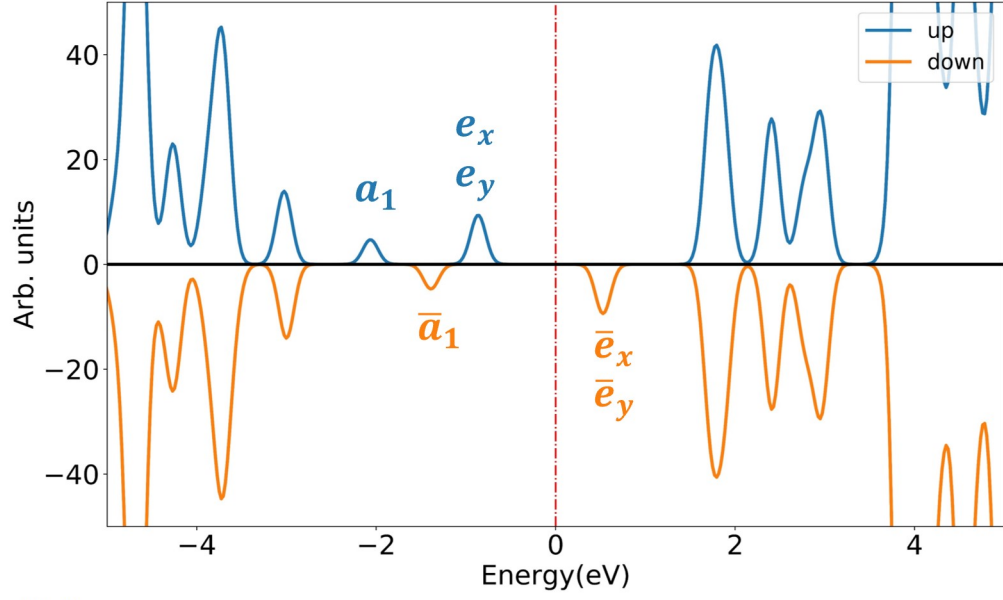
7.3 Results and discussion

7.3.1 Pure NV

The results of pure NV^- at 0K are present in Figure 7.3 where the density of states and corresponding identical transition orbitals are illustrated. It can be extracted from the DOS graph that the calculated NV^- agrees with the theoretical reference in terms of the electronic distribution. Specifically, in the spin-up region, the a_1 and two degenerated e_x , e_y orbitals are located below the Fermi level while in the spin-down state, only a_1 accommodates below the Fermi level. The featured transition on NV^- refers to an electron being pumped from a_1 orbital to e_x or e_y degenerated manifold in the spin-down area. This can be observed from Figure 7.3 graph (b) where the left one shows the localization of a orbitals and the right two graphs present the two target degenerated orbitals.

In terms of the results of pure NV^- at 300K. There is an energy split on the e_x , e_y orbitals which can be found on its corresponding DOS graph in Figure 7.4. Specifically, the energy splitting of the two degenerated orbitals is around 0.1 eV.

(a)



(b)

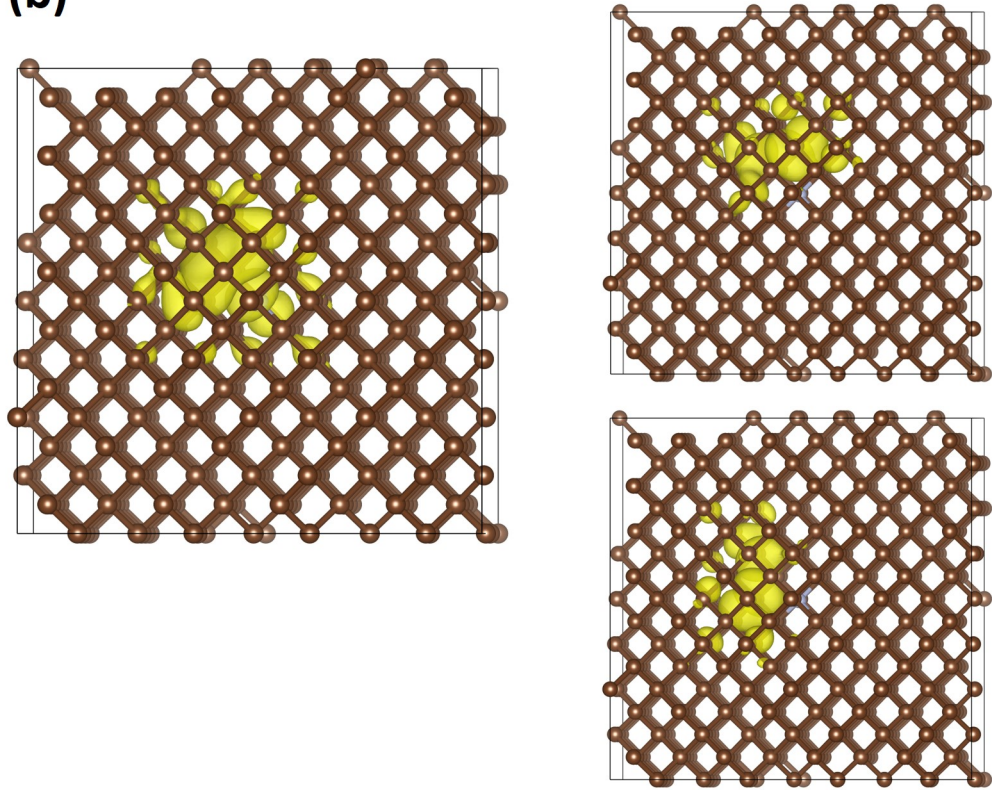


Figure 7.3: **(a)**: Density of state(DOS) on pure NV⁻ at 0K.**(b)**: Identical transition of NV⁻ from spin down a orbital to spin down degenerated e_x, e_y manifolds.

This implies that the thermal effect on lattice distortion at 300K would potentially split the excited states on e_x , e_y orbitals, thus affecting the absorption properties. However, the transition from a_1 orbital to e_x or e_y can still be detected on the TDDFT electron-hole profile which is shown in Figure 7.4 **(b)**. Similarly, graph **(b)** illustrates the transition from the a_1 orbital to the lower energy state of e_x or e_y in the spin-down configuration.

A further investigation on the comparison of absorption spectrum between NV^- at 0K and 300K is demonstrated in Figure 7.5 **(a)**. The absorption intensity as a function of photon energy E is represented by:

$$I(E) = \sum_i f_i \exp\left(-\frac{(E - E_i)^2}{2\sigma^2}\right)$$

where:

- $I(E)$: The absorption intensity at a given photon energy E .
- E : The photon energy, typically in electron volts (eV). It is converted to wavelength for comparing to the experimental data.
- f_i : The oscillator strength for the i -th electronic transition, which determines the intensity or probability of that transition.
- E_i : The excitation energy of the i -th electronic transition, representing the difference in energy between the ground and excited states.
- σ : The broadening parameter, which defines the width of each peak and accounts for factors such as thermal effects or instrumental resolution, resulting

in Gaussian broadening.

- $\exp\left(-\frac{(E-E_i)^2}{2\sigma^2}\right)$: The Gaussian function centered at E_i with a standard deviation of σ , used to approximate the shape of each absorption peak.

The absorption spectrum uses the excitation energies and oscillator strengths to determine the location and intensity of the absorption peaks, while the lifetime data is used to determine the broadening of the Gaussian fit.

In the absorption spectrum, the green dashed line presents the induced laser for photoluminescence experiments whose wavelength is 532 nm. It can be summarized from the graph that under a thermal environment at 300K, the splitting of degenerate states will result in the broadening of absorption peaks as well as a decrease in absorption strength. This would potentially increase the fluorescence efficiency due to the left shift of the absorption peak.

According to the Franck-Condon theory, if the potential energy surfaces of the ground and excited states are approximately harmonic, the absorption and emission spectra will be symmetric about the ZPL. In this case, the absorption spectrum can be transformed into the emission spectrum by applying a mirror symmetry to the zero-phonon line (ZPL) located at a wavelength of 637 nm. The ZPL is not presented in the spectrum since this calculation only involves vertical transition. The comparison between experimental data and simulation can be found in graph **(b)**. It can be observed from the graph that, the emission spectrum from pure NV^- at 300 K fits well with the experimental data. However, this influence is not strong enough to affect the PL signal since its emission can still be detected. The following part will

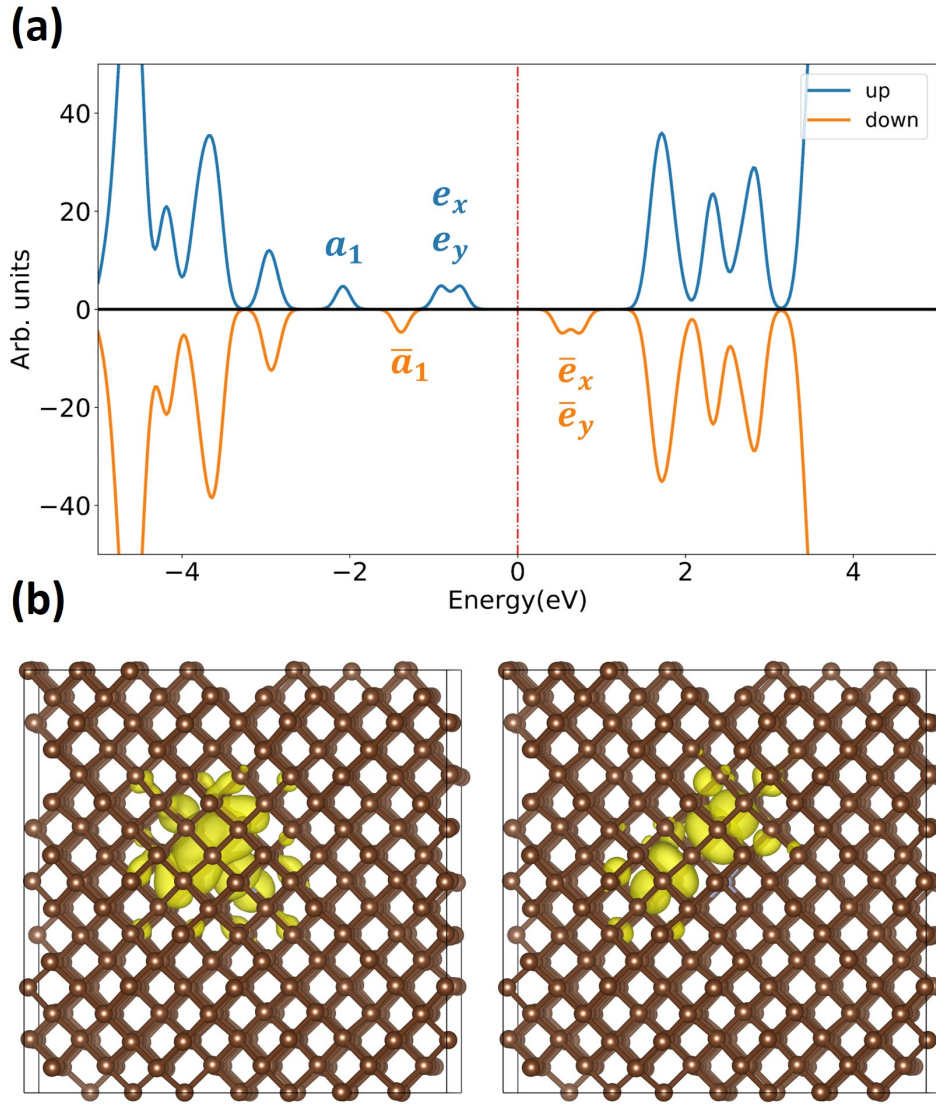


Figure 7.4: **(a)**: Density of state(DOS) on pure NV^- at 300K. **(b)**: Transition of NV^- from spin down a_1 orbital to spin down split e_x or e_y manifolds.

analyse the results of the absorption spectrum on random structures containing one NV^- and one C_i .

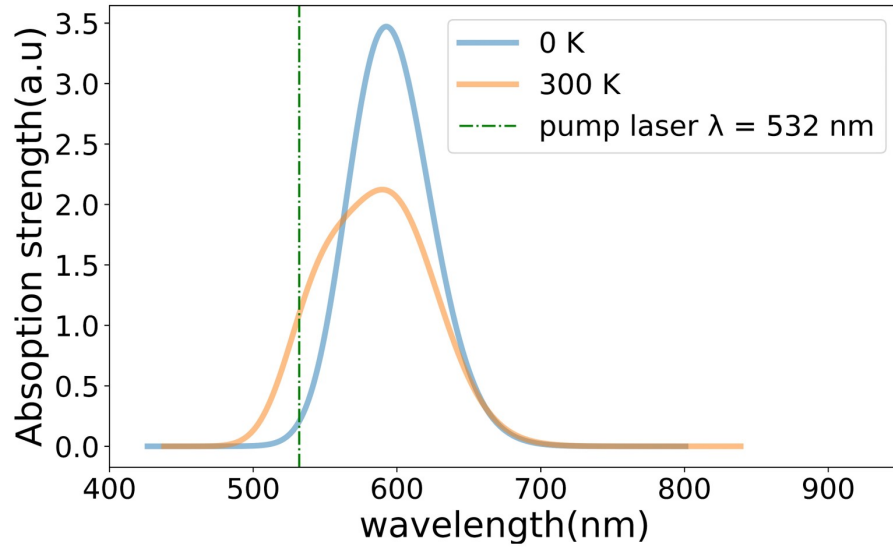
7.3.2 NV and interstitial carbon

This section will analyse the results of the change of excited state when an extra carbon atom is added to the pure NV^- system. To begin with, an overview of the absorption spectrum on all the simulated combinations is demonstrated in Figure 7.6. A further discussion will be held later, trying to decouple the reasons behind this spectrum and have a better understanding of it. According to the changes of their excitation, it can be mainly defined into three types, namely non-hybridization, weak-hybridization and others. This will be discussed in the following sections.

7.3.3 Non-hybridization

The first type can be called as non-hybridization. Similar to the classification in the previous chapter, non-hybridization means the orbitals of NV^- and interstitial carbon can be analyzed separately. An illustration of the absorption spectrum for all the non-hybridized situations can be found in Figure 7.7 where two main peaks can be addressed at around 1300 nm and 600 nm. To further investigate the transition behind these peaks, their corresponding hole states and electron states are present in Figure 7.8 (b) and (c). Meanwhile, a typical density of state from the non-hybridization situation is present in graph (a). Combining the DOS plot and hole-electron orbitals, the absorption peak located at around 1300 nm refers to the transition from NV^- 's

(a)



(b)

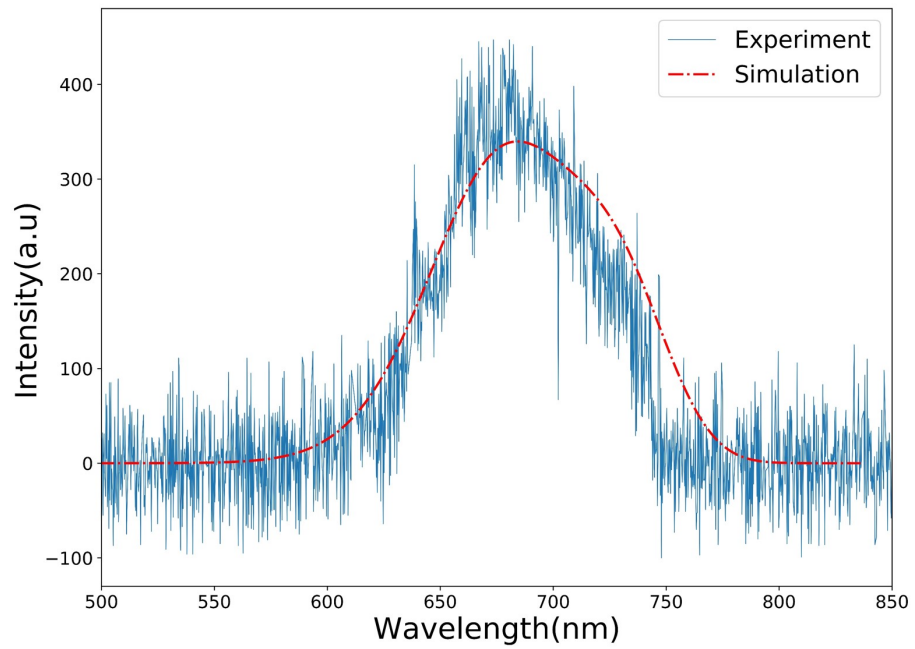


Figure 7.5: **(a)**: Absorption spectrum comparison between pure NV^- at 0K and 300K. **b**: Emission spectrum between pure NV^- at 300 K and experimental data.

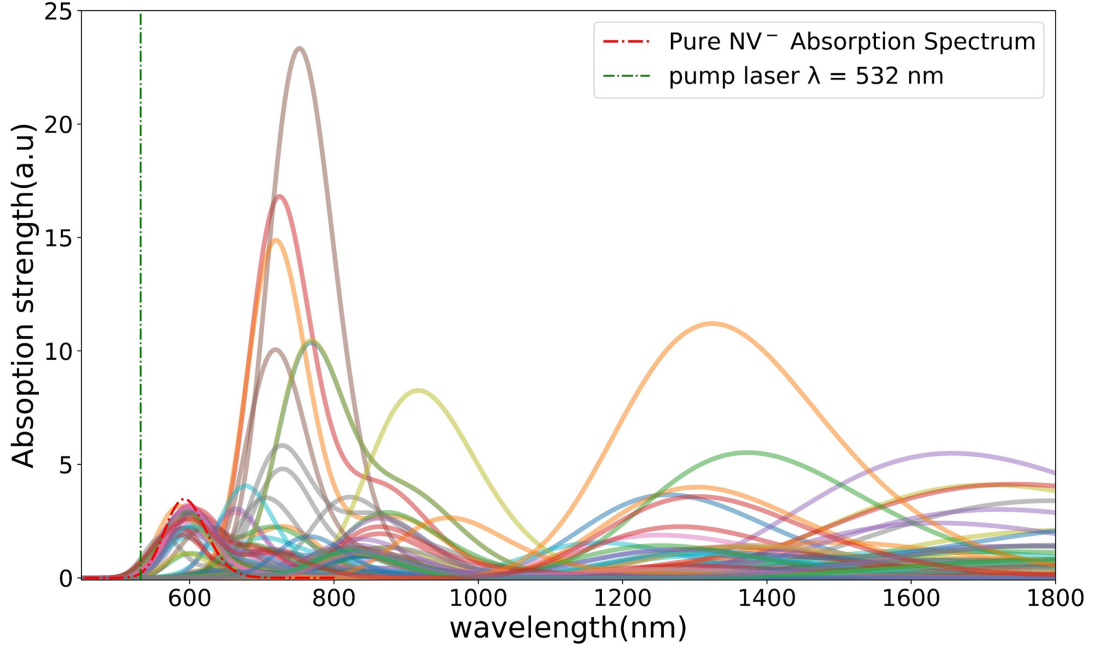


Figure 7.6: A graph of absorption spectrum on all the simulated situations containing one NV^- and one interstitial carbon

e_x, e_y manifolds to C_i 's π bond in the spin-up configuration while the peak at 600 nm can be interpreted as a featured transition from NV^- colour centre which is from a_1 orbital to degenerated e_x, e_y orbitals. Since the identical transition from NV^- colour centre remains and no obvious shift on its corresponding absorption peak, it can be concluded that in non-hybridization, the absorption procedure will not be affected significantly.

7.3.4 Weak-hybridization

From the previous part, we learn that some absorption spectra can be explained as the consequence of non-hybridization. In this part, another situation will be present, called weak-hybridization. In this situation, a hybridized state between NV^- centre and C_i transition is detected at the wavelength around 700 nm and the transition

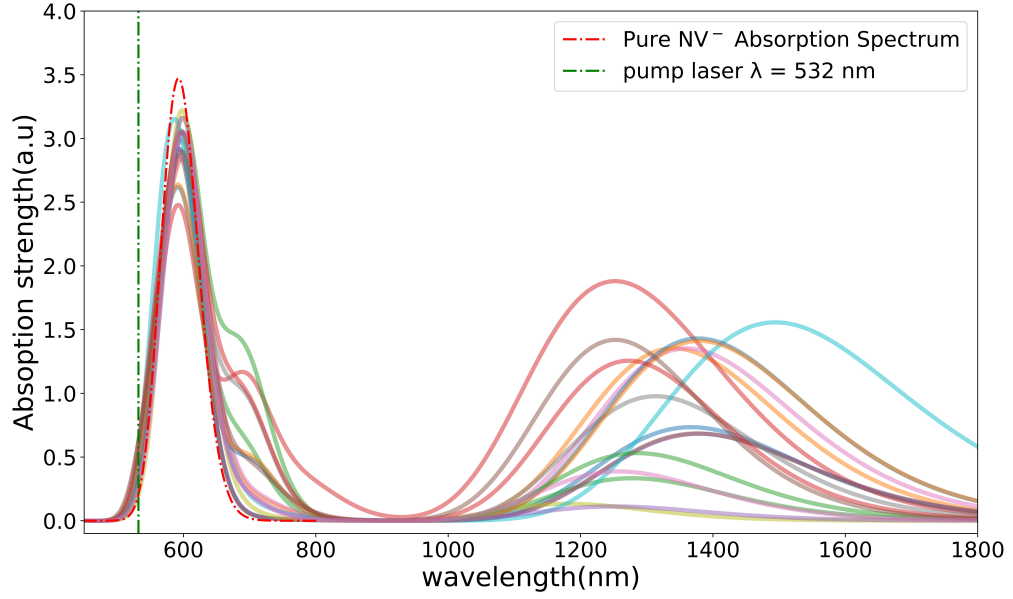


Figure 7.7: An illustration of absorption spectrum on all the non-hybridized situations.

from NV^- colour centre will be weaker as the increase of hybridized component between NV^- centre and C_i . This tendency can be observed from Figure 7.9 where the absorption peak from around 600 nm decreases gradually as the absorption strength at 700 nm becomes stronger. Details on the absorption peak interpretations can be found in Figure 7.10 where an example of weak-hybridization is present. In this graph, there are three main absorption peaks accommodated at the wavelength of around 600 nm, 700 nm and 1300 nm. Because the excited pump laser is at the wavelength of 532 nm, marked as a dashed line in green, the absorption peak localized at 1300 nm may not be transferred to the excited state. In terms of the transition at 600 nm, it can be interpreted as an internal transition within the NV^- centre, specifically from the a_1 orbital to the degenerate e_x and e_y orbitals. However, it is worth noting that the absorption strength of this transition is weakened compared to the

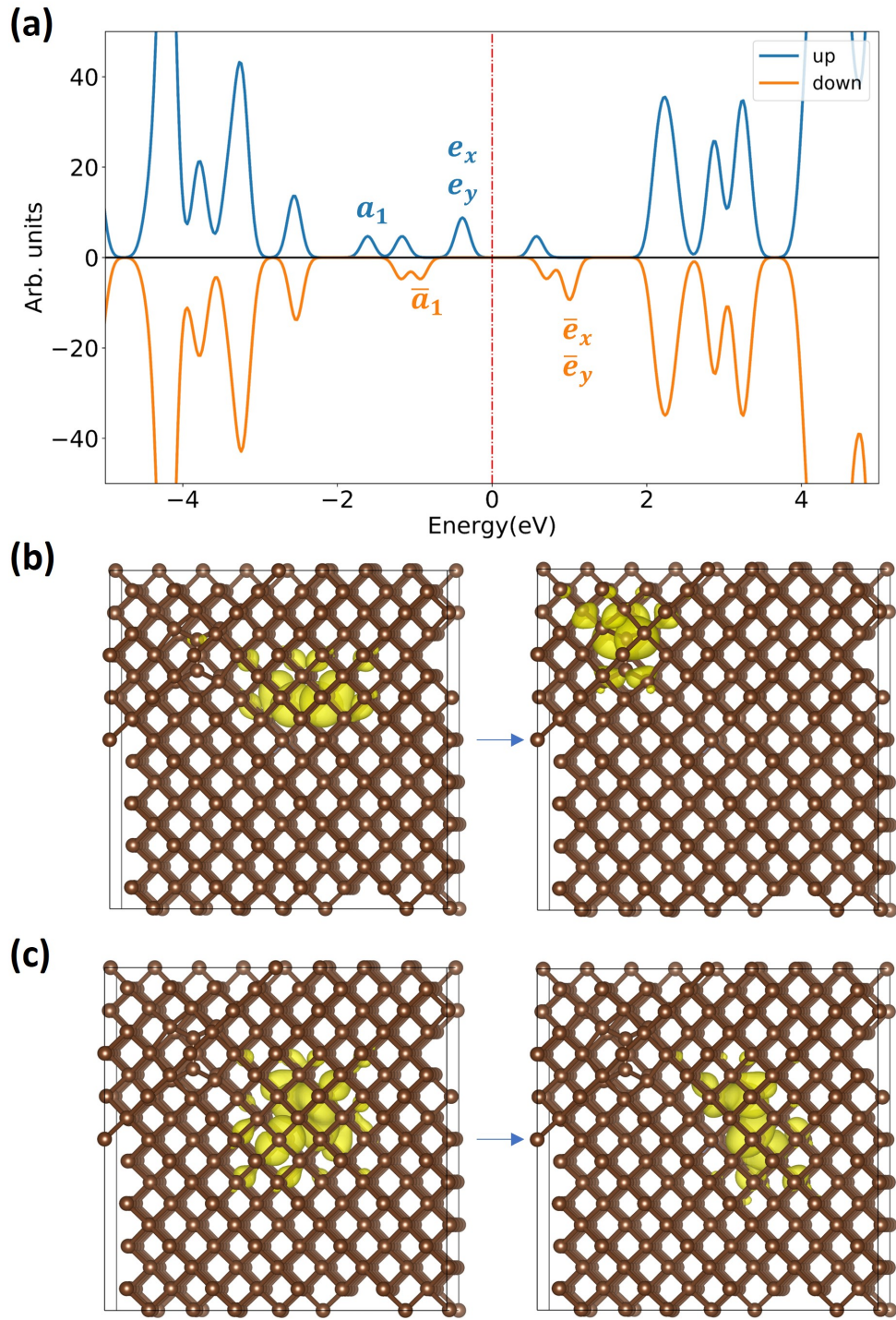


Figure 7.8: (a): Density of state(DOS) on non-hybridized situations.(b): Corresponding transition at around 1300 nm, referring to pump from degenerated e_x, e_y to orbitals from interstitial carbon.(c):Identical transition of NV^- from spin down a_1 orbital to spin down degenerated e_x, e_y manifolds.

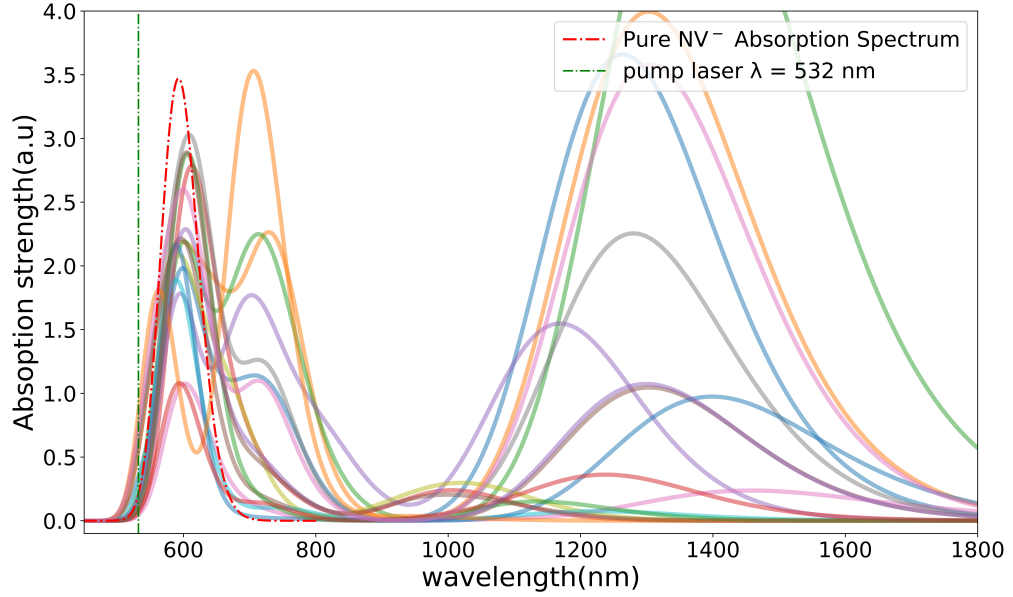


Figure 7.9: An illustration of absorption spectrum on all the weak-hybridized situations.

pristine NV^- absorption peak. An interesting part happens at the peak from 700 nm, where a transition initializes at a_1 from NV^- to a 'weak-hybridized' state whose electronic orbitals is a hybridization of e_x, e_y in NV^- and π bond in the C_i defect. This 'weak-hybridized' phenomenon would directly weaken the intensity transition at 600 nm, potentially responsible for the blinking signal detected in the fluorescence procedure. Furthermore, with the increase of hybridization, the transition at 700 nm will be stronger whereas the transition at approximately 600 nm will weaken and vanish eventually. This suggests that the absorption will experience a process of weakening to disappear with the strength of hybridization.

To better understand the progress of hybridization and its influence on the transition within NV^- colour centre, further absorption spectrum analysis is performed on three different levels of hybridization which are shown in Figure 7.11. As can be ex-

tracted from the graph, with the increase of absorption strength for the marked peak, identified as the signal of hybridization, the identical transition from NV^- drops down gradually. The corresponding electron-hole configuration for those marked absorption peaks is shown at the right where the volume of the isosurface around interstitial carbon highly determines the level of hybridization intensity. Another key piece of information that can be found from the graph is that for the bottom situation, all the orbitals from interstitial carbon are hybridized with NV^- centre, presenting no peaks around 1300 nm.

7.3.5 Others

The rest of the absorption spectrum is relatively complicated and its summary can be found in Figure 7.13. Although we are not able to have a systematic classification for decoupling these spectrums, it can be observed from the graph that all of these peaks are shifting further away from the wavelength of the pump laser at 532 nm. This indicates that there will be no excitation among all of these other situations which will be out of scope on the interest of this project. By digging into some of the results for the 'others' absorption, it could be potentially caused by strong hybridisation together with energy level shifting, charge relocation etc. One example of strong hybridisation together with energy levels shifting situations is shown in Figure 7.12 where the hole-state of the first absorption peak presents strong hybridization and significant right shift can be observed.

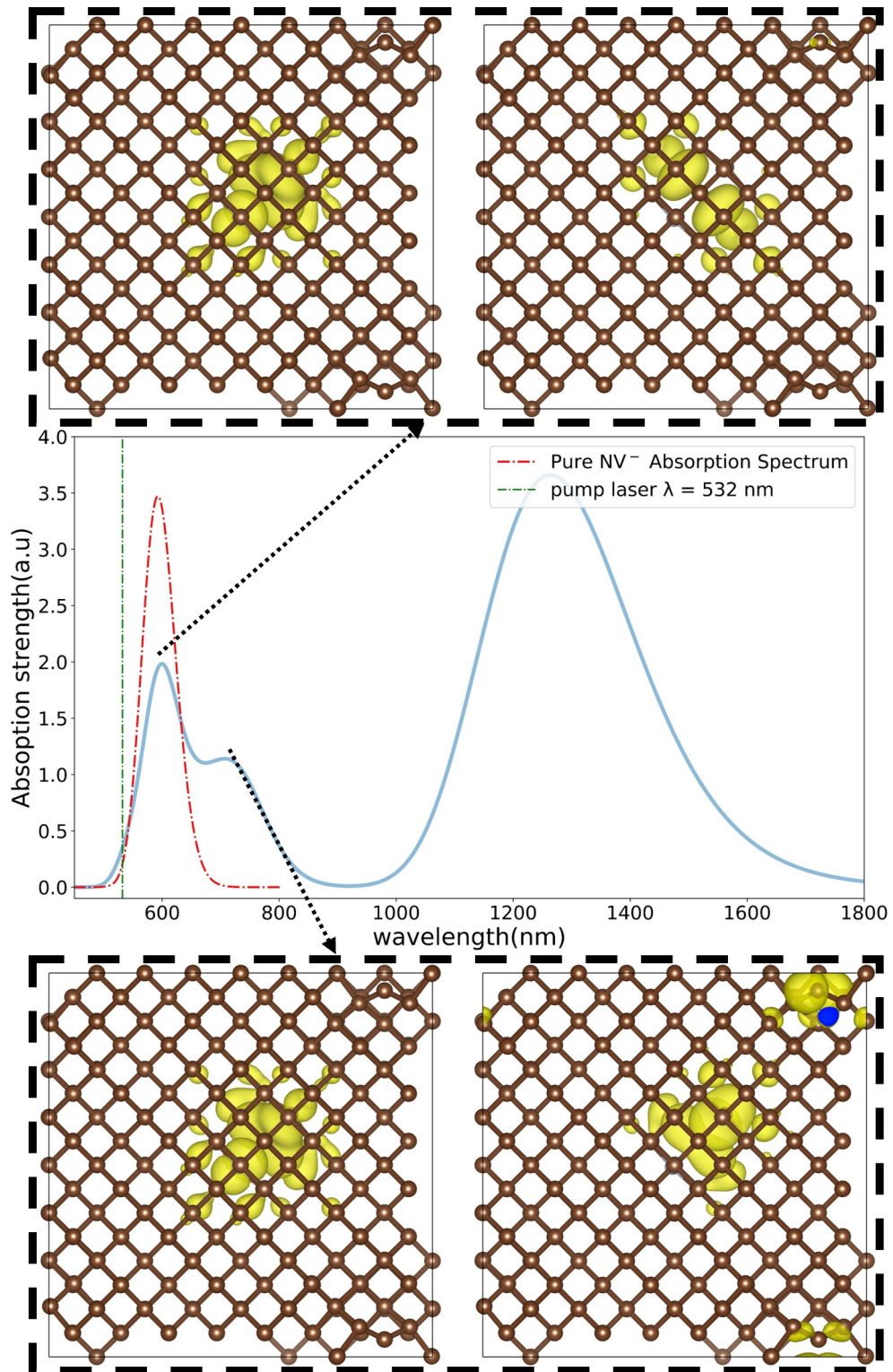


Figure 7.10: An example of weak-hybridized on both absorption spectrum and its corresponding transition manifolds

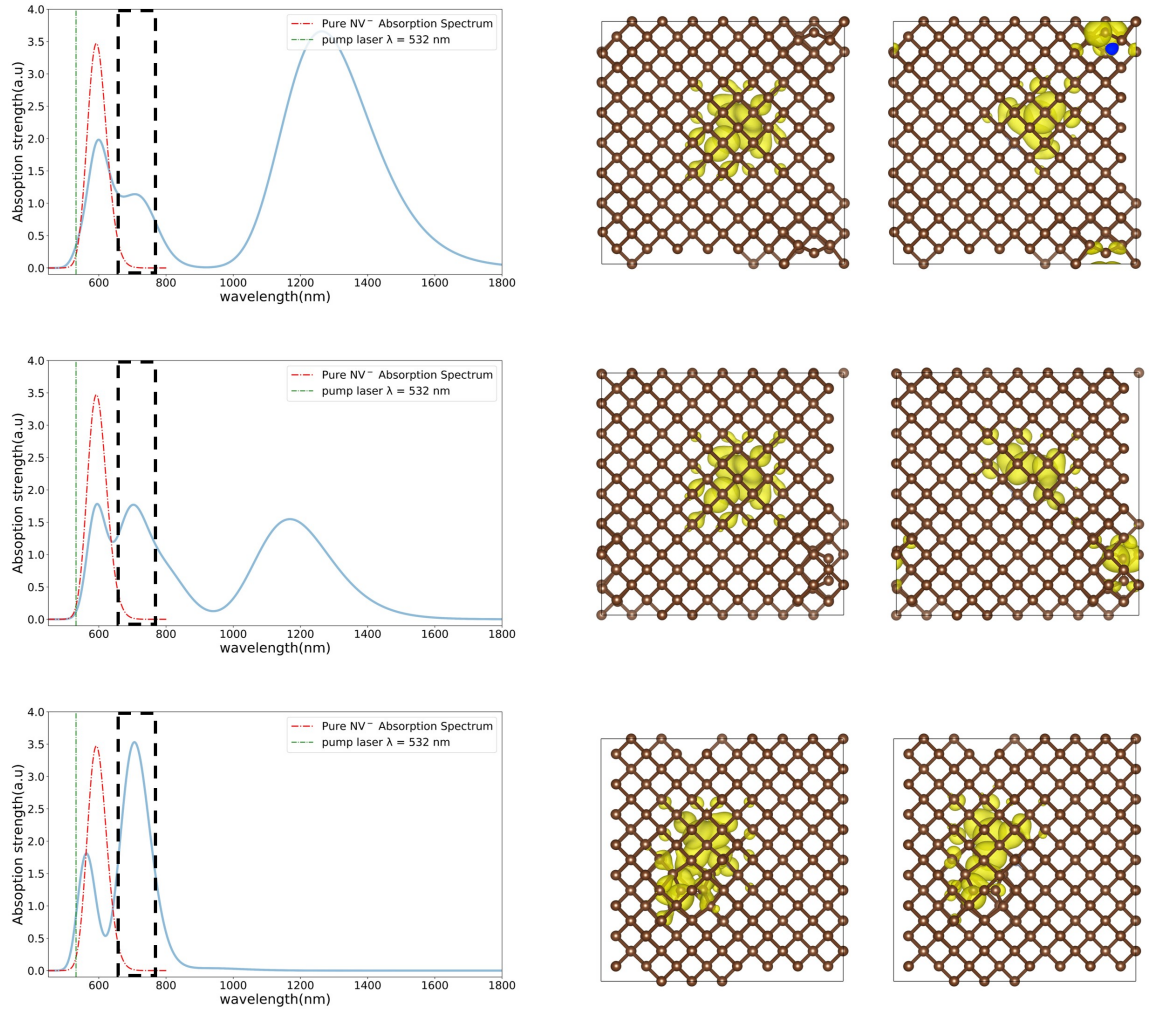


Figure 7.11: An illustration of progression in absorption spectrum in the weak-hybridized situation and its corresponding hole-electron states.

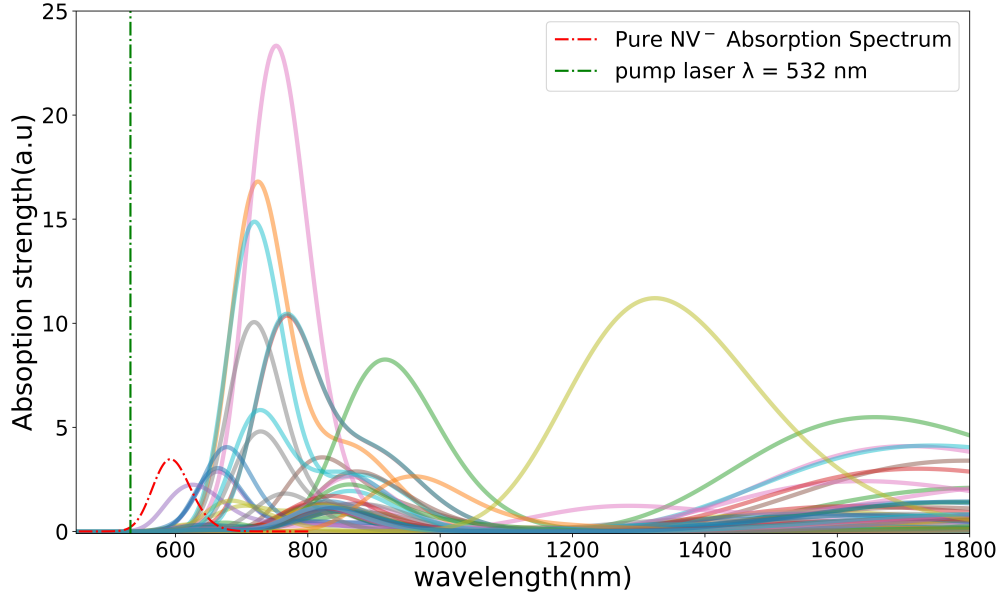


Figure 7.12: An illustration of absorption spectrum on all the other situations.

7.3.6 Spatial distribution

After investigating some individual situations on non-hybridization, hybridization and the rest of them, the overview of the absorption spectrum can be re-plotted by the classification, shown in 7.14 (a). In the graph, non-hybridization is marked in cyan, presenting 'bright' states in the absorption procedure while hybridization is coloured in blue, showing 'blinking' states. Finally, due to the right shift of all the 'others' situations, they are tagged in night blue, showing 'dark' states during the excitation procedure.

The graph (b) in Figure 7.14 demonstrates the spatial distribution of all the situations contained in this research. For better visualization, the carbons located at the pristine diamond lattice are eliminated by the Wigner-Seitz approach[115]. From the previous study[1], we learn that under the annealing procedure, the interstitial

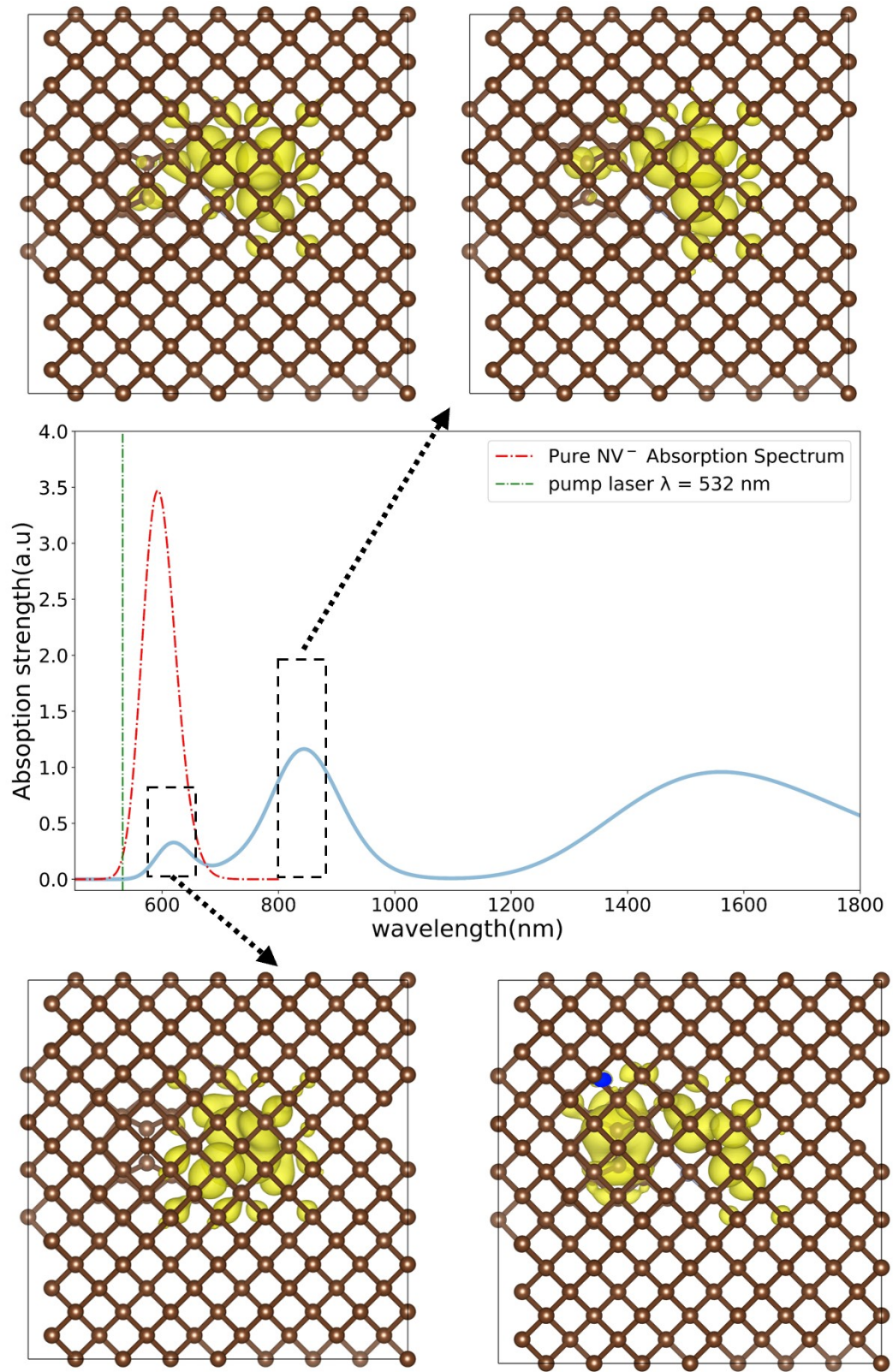


Figure 7.13: An illustration of absorption spectrum on an example of strong-hybridization and its corresponding electron-hole configuration.

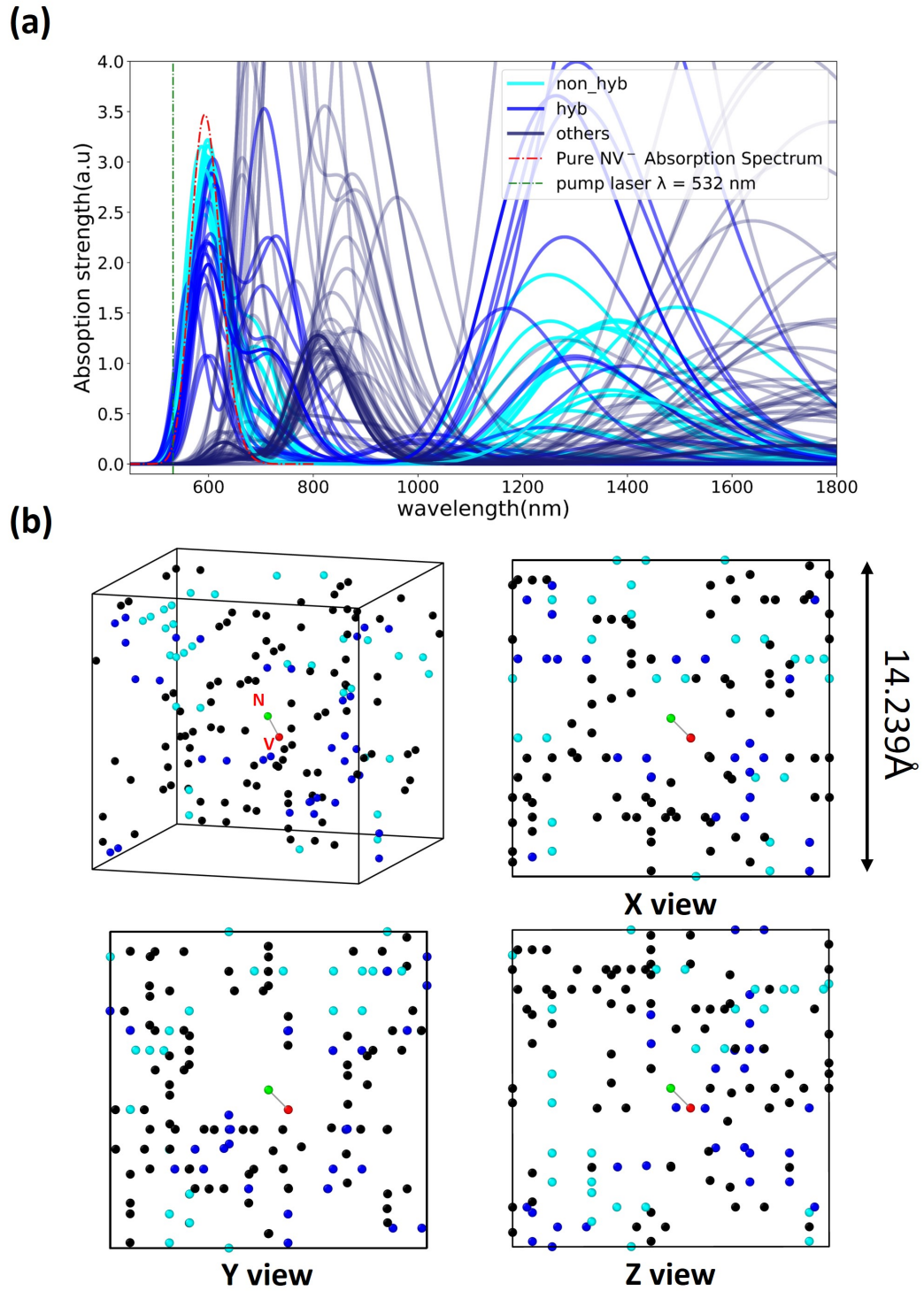


Figure 7.14: (a): Classification on absorption spectrum in terms of non-hybridization, weak-hybridization and other situations. (b): Spatial distribution on all the classified situations

carbon is mobile with a possibility to diffuse around the formed NV^- centre. This implies that interstitial carbon can migrate all of these positions, hopping between the states of 'bright', 'blink' and 'dark'.

Among all the simulated situations, around 20% of them are shown as 'bright', 20% of them are marked as 'blink' and the rest of them are present in the 'dark' state. The outcomes associated with these states are significantly influenced by atomic configurations, the spatial proximity of defects and charge states.

7.4 Conclusion

In this chapter, linear-scaling TDDFT simulations are performed to investigate the absorption properties of two main situations. The first study aims to explore the absorption difference between NV^- at 0K and 300K. The findings indicate that thermal effects induce energy splitting in the degenerate orbitals e_x and e_y , leading to distortion in the absorption spectrum. This distortion is further verified by comparing it to the experimental emission spectrum. The second task focuses on the variety of absorption features on different ensembles of NV^- and C_i . The outcomes can be classified as non-hybridization, hybridization and others. In the situation of non-hybridization, the electronic structure of two defects can be separately treated while the transition within NV^- remains. This would result in 'bright' states where a stable fluorescence signal might occur. In hybridization situations, the strength of absorption highly depends on the hybridized intensity. The increase in hybridized intensity would finally vanish the absorption procedure. In the 'others' situation, all of their absorption spectrum shifts away from the pump laser, which implies that no excitation would happen, known as 'dark' states. Finally, a spatial distribution of all the simulated configurations is illustrated, showing the possible sites for interstitial carbon to migrate under the annealing procedure. However, the correlation between absorption properties and their corresponding spatial locations remains to be discovered.

Chapter 8

Summary and outlook

8.1 Summary

This thesis conducts a simulation study on the interaction between defects in nitrogen-doped diamond. In chapter 4, an *ab initio* simulation on the electronic interaction between a neutral vacancy and a neutral split- $\langle 100 \rangle$ interstitial carbon is performed to investigate the influence of GR1 signal with the presence of interstitial carbon. Among all of the combinations of neutral vacancy and split- $\langle 100 \rangle$ interstitial carbon, there are mainly three types of situations, non-hybridization, hybridization and recombination. In the situation of non-hybridization, there is no significant influence on the electronic structure of neutral vacancy and therefore, the GR1 signal might be unchanged. While the recombination corresponds to the combination of interstitial carbon to the position of vacancy, the hybridization refers to the orbital hybridization between a neutral vacancy and a neutral split- $\langle 100 \rangle$ interstitial carbon, where their electronic structure would be affected significantly, causing a quench of GR1. On further spatial

analysis with a separation less than 5 Å, the vanish of the GR1 signal would be highly dependent on the relative positions between these two defects.

Chapter 5 illustrates the interaction between a NV^- and a split- $\langle 100 \rangle$ self-interstitial carbon(C_i) at the aspect of strain effects and electronic structure. In the strain effect research, the strain produced by split- $\langle 100 \rangle$ self-interstitial carbon(C_i) with a separation from 4.5 to 6 Å will cause an energy-splitting around 75 to 280 meV of the two degenerated orbitals ex , ey in NV^- colour centre. This might not be the consequence of the blinking signal in the photoluminescence monitor. In the electronic interaction study, the hybridization between degenerated orbitals ex , ey in NV^- colour centre and π bond from C_i might be responsible for the blinking signal. The hybridized electronic bandstructure implies that electrons could relax back to the ground state by radiative transition or non-radiative pathway, causing the presence of blink or quench in the photoluminescence signal. This hybridized phenomenon would happen when an interstitial carbon is located at the vacancy site of a NV^- colour centre in diamond. Due to the restriction of computational resources, *ab initio* molecular dynamics(AIMD) is not able to investigate the diffusion mechanism upon defects in adequate duration time and scales where an alternative will be applied, demonstrated in the next Chapter.

Chapter 6 describes the procedure for training a carbon-nitrogen(CN-GAP) potential and its application in a continuous investigation of the diffusion behaviour of interstitial carbon with a nearby NV^- colour centre. The database samples are constructed by **1**): crystalline structure from GAP-20 and **2**): nitrogen-doped structures along with their respective defect configurations. The constructed database

is then applied in a self-iteration algorithm with accuracy regarding force and energy. Further validation is performed on the diffusion barriers on interstitial carbon, vacancy and NV swapping energy. Meanwhile, the formation energy on nitrogen-vacancy(NV), vacancy(V), interstitial carbon(C_i), substitutional nitrogen(N_s) and interstitial nitrogen(N_i) are taken into comparison with results of DFT and relative reference publications. After a series of validation tests, the formed CN-GAP potential is then applied to molecular dynamics simulation to estimate the diffusion behaviour on an interstitial carbon around an NV centre. The results indicate that the interstitial carbon will recombine to vacancy or diffuse away. Also, the maximum distance for an interstitial carbon to recombine within 3000 fs under 2600 K is around 6 Å.

Chapter 7 illustrates that the blinking and quenching of photoluminescence might be derived from the changes in the absorption spectrum. Two main situations are employed in linear-scaling TDDFT simulation. The first one refers to investigating the difference in the absorption spectrum between pure NV^- in 0 K and 300 K(room temperature) where the 300 K results agree with the experimental spectrum. The second situations refer to a random generation of an ensemble containing one NV^- and one C_i in diamond. Among all the simulated situations, it can be mainly classified as 'bright', 'blink' and 'dark' states. While 'bright' refers to non-hybridization between NV^- and C_i with slight changes in absorption procedure, 'blink' and 'dark' states are more complicated and can be interpreted as the results of hybridization of different orbitals, charge delocalization or atomic configuration distortion.

8.2 Future prospects

To accurately simulate the interactions between defects in diamond and compare them to experimental data, two main factors are of significant. One might have to simulate accurately enough which might potentially increase the computational cost while the other is to approach experimental environments as closely as possible.

For the first standpoint, perhaps accuracy could be increased by applying more expensive hybrid exchange-correlational functionals like HSE06. This would reveal more information on the electronic structure quantitatively whereas this thesis analyzes them qualitatively. Another aspect of the undiscovered field of this project is the minimum distance to eliminate hybridization. A larger supercell should be applied in the simulation to investigate this question. Unfortunately, the problems mentioned above could not be solved due to the limitation of computational resources in our group.

In terms of the imitation of experimental conditions, simulations should take more factors into account. For example, the currently generated CN-GAP machine-learning potential can only be applied in the thermal annealing process whereas in reality, the annealing procedure is induced by laser. The investigation of laser-induced molecular dynamics is a yet-to-developed research topic because it is a non-equilibrium dynamics problem and the coupling between electrons and phonons requires careful treatment. To the best of my knowledge, the machine-learning potential for excited states molecular dynamics remains a challenge at the moment.

Finally, I believe that what I have accomplished thus far is merely scratching the surface, and what lies ahead is simple: keep exploring.

Supplemental Information

Spin polarized cases study

Given the need to balance computational cost and accuracy, the DFT simulations in Chapters 4 and 5 are based on non-spin-polarized calculations. This setting could potentially alter the ground state of the electronic configuration. For example, when simulating the electronic properties of pure NV^- in diamond, the non-spin-polarized DFT simulation would converge to the ^1E state rather than the $^3\text{A}_2$ state. Due to the scope of this research, Chapters 4 and 5 aim to provide a comprehensive qualitative understanding of the influence of a nearby interstitial carbon on pure vacancy or pure NV centres. This thesis suggests that in non-spin-polarised cases, the electronic structure of defect sites (NV^- or V_0) may be affected by the presence of a nearby interstitial carbon due to hybridisation between the orbitals of V_0 and C_i , or NV^- and C_i .

The supplement provides an example of a spin-polarised DFT calculation for a structure containing one NV and one C_i . The structure was tested as hybridised in the non-spin-polarised simulation, and hybridised orbitals were displayed according

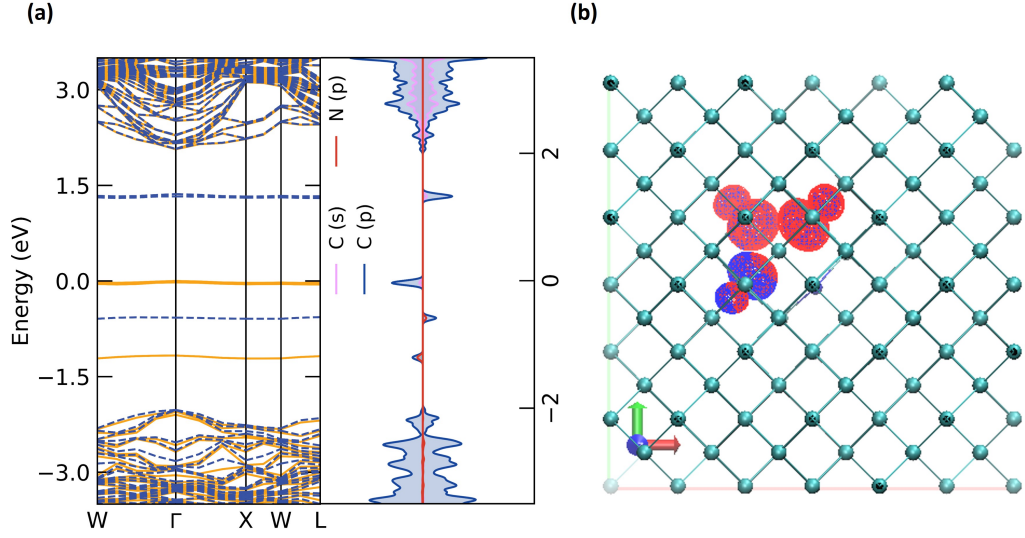


Figure 1: Spin-polarized DFT simulation on pure NV^- in diamond while (a) is its bandstructure plot together with DOS plot and (b) is its corresponding molecular orbitals on e_x and e_y . For the electronic orbitals, an isovalue of 0.02 in VMD (Visual Molecular Dynamics) is chosen.

to its molecular orbital manifold. The computational settings are the same as those used in Chapters 4 and 5, except that spin polarisation is enabled here.

In Figure 1, a spin-polarised ground-state DFT calculation is performed on a pure NV^- in a $3 \times 3 \times 6$ supercell. According to the band structure and density of states plot, in the spin-up channel, the a_2 , e_x , and e_y orbitals are fully occupied, while in the spin-down channel, only the $\bar{a}_2$ orbital is occupied. This configuration corresponds to the ground-state $^3\text{A}_2$ state of NV^- .

In Figure 2, the same hybridised case containing one NV^- and one C_i discussed in Chapter 5 is computed using spin-polarised ground-state DFT implementations. It can be concluded from the figure that, in the presence of C_i , both e_x and e_y orbitals in the two spin channels likely experience energy splitting. Meanwhile, the states around the Fermi level demonstrate strong hybridisation between NV^- and C_i , which

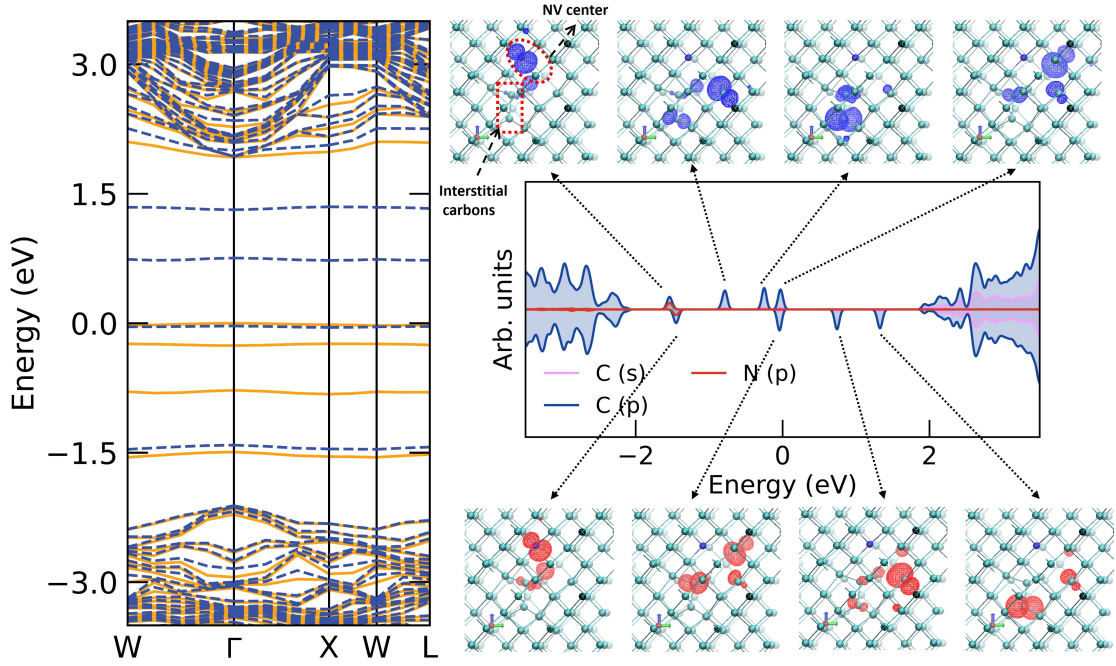


Figure 2: An example of spin-polarized DFT calculation in where bandstructure, DOS and its corresponding molecular orbitals are illustrated.

can be observed in the projected orbital graphic.

The remaining hybridised configurations mentioned in Chapter 5 are all recalculated using spin-polarised DFT simulations. The results indicate that hybridised orbitals are present in all simulated cases. This suggests that the presence of C_i may potentially cause orbital hybridisation in either the 1E or 3A_2 state of the NV^- colour centre. Additionally, a comparison of the final energies between spin and non-spin calculations is presented in Figure 3, showing a similar fluctuation trend with differences ranging from 0.2 to 0.4 eV.

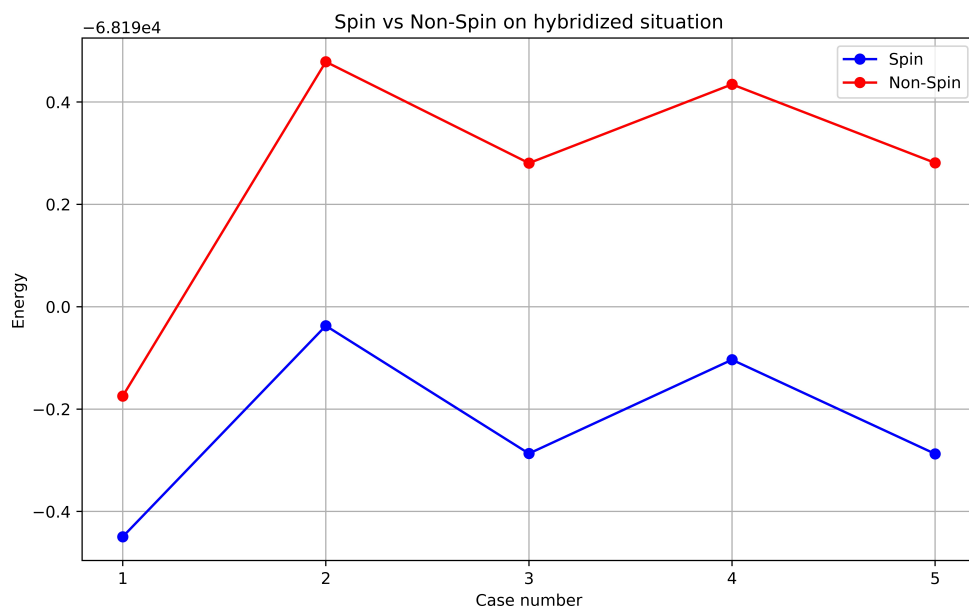


Figure 3: A comparison of spin and non-spin DFT calculations for final energies across various hybridization conditions.

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