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Solid-State Qubits for Second-Generation Quantum Technologies: A Comprehensive Theoretical Investigation

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Abstract

Recent advancements in quantum technologies have generated significant interest in the development of various quantum applications, including quantum emitters, quantum memories, and quantum sensors for applications in quantum communication, quantum metrology, and quantum computing. Such quantum applications can in principle be built based on several physical systems, one of which is solid-state materials; for example, hexagonal boron nitride (hBN) color centers, quantum dots, nitrogen-vacancy centers in a diamond, and transition metal dichalcogenides. Among these materials, hBN is the most promising in terms of room-temperature operation, flexible integration with other components, high coupling efficiency, and wide coverage of emission wavelengths. However, hBN has only recently been discovered for quantum technologies, so its development lags behind that of other systems. This dissertation, therefore, aims to characterize photophysical and optical properties as well as spin-qubit properties of a large number of color centers. The potential of hBN solid-state qubits across quantum technology applications is also evaluated.

Firstly, the dissertation characterizes hBN color centers for quantum emitter applications by analyzing the emission wavelength distribution from various defects from periodic groups III to IV. The emission wavelengths span from ultraviolet to near-infrared, though no direct correlation with periodic groups is observed. To address slight shifts from target wavelengths, strain engineering is proposed. Then, the simulation is compared with an experiment of a yellow quantum emitter fabricated through electron beam irradiation. A detailed theoretical simulation identifies the most promising defect candidate and explains the temporal polarization dynamics, highlighting the importance of multiple photophysical properties for accurate defect identification. The study concludes that the $C_B C_N C_B C_N$ defect emerges as the most promising candidate. This defect consists of four carbons substituting at two boron and two nitrogen sites. Additionally, two novel defects are proposed for quantum emitters based on these findings.

Secondly, the dissertation explores hBN color centers for quantum memory applications. Initial investigations into Raman quantum memory reveal that hBN defects support the desired electronic transitions and require a quality factor reachable by an experiment to achieve a writing efficiency of 95%. The study also demonstrates the compatibility of hBN defects for Raman-based quantum memory with other quantum technologies, emphasizing its low noise from wavelength conversion. However, the storage time in this Raman model is constrained by the electron spin coherence time, which is typically shorter than that of nuclear spin. In light of that, the study also focuses on nuclear spin-based quantum memory. The $h^{10}B^{15}N$ isotope is identified as the optimal

one due to its longest coherence time and its similarity in mechanism to ^{13}C in NV center-based quantum memory systems in diamond. The spin relaxation time is also modeled to assess the impact of potential decoherence mechanisms.

Thirdly, the dissertation investigates hBN color centers for quantum sensing applications. Given the unique properties observed in this application, such as optically detected magnetic resonance (ODMR) and electron paramagnetic resonance (EPR), both spectra are leveraged to identify hBN defects. Selected point defects are characterized via their EPR spectra. In addition, ODMR properties are employed to illustrate linewidth broadening across different hBN isotopes, allowing for a comparative analysis of the contributions to decoherence.

Finally, the findings of this research are compiled into an online database (<https://h-bn.info>), which features an interactive search engine for all photophysical properties and provides graphical lattice structure files for future studies. Crucially, the electronic transitions of all collected defects are mapped to quantum emitter, quantum memory, and quantum sensing applications. Consequently, this dissertation not only establishes solid-state qubits in hBN color centers as a promising quantum system with the potential to serve as a foundational element for various quantum technologies, but it also develops a comprehensive methodology applicable across a wide range of quantum technologies. This methodology, which includes the detailed characterization and modeling of solid-state quantum systems, can be adapted to investigate and optimize other solid-state quantum systems, thereby contributing broadly to the advancement of quantum science and technology.

Zusammenfassung

Durch die jüngsten Fortschritte in der Quantentechnologie gibt es ein großes Interesse an deren Anwendung in der Quantenkommunikation, Quantenmetrologie, und dem Quantencomputing. Dazu zählt die Entwicklung von Quantenanwendungen wie Quantenemitter, Quantenspeicher und Quantensensoren. Diese können durch verschiedene physikalische Systeme umgesetzt werden. Eine mögliche Umsetzung besteht in der Nutzung von Festkörpermaterien, wie zum Beispiel hexagonales Bornitrid (hBN) Farbzentren, Quantenpunkte, Stickstoff-Fehlstellen in einem Diamanten und Übergangsmetall-Dichalcogenide. Unter diesen Materialien ist hBN das vielversprechendste in Bezug auf die Benutzung bei Raumtemperatur, die flexible Integration mit anderen Komponenten, die hohe Kopplungseffizienz und die breite Abdeckung von Emissionswellenlängen. Allerdings ist hBN noch nicht lange Gegenstand der Aufmerksamkeit in der Quantentechnologie, so dass seine Entwicklung hinter der anderer Systeme zurückbleibt. Ziel dieser Dissertation ist es daher, die photophysikalischen und optischen Eigenschaften sowie die Spin-Qubit-Eigenschaften einer großen Anzahl von Farbzentren in hBN zu charakterisieren. Das Potenzial von hBN-Festkörper-Qubits für Anwendungen in der Quantentechnologie wird ebenfalls bewertet.

Zuerst widmet sich diese Dissertation der Charakterisierung von hBN-Farbzentren für Quantenemitter-Anwendungen, indem die Verteilung der Emissionswellenlängen verschiedener Defekte der Periodengruppen III bis IV analysiert wird. Die Emissionswellenlängen reichen von Ultraviolett bis zum nahen Infrarot, wobei keine direkte Korrelation mit den periodischen Gruppen beobachtet wird. Um leichte Verschiebungen von den Zielwellenlängen auszugleichen, wird ein Dehnungsversuch vorgeschlagen. Anschließend wird die Simulation mit einem Experiment verglichen, bei dem ein gelber Quantenstrahler durch Elektronenbestrahlung hergestellt wurde. Eine detaillierte theoretische Simulation identifiziert den vielversprechendsten Defektkandidaten und erklärt die zeitliche Polarisationsdynamik, wobei die Bedeutung mehrerer photophysikalischer Eigenschaften für eine genaue Defektidentifizierung beleuchtet wird. Die Studie kommt zu dem Schluss, dass sich der $C_B C_N C_B C_N$ -Defekt als der vielversprechendste Kandidat herausstellt. Dieser Defekt besteht aus vier Kohlenstoffen, die an zwei Bor- und zwei Stickstoffstellen substituiert sind. Außerdem werden auf der Grundlage dieser Erkenntnisse zwei neue Defekte für Quantenemitter vorgeschlagen.

Zweitens erforscht diese Dissertation hBN-Farbzentren für Quantenspeicheranwendungen. Erste Untersuchungen zum Raman-Quantenspeicher zeigen, dass hBN-Defekte die gewünschten elektronischen Übergänge unterstützen und einen experimentell umsetzbaren Qualitätsfaktor ergeben, welcher eine Schreibeffizienz von 95% ermöglicht. Die

Studie zeigt auch die Kompatibilität von hBN-Defekten für Raman-basierte Quantenspeicher mit anderen Quantentechnologien, wobei das geringe Rauschen der Wellenlängenkonversion hervorgehoben wird. Allerdings wird die Speicherzeit in diesem Raman-Modell durch die Kohärenzzeit des Elektronenspins begrenzt, die in der Regel kürzer ist als die des Kernspins. Unter diesem Hintergrund konzentriert sich die Studie auch auf Quantenspeicher auf der Basis von Kernspins. Das Isotop $h^{10}B^{15}N$ wird aufgrund seiner längsten Kohärenzzeit und seiner Ähnlichkeit mit dem Mechanismus von ^{13}C in NV-Zentrum-basierten Quantenspeichersystemen in Diamant als das optimale Isotop identifiziert. Außerdem wird die Spin-Relaxationszeit modelliert, um die Auswirkungen möglicher Dekohärenzmechanismen zu bewerten.

Drittens werden in dieser Dissertation hBN-Farbzentren für Quantensensoranwendungen untersucht. Angesichts der einzigartigen Eigenschaften, die bei dieser Anwendung beobachtet werden, wie die optisch detektierte magnetische Resonanz (ODMR) und die paramagnetische Elektronenresonanz (EPR), werden beide Spektren zur Identifizierung von hBN-Defekten genutzt. Ausgewählte Punktdefekte werden über ihre EPR-Spektren charakterisiert. Darüber hinaus werden die ODMR-Eigenschaften genutzt, um die Linienverbreiterung bei verschiedenen hBN-Isotopen zu veranschaulichen, was eine vergleichende Analyse der Beiträge zur Dekohärenz ermöglicht.

Schließlich werden die Ergebnisse dieser Forschung in einer Online-Datenbank (<https://h-bn.info>) zusammengestellt, die eine interaktive Suchmaschine für alle photophysikalischen Eigenschaften enthält und grafische Gitterstrukturdateien für zukünftige Studien bereitstellt. Dabei ist entscheidend, dass die elektronischen Übergänge aller gesammelten Defekte auf die jeweilige Anwendung als Quantenemitter, Quantenspeicher und Quantensensor bezogen sind. Folglich etabliert diese Dissertation nicht nur Festkörper-Qubits in hBN-Farbzentren als vielversprechendes Quantensystem mit dem Potenzial, als grundlegendes Element für verschiedene Quantentechnologien zu dienen, sondern sie entwickelt auch eine umfassende Methodik, die für ein breites Spektrum von Quantentechnologien anwendbar ist. Diese Methodik, die die detaillierte Charakterisierung und Modellierung von Festkörper-Quantensystemen umfasst, kann zur Untersuchung und Optimierung anderer Festkörper-Quantensysteme angepasst werden und so einen umfassenden Beitrag zum Fortschritt der Quantenwissenschaft und -technologie leisten.

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List of Abbreviations

CCE	cluster correlation expansion
DFT	density functional theory
DW	Debye Waller
EPR	electron paramagnetic resonance
ESLAC	excited-state level anti crossing
GSLAC	ground-state level anti crossing
hBN	hexagonal boron nitride
HR	Huang Rhys
ISC	intersystem crossing
MW	microwave
NV	nitrogen vacancy
ODMR	optically detected magnetic resonance
PAW	projector augmented wave
PL	photoluminescence
PSB	phonon side band
QD	quantum dot
QE	quantum efficiency
RF	radio frequency
SiC	silicon carbide
SPE	single photon emitter
SPS	single photon source
T_1	spin relaxation time
T_2	spin coherence time
T_ϕ	pure dephasing time
T_2^*	inhomogeneous dephasing
TDM	transition dipole moment
TDS	two-decoy states
TMDs	transition metal dichalcogenides
VASP	Vienna Ab initio Simulation Package
WCS	weak coherent source
ZFS	zero-field splitting
ZPL	zero phonon line

List of Publications

Peer-review articles included in this dissertation

1. **Chanaprom Cholsuk**, Ashkan Zand, Aslı Çakan, and Tobias Vogl. *The hBN Defects Database, A Theoretical Compilation of Color Centers in Hexagonal Boron Nitride*. The Journal of Physical Chemistry C **2024**, 128 (30), 12716–25.
2. **Chanaprom Cholsuk**, Aslı Çakan, Sujin Suwanna, and Tobias Vogl. *Identifying Electronic Transitions of Defects in Hexagonal Boron Nitride for Quantum Memories*. Advanced Optical Materials, **2024**, 12, 2302760.
3. **Chanaprom Cholsuk**, Sujin Suwanna, and Tobias Vogl. *Comprehensive Scheme for Identifying Defects in Solid-State Quantum Systems*. The Journal of Physical Chemistry Letters, **2023**, 14 (29), 6564–6571.
4. **Chanaprom Cholsuk**, Sujin Suwanna, and Tobias Vogl. *Tailoring the Emission Wavelength of Color Centers in Hexagonal Boron Nitride for Quantum Applications*. Nanomaterials, **2022**, 12, 2427.
5. Takla Nateeboon, **Chanaprom Cholsuk**, Tobias Vogl, and Sujin Suwanna. *Modeling the Performance and Bandwidth of Single-Atom Adiabatic Quantum Memories*. APL Quantum, **2024**, 1 (2), 026107.
6. Anand Kumar, Çağlar Samaner, **Chanaprom Cholsuk**, Tjorben Matthes, Serkan Paçal, Yağız Oyun, Ashkan Zand, et al. *Polarization Dynamics of Solid-State Quantum Emitters*. ACS Nano, **2024**, 18 (7), 5270–5281.
7. Anand Kumar, **Chanaprom Cholsuk**, Ashkan Zand, Mohammad N. Mishuk, Tjorben Matthes, Falk Eilenberger, Sujin Suwanna, and Tobias Vogl. *Localized Creation of Yellow Single Photon Emitting Carbon Complexes in Hexagonal Boron Nitride*. APL Materials, **2023**, 11 (7), 071108.

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8. **Chanaprom Cholsuk**, Siavash Davani, Lorcan O. Conlon, Tobias Vogl, Falk Eilenberger. *Efficient Light Propagation Algorithm using Quantum Computers*. Physica Scripta. **2024**, 99 (4), 045110.

9. Anand Kumar, **Chanaprom Cholsuk**, Mohammad N. Mishuk, Mouli Hazra, Clotilde Pillot, Tjorben Matthes, Tanveer A. Shaik, et al. *Comparative Study of Quantum Emitter Fabrication in Wide Bandgap Materials Using Localized Electron Irradiation*. ACS Applied Optical Materials, **2024**, 2 (2), 323–32.
10. Najme Ahmadi, Sven Schwertfeger, Philipp Werner, Lukas Wiese, Joseph Lester, Elisa Da Ros, Josefine Krause, Sebastian Ritter, Mostafa Abasifard, **Chanaprom Cholsuk**, et al. *QUICK³ – Design of a Satellite-Based Quantum Light Source for Quantum Communication and Extended Physical Theory Tests in Space*. Advanced Quantum Technologies, **2024**, 7 (4), 2300343.
11. Mostafa Abasifard, **Chanaprom Cholsuk**, Roberto G. Pousa, Anand Kumar, Ashkan Zand, Thomas Riel, Daniel K. L. Oi, and Tobias Vogl. *The Ideal Wavelength for Daylight Free-Space Quantum Key Distribution*. APL Quantum, **2024**, 1 (1), 016113.
12. Aniwat Kesorn, Rutchapon Hunkao, Cheewawut Na Talang, **Chanaprom Cholsuk**, Asawin Sinsarp, Tobias Vogl, Sujin Suwanna, Suraphong Yuma. *Formation Energy Prediction of Neutral Single-Atom Impurities in 2D Materials using Tree-based Machine Learning*. Machine Learning: Science and Technology, **2024**, 5(3), 035039.
13. Asli Çakan, **Chanaprom Cholsuk**, Angus Gale, Mehran Kianinia, Serkan Pacal, Serkan Ates, Igor Aharonovich, Milos Toth, and Tobias Vogl. *Quantum Optics Applications of Hexagonal Boron Nitride Defects*, Advanced Optical Materials, **2025**, 13 (7), 2402508.
14. Gia Quyet Ngo, **Chanaprom Cholsuk**, Sebastian Thiele, Ziyang Gan, Antony George, Jörg Pezoldt, Andrey Turchanin, Tobias Vogl, and Falk Eilenberger *Photoluminescence Based Gas Sensing with MoS₂ Monolayers*, Accepted in Optics Express, **2025**.

Conference articles

15. **Chanaprom Cholsuk**, Asli Çakan, Sujin Suwanna, and Tobias Vogl. *Theoretical investigation of fluorescent defects in hexagonal boron nitride and their applications in quantum technologies*. Quantum Technologies, **2024**, 129930G.
16. Tjorben Matthes, Anand Kumar, **Chanaprom Cholsuk**., Mohammad N. Mishuk, Josefine Krause, Mouli Hazra, Asli Çakan, Kabilan Sripathy, Giacomo Corrielli, and Tobias Vogl. *Near-ideal room-temperature single photon emitters coupled with photonic integrated circuits*. Quantum Technologies **2024**, 129930D.

Chapter 1

Introduction

In the early 20th century, the first quantum revolution began with the discovery of key principles in quantum mechanics, such as quantization, wave-particle duality, and the uncertainty principle. This revolution significantly advanced semiconductor technology but eventually reached a limit owing to incapability of controlling individual quantum states. Building on the foundations of the first revolution, a second quantum revolution emerged, often called the “information era”. This new phase has shifted paradigm by overcoming earlier limitations and precisely manipulating individual quantum states, such as single photons. Alain Aspect, awarded the 2022 Nobel Prize in Physics, highlighted this transition, stating

“The main ingredient of the first quantum revolution, wave-particle duality, has led to inventions such as the transistor and the laser that are at the root of the information”.

This newfound capability to manipulate individual quantum states has engendered some novel advanced second-generation quantum applications by harnessing fundamental quantum properties such as superposition, entanglement, and no-cloning theorem. Notable among these applications are quantum communication, quantum sensing, and quantum computing, as detailed below.

1.1 Quantum Technology Applications

Second-generation quantum technology can generally be categorized into several applications. This dissertation focuses on only the following three key pillars: quantum communication, quantum computing, and quantum sensing, whose cutting-edge principles are summarized below.

1.1.1 Quantum Communication

Classical communication systems employ encryption using bits (0 and 1) to transmit data through fiber optics or free space. Despite its current practicality, the advent

of quantum computing over the past five years has posed significant threats to security, particularly concerning the RSA algorithm (Rivest-Shamir-Adleman), a widely used encryption protocol in classical communication [1]. Specifically, the security of the RSA algorithm hinges on the difficulty of factoring two large integers into primes, a problem that is challenging to solve by classical computers within a practical timeframe. However, the development of quantum computing, leveraging controllable individual quantum states, introduces a powerful algorithm—namely Shor’s algorithm—capable of potentially breaking the RSA protocol in a short time [2]. In anticipation of this potential security threat, quantum communication and quantum cryptography have emerged as crucial areas of focus. Instead of relying on a mathematical algorithm, quantum communication capitalizes on quantum properties to create unhackable encryption.

Single photons are commonly used as flying qubits (or quantum bits) to transmit quantum information due to their inherent advantages: they travel at the speed of light, enabling rapid transmission; and they interact weakly with the environment, ensuring robust qubit states [3, 4, 5]. Quantum properties, such as superposition, enable single photons to encode information in multiple states (2^N states for N photonic qubits), based on various degrees of freedom such as polarization [6], time-bin encoding [7], and orbital angular momentum [8]. Although photonic qubits can be transmitted through fiber optics, they are subject to finite communication distances due to intrinsic channel attenuation, including loss and errors in fibers. To overcome this limitation, satellite-based quantum communication has been proposed [4, 9, 10, 11]. Utilizing the entanglement quantum property, satellite-based quantum networks can connect qubits over extended distances through quantum repeater protocols. Additionally, the no-cloning theorem, which prohibits the duplication and amplification of quantum states, ensures the security of the transmitted information from copying attempts.

Up until now, several physical sources have been developed to establish a secured quantum communication system. For instance, a weak coherent source (WCS) attenuates the laser intensity so that its probability of having multiple photons is low. The advantage of this type is simplicity for implementation in an experiment; nonetheless, its disadvantage is the shorter communication distance and the more vulnerability from photon-number splitting (PNS) attacks than those in decoy source and single-photon source (SPS). For the decoy protocol, this is still a laser source, but it exploits multiple intensities of WCPs to restrict the multiphoton events [12]. This, thus, can potentially prevent the PNS attack and turn out to vastly enhance the communication distance in quantum communications as demonstrated in previous satellite-based experiments [4, 10, 11]. However, instead of relying on multiple source intensities like the decoy source, an alternative quantum source is the SPS, which relies only on the “true” single photon. This ensures the prevention of PNS attacks due to the significantly low multiphoton probability. Recently, the systems served SPS include quantum dots (QDs), negatively-charged nitrogen-vacancy (NV) centers in a diamond, color centers in silicon carbide (SiC), transition metal dichalcogenides (TMDs), and color centers in hexagonal boron nitride (hBN).

Another required component is quantum memory. Though free-space quantum communication can offer long communication distances, there are still some unavoidable limitations from noise and loss, causing finite communication distance. To circumvent this issue, distant communication can be split into smaller segments. Each segment is then linked by entanglement swapping, the process in which the photons in each segment become entangled and hence extend the communication range by the transfer of entanglement, namely swapping. A device that allows for high-quality entanglement to be shared between distant nodes is referred to as a quantum repeater. This implies that a quantum repeater can be used to extend the communication range. One of the necessary components in each node is a quantum memory, whose functions include handling quantum information, entailing the reliable storage of quantum states, preserving them over time, and transmitting them to successive communication nodes. Significant research efforts have been directed toward exploring various physical systems. For instance, warm atomic vapor memories, such as Cs, have recently been demonstrated to achieve the storage of GHz-bandwidth based on two-photon off-resonant cascaded absorption (ORCA) at room temperature [13]. Cold atoms require laser-cooled atomic systems to suppress thermal noises, hence storing light with long coherence time in Bose-Einstein condensates based on electromagnetically induced transparency (EIT) [14] and Autler–Townes-splitting (ATS) quantum-memory protocol [15]. Rare-earth ion doped crystals (REIDs), such as a $^{151}\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ crystal, have offered one-hour coherence storage time at cryogenic temperatures [16]. In addition to the indicated metrics, the interface between quantum memories and other on-chip micron-scale photonic quantum elements has become desirable for consideration. As a result, developing quantum memories has also been extended to investigate solid-state quantum systems such as QDs, NV centers, and defects hosted by hBN.

1.1.2 Quantum Computing

In contemporary computing, classical computers encode information using binary bits, represented by 0 and 1. In contrast, quantum computers utilize qubits to encode information. These qubits can exist in a quantum state that is a mixture of both $|0\rangle$ and $|1\rangle$ states, the so-called superposition quantum property. This capability potentially results in exponential speedups in some quantum algorithms compared to the classical counterparts, such as Deutsch-Jozsa algorithm [17], Grover’s algorithm [18], quantum beam propagation algorithm [19], as depicted in Fig. 1.1, as well as quantum algorithms for solving equations of motion [20, 21, 22] etc. While the quantum algorithms have been developed so far, physical systems that can be applied to create qubit states $|0\rangle$ and $|1\rangle$ have also been explored in parallel.

Nowadays, several systems have been used for qubits, such as Josephson junctions [23, 24], topological insulators [25, 26], trapped ions [27, 28], color centers in solids [29, 30], and photons [31, 32]. Each system has its own way of producing qubits. That is, Josephson junctions are typically used in superconducting qubits, which exploit the

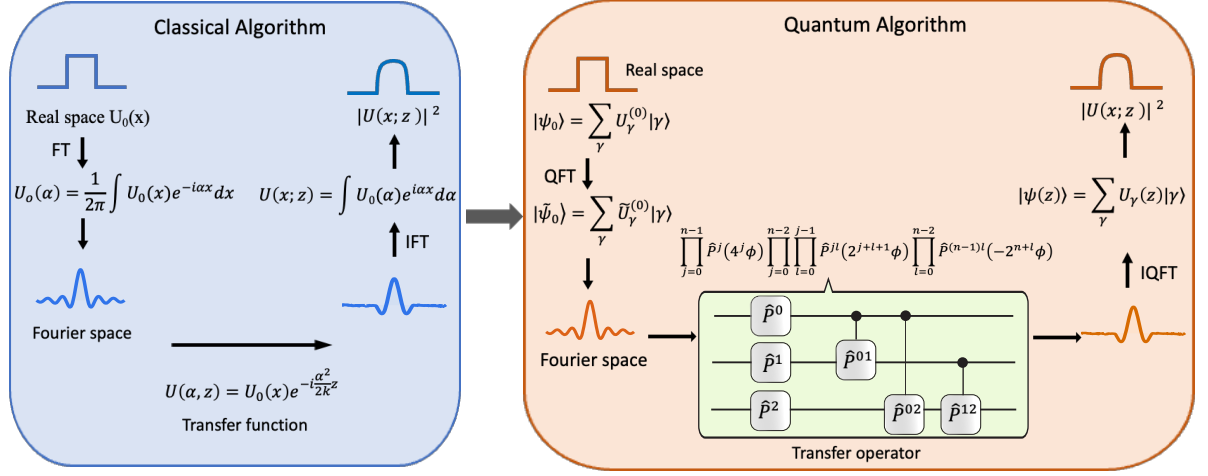


Figure 1.1: A schematic diagram of classical and quantum algorithms for light propagation. In each case, the Helmholtz equation is solved by first transforming the initial wavefunction from real space to Fourier space, using either the classical or quantum Fourier transform. The transfer function is then applied, followed by an inverse Fourier transformation to retrieve the propagated wave in real space. The operator P^j is indexed by the qubit j , and P^{jl} is indexed by qubits j and l with the specific phase shift value. This figure is adapted from Ref. [19] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

direction of current for representing $|0\rangle$ and $|1\rangle$ states. Topological insulators can use anyons as qubits. Trapped ions can exploit differences in atomic energy levels by spins up and down to assign qubit states. Color centers in solid-state systems can exploit their nuclear spin as spin qubits, such as NV center and SiV in diamond [29, 33]. Alternatively, the color center can also generate single photons, which can then be used as qubits by exploiting the degrees of freedom in the polarization, time-bin encoding, and spatial mode, etc. Note that several other mechanisms can be employed for qubit representation. Considering the implementation, most of the systems require cryogenic temperature conditions, while some systems in solid states can be operated under room temperatures, such as NV center and hBN. Therefore, using single photons as qubits becomes promising.

For optical quantum computers in particular, the horizontal and vertical polarizations of single photons are commonly used to encode these states due to the ease of manipulating single photons with linear optics to process quantum information. However, this approach has the drawback of complicated multi-qubit operations, as photons do not naturally interact with each other. The controlled-NOT (CNOT) gate, which is crucial for universal quantum computing, cannot be implemented with linear optics alone

and requires a nonlinear medium to mediate interactions, such as through cross-phase modulation [34, 35]. This necessity can be circumvented with one-way or measurement-based quantum computing. This approach uses entangled qubits as a resource and performs universal quantum computations using single-qubit gates implemented with linear optics [36, 37]. However, generating entangled states from single photons requires a high-quality single-photon source (SPS). Thus, ensuring the SPS quality is essential for the successful implementation of optical quantum computing.

1.1.3 Quantum Sensing

The final quantum technology application examined in this dissertation is quantum sensing. Traditionally, microscopy resolution is constrained by the diffraction limit to roughly half the wavelength. While non-linear imaging techniques can overcome this limitation [38, 39], they remain insufficient for achieving nanoscale resolution. On the other hand, in magnetic resonance imaging (MRI), spatial resolution is not restricted by diffraction but rather by magnetic field sensitivity, potentially allowing the resolution below optical wavelengths. Recent advancements in MRI sensitivity have enabled the imaging of individual cells [40]. Furthermore, magnetic resonance force microscopy can detect single electrons and small ensembles of nuclear spins [41]. However, this method currently requires cryogenic temperatures, which restrict its deployment in most biological applications.

To overcome this challenge, several physical systems have been proposed, such as topological insulators [42], complex oxide interfaces [43], and solid-state systems [44, 45, 46] to achieve nanoscale detection. For application with room temperature operation, solid-state quantum systems are intriguing. The well-known system includes an NV center in diamond [44, 45], which can work at room temperature. So far, its applications have been extended to various domains, including magnetic sensing, cellular and tissue imaging, and nuclear magnetic resonance (NMR). Another recent well-known system is a color center in hBN [46]. The sensitivity from solid-state systems relies on the electronic structures of a defect. This implies that it is an intrinsic property of a quantum system, so the reliability of quantum sensing does not degrade over time. Therefore, the characterization of electronic structure is of great importance, especially the triplet ($S = 1$) or doublet ($S = 1/2$) states. This is because these two states enable the Zeeman splitting of sub-spin levels such as $m_s = \pm 1/2$ for $S = 1/2$ or $m_s = 0$ and ± 1 for $S = 1$ when the magnetic field is applied. This brings about the ability to be sensors through changes in the photoluminescence (PL) spectrum.

1.2 Solid-State Quantum Systems

As introduced in the previous section, various physical systems have been developed for quantum technology applications. Nevertheless, when considering the room-

temperature operation, the solid-state systems become outstanding. Such systems include NV centers, TMDs, and hBN defects. In this section, all three materials are investigated and compared in terms of their usage in quantum emitter, quantum memory, and quantum sensor. These three essential components can be applied in quantum communication, quantum computing, and quantum sensing.

1.2.1 Color Centers for Quantum Emitter

The SPS has become one of the most generic required components across quantum communication, quantum computing, and quantum sensing. In a solid-state system, its electronic structure can be altered and then generates single photons. For instance, creating point-like defects can result in additional energy states in the in-gap region, or introducing some strain can bend the electronic structure to trap an excited electron. For NV centers, it is a defect in a three-dimensional host material from a diamond with a wide bandgap of approximately 5.5 eV [47]. Its color is derived from a specific point defect consisting of a nitrogen atom substituted at a carbon site adjacent to a vacancy site with the negative charge applied. NV centers exhibit PL peaked at around 637 nm with a strong contribution from phonon sidebands (PSB) [48, 49]. As the 637-nm ZPL peak in the PL spectrum has less intensity than the luminescence from PSB, this reflects the low Debye-Waller (DW) factor to below 4% at room temperature [50], which consequently limits high quantum efficiency. Another limitation is the outcoupling efficiency, which is lower than that of 2D materials. This is limited by the total internal Fresnel reflection due to a high refractive index in the diamond.

For TMDs, they are a class of two-dimensional materials that exhibit band gaps ranging from approximately 0.8 to 2.5 eV, depending on the specific material. Examples of TMDs include MoS₂ [51], MoSe₂ [52], MoTe₂ [53], WS₂ [54], and WSe₂ [55]. Their single photons can be induced by both defect states and band bending. Since their bandgaps are not comparatively large, some TMDs can possibly offer the photon emission at the telecommunication wavelength [51, 53]. This makes them promising for integration into existing telecommunication infrastructure. A key limitation, however, is that many 2D-TMDs require cryogenic temperatures, typically below 15 K, to maintain efficient operation. At higher temperatures, thermal excitation of charge carriers increases, introducing additional non-radiative pathways that can degrade single-photon emission efficiency.

So far, properties in both diamond and TMDs depend on the limited types of color centers for generating single photons. Thus, they need to hinge on another component to convert the wavelength to the target one. This is, however, not the case for color centers in hBN. In hBN, it inherits a wide bandgap of approximately 6 eV. Its application as the SPS was first discovered in 2016 [56]. The color centers in hBN are considered more promising than those in other materials due to their robustness against aging [57, 58], resistance to radiation [59], and stability across a wide temperature range [60]. Additionally, these color centers exhibit high single-photon luminosity [56], pure single-photon

emission [61], and a short excited state lifetime [57]. Quantitatively, some color centers in hBN have demonstrated DW factors as high as 82.4% [57] and quantum efficiencies of 87% at room temperature [62]. The single-photon emission from hBN is due to defect localization, which can emit single photons at a specific wavelength. As the hBN can host many different defects, it can emit photons over a broad range of wavelengths, including ultraviolet (UV) [63], visible [64], and near-infrared (IR) [65]. This broad emission range allows for the flexibility to select the optimal defect for specific quantum applications.

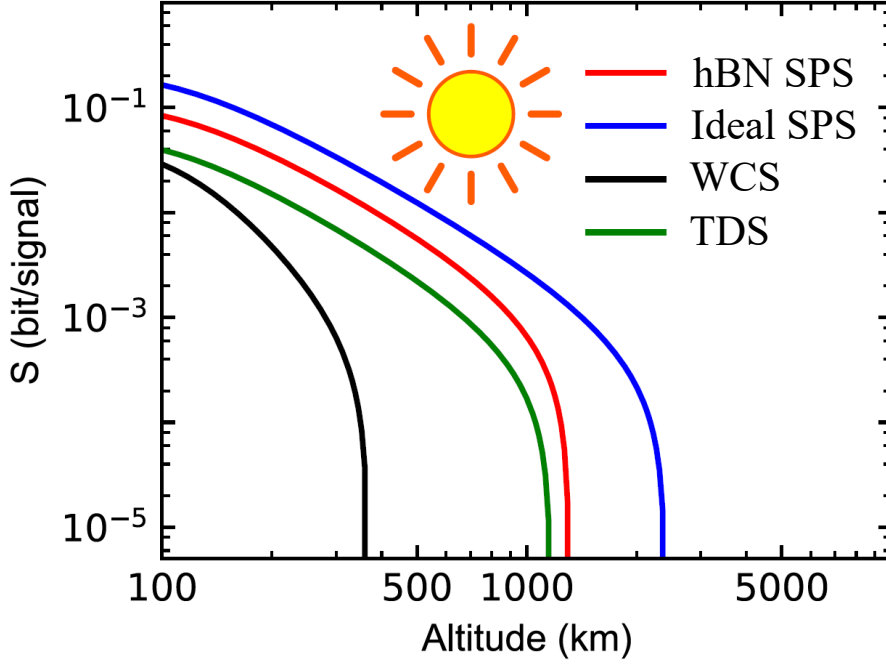


Figure 1.2: The extractable secret bit per signal for a satellite-based quantum communication as a function of satellite altitudes for different light sources, namely weak coherent state (WCS), two-decoy source (TDS), cavity coupled hBN single photon source (hBN SPS), and ideal SPS, all of which emit at 854.445 nm in daylight, visualized by the sun. This figure is adapted from Ref. [66] available under a [CC-BY 4.0 license](#). Copyright 2024 Abasifard *et al.*

Focusing on the performance of hBN defects to generate single photons for quantum communications, Fig. 1.2 compares the performance of various SPSs, including WCS, TDS, hBN-based SPS, and an ideal SPS on the number of input signals that can be made into the key or the so-called secret key bit per signal. WCS are light pulses generated by attenuating a laser to achieve an average photon number close to one. As a result, most pulses contain no photons, some contain a single photon, and a smaller fraction contain multiple photons. The presence of such multi-photon pulses introduces higher noise levels, which significantly reduces the effective communication range com-

pared to other methods. In contrast, TDS is a technique used to enhance the security of quantum key distribution by randomly varying the intensity of laser pulses, utilizing a few decoy states with different average photon numbers. This method counteracts potential eavesdropping by making it difficult for an attacker to distinguish between the different photon number states without being detected [12]. As a result, this approach enables stronger signal strength and, thus, longer communication distances than WCS [12, 67]. Comparing several wavelengths, Ref. [66] found certain wavelengths offering high extractable secret key rates. These include the wavelengths at 656 nm and 854 nm, corresponding to the H α and Ca-II Fraunhofer lines, respectively. This can be justified by the fact that the Fraunhofer lines can have low solar background noise if the filter is applied at this wavelength. Fig. 1.2 exemplifies the extractable secret bit per signal performance at 854-nm wavelength. The hBN SPS outperforms TDS, though this behavior can be different for other wavelengths. For further details, see Ref. [66]. Overall, the results suggest that using a true SPS from a quantum system is a promising approach for achieving efficient quantum communication, including in satellite-based and fiber-based platforms.

Having considered all the above properties, this dissertation focuses on hBN color centers. Although they have been demonstrated throughout, some crucial in-depth investigations remain unexplored. For example, color centers inheriting emission wavelength consistent with each quantum application have not yet been specified. Tailoring mechanisms for wavelength tuning remain unexplored. Finally, accurate defect identification between theory and experiment has not yet been achieved. All these research questions will be consequently addressed in Chapter 4 in this dissertation.

1.2.2 Color Centers for Quantum Memory

Another critical component for quantum communication and (distributed) quantum computing is quantum memory, which has been investigated extensively in solid-state systems. For instance, spin properties of NV center are exceptional for quantum memory [68, 69, 70, 71, 72]. The NV center is surrounded by carbon nuclear spins, with 99% of carbon isotopes being ^{12}C , which has no nuclear spin, and the remaining being ^{13}C , which has a nuclear spin (I) of $1/2$. This composition results in low decoherence from environmental nuclear spins, providing long spin relaxation time (T_1) and coherence time (T_2) as well as potential for coherent control [69, 73, 74, 75, 76]. Compared to hBN counterpart in V_B^{-1} defect, its nuclear spins consist of ^{10}B ($I = 3$ with 20% natural abundance), ^{11}B ($I = 3/2$ with 80% abundance), ^{14}N ($I = 1$ with 99.6% abundance), as well as ^{15}N ($I = 1/2$ with 0.4% abundance). These non-zero nuclear spins significantly lead to decoherence and, in turn, shorten T_1 and T_2 times. The comparison of T_1 and T_2 between NV centers and hBN is shown in Tab. 1.1. It is worth noting that TMDs also suffer from strong decoherence due to the non-zero nuclear spins. Given the more intrinsic disadvantages than that in hBN, TMDs become less attractive.

While the NV centers can offer long T_1 and T_2 times, their optical properties fall

behind those in hBN defects such as lower DW factor, lower outcoupling efficiency, and lower quantum efficiency, as discussed in Sec. 1.2.1 and listed in Tab. 1.1. In addition, the diamond hosts the NV center and a few more, whereas the hBN can host a large number of different defects. This restricts the diamond to having the ZPL only at 637 nm from the NV center, implying that another component for wavelength conversion is needed to convert the ZPL to the target values. Note that the specific wavelength is necessary for quantum communication to achieve the minimum losses. For instance, the 637-nm wavelength encounters propagation loss in optical fibers around 8 dB/km [77], while the 1330-nm and 1550-nm wavelengths encounter fiber losses of only around 0.35 dB/km and 0.20 dB/km, respectively [78]. This wavelength conversion component, therefore, introduces some additional noises due to conversion efficiency.

As a result, hBN is more intriguing than the diamond; nonetheless, the challenge in hBN defects is whether their spin coherence times can be prolonged so that they are comparable to those in the NV center. Hence, this dissertation aims to investigate the potential of hBN color centers as quantum memories. Given that no prior works have investigated hBN defects for this application before, this dissertation explores comprehensive properties, comprising the suitability of electronic structures in hBN defects, compatibility of emission wavelength in hBN defects with other quantum components, understanding causes of decoherence, and enhancement in T_1 and T_2 times. All these aspects will be addressed in detail in Chapters 5 and 6 of this dissertation.

Table 1.1: Comparison of spin and optical properties between NV centers and negatively charged boron vacancy (V_B^{-1}) defect in hBN. The experimental T_1 and T_2 at 295 K exclude any enhancement mechanism.

Spin properties					
Time	hBN isotopes				NV centers ¹³ C
	hBN _{nat}	h ¹⁰ BN	h ¹¹ BN	h ¹⁰ B ¹⁵ N	
T ₁	15 - 18 μs [79, 80, 81] for all isotopes				2.8 s [74]
T ₂	82.12 ns [82]	62 ns [83]	46 ns [83]	186 ns [79]	1.1 s [74]
Optical properties					
Properties	hBN defects				NV centers
DW factor	82.4% [57]				4% [50]
Quantum efficiency	87% [62]				70% [84]
Coupling efficiency	high				low

1.2.3 Color Centers for Quantum Sensing

Solid-state quantum systems can offer electronic structures suitable for quantum sensing. This enables high accuracy, sensitivity, and resolution, thus overcoming the limitations of classical sensing. For instance, NV centers inherit the triplet and singlet

electronic structures, featuring two pathways for electron decay [48, 49]. One is within the triplet state, while the other is via intersystem crossing between triplets and singlets, as will be discussed in Sec. 3.3. This can be used for sensors and can also be observed in the optically detected magnetic resonance (ODMR) spectrum. Meanwhile, a V_B^{-1} in hBN can also offer a similar electronic structure to the NV center, enabling quantum sensing application. These two color centers have been demonstrated in sensing, as summarized in Tab. 1.2.

Tab. 1.2 suggested that the V_B^{-1} in hBN outperforms the NV center, especially in pressure sensing due to its ability to detect pressure through monitoring changes in the zero-field splitting (ZFS). However, its response is anisotropic, reflecting pressure asymmetrically along the x , y , and z directions. This anisotropy arises because the ZFS shifts are linked to the elastic tensor of the host material, and since the V_B^{-1} center experiences different elastic coefficients along each axis, it reacts accordingly [46]. In particular, the out-of-plane sensitivity along the z -axis is higher due to the smaller elastic coefficient in this direction.

Table 1.2: Comparison of quantum sensing resolution from NV centers in a diamond and V_B^{-1} in hBN.

Detection	Sensitivity at 295 K			
	NV in diamond	Reference	hBN	Reference
Magnetic field	3 nT/ $\sqrt{\text{Hz}}$	[45]	85.1 $\mu\text{T}/\sqrt{\text{Hz}}$	[46]
Temperature	0.76 mK/ $\sqrt{\text{Hz}}$	[44]	3.82 K/ $\sqrt{\text{Hz}}$	[46]
X Pressure	-	-	17.5×10^6 Pa/ $\sqrt{\text{Hz}}$	[46]
Y Pressure	-	-	11.2×10^6 Pa/ $\sqrt{\text{Hz}}$	[46]
Z Pressure	-	-	2.62×10^6 Pa/ $\sqrt{\text{Hz}}$	[46]

However, the major obstruction in NV centers and V_B^{-1} is wide ODMR linewidth, which limits the sensing precision. Recently, a novel carbon-based defect in hBN has been discovered and found a narrower linewidth [85, 86]. While a specific defect type remains under investigation, this suggests that hBN color centers still have some unknown available defects, offering narrow linewidth that is useful for quantum sensing. As there are still a large number of hBN defects that have not yet been characterized theoretically and experimentally, this dissertation aims to fill this crucial gap.

The other important feature is from ODMR and electron paramagnetic resonance (EPR) spectra. In addition to being sensors, these two spectra can be used for defect assignments as this strongly depends on the defect type. While this has been achieved in identifying V_B^{-1} before, the spectra for a large number of hBN defects are not yet characterized. Thus, this dissertation aims to not only explore a large number of defects that inherit electronic structures suitable for quantum sensing, but also exploit ODMR and EPR spectra for defect identification purposes. These research questions will be addressed in Chapter 7 of this dissertation.

1.3 Scope of This Dissertation

Solid-state quantum systems can be created from various materials. However, this dissertation focuses specifically on hBN color centers due to the aforementioned unique advantages. These hBN color centers are examined for their potential applications as quantum emitters, quantum memories, and quantum sensors.

Regarding quantum emitter application, density functional theory (DFT) and post-processing DFT methods are utilized to comprehensively reveal the electronic and optical properties of color centers in hBN monolayer. The investigation covers vacancy defects, antisite defects, substitutional defects, and defect complexes from periodic groups III to VI as well as certain transition metals. The accuracy of these DFT predictions is also benchmarked against experimental data to ensure reliable theoretical results. Especially in the experiment for the yellow emitter, a comprehensive investigation has been conducted and consistent results have been found. In addition, this theoretical study has also been extended to analyze the underlying cause of the temporal dynamics of polarizations observed in the yellow emitter experiment. This dissertation also emphasizes the importance of comparing simulations and experiments across multiple properties rather than a single property to prevent misidentifying the microscopic origins.

For quantum memory, this dissertation addresses two primary types: off-resonance Raman quantum memory and nuclear-spin quantum memory. For Raman quantum memory, an hBN color center is assumed to be embedded in a cavity. Then, a theoretical model is developed to assess the minimum required quality factor of a cavity for each color center to achieve the desired writing and reading efficiency. To serve the theoretical model, DFT is used to reveal the intrinsic properties of each defect, especially the possibility of having the Λ electronic structures derived from the triplet and singlet defects. This study involves up to 257 electronic defect transitions and can classify quantum memory from hBN defects according to other quantum components. For the nuclear-spin quantum memory, instead of evaluating the hBN quantum memory performance directly, this dissertation investigates only the effects of quantum decoherence on T_1 and T_2 times, using open quantum system techniques. The study assumes low-temperature conditions, where the decoherence primarily arises from interactions between central spins and environmental nuclear spins. To capture these interactions, DFT calculation is employed to determine the hyperfine interaction for each defect, and an open quantum systems-based model is used to investigate the dynamics between electron spins and nuclear spins. While this analysis exemplifies through V_B^{-1} defect, the models can be used for other hBN defects. Although these findings do not directly determine quantum memory performance, they provide valuable insights into the feasibility of hBN as a quantum memory in terms of the T_1 and T_2 times. A full performance evaluation of the nuclear-spin quantum memory is then beyond the scope of this dissertation.

In quantum sensing application, this dissertation characterizes ODMR and EPR spectra with the purpose of defect identification. Enhancing the quantum sensing performance of hBN, however, is beyond the scope of this work. The investigation is based

on DFT calculations and a numerical model. The DFT calculation determines the intrinsic properties of hBN defects, which serve as inputs for the numerical model used in spectral characterization. These characterizations are limited to some point defects only.

1.4 Organization of This Dissertation

This dissertation provides comprehensive theoretical investigations of the photo-physical and spin qubit properties of color centers in hBN. These investigations provide useful insights not only for identifying microscopic origins that align well with experimental observations but also for assessing the performance of hBN color centers as quantum emitters, quantum memory, and quantum sensing for applications in quantum technology.

To cover such investigations, the integration among solid-state physics, density functional theory, and open quantum systems is employed in this dissertation. Key theory points are detailed in Chapter 2. Since these theoretical approaches are not specific enough to fully account for the fundamental mechanisms underlying quantum technologies, Chapter 3 elaborates on this critical discrepancy. The later chapters include analyses and results discovered in this dissertation.

Fig. 1.3 displays the overview of the comprehensive theoretical investigation conducted in this dissertation. That is, Chapter 4 is aimed to comprehensively investigate the color centers in hBN for SPS or quantum emitters together with a comparison with experiments. Then, this chapter details the distribution of various hBN defects. Although this primarily relies on simulations, this chapter also compares the computed properties with experimental results, demonstrating the consistency between the simulations and experimental data. Among studied numerous defects, several promising defects are identified and examined in in-depth detail.

In the following Chapter 5, the application of hBN color centers is extended to quantum memory. As quantum memory can operate through two distinct mechanisms, Chapter 5 focuses on evaluating the performance of hBN for the Raman-based scheme, while Chapter 6 emphasizes access to the feasibility of hBN for the nuclear-spin-based quantum memory. For Chapter 5, it elaborates on comprehensive properties and also lists promising defect candidates that are likely compatible with other systems. Given the complexity of calculating T_1 and T_2 times due to decoherence effects, Chapter 6 is dedicated to understanding the decoherence mechanisms affecting T_1 and T_2 .

Furthermore, it is observed that hBN color centers with the potential for quantum memory can also be implemented in quantum sensing applications. Therefore, Chapter 7 analyzes the behavior of hBN color centers in EPR and ODMR. Since these two spectra can be used for defect identification, several point defects are characterized in this chapter.

Finally, all properties of hBN color centers are then summarized and visualized

through an online database available at <https://h-bn.info>, as presented in Chapter 8. The dissertation concludes with a summary of the findings and proposes an outlook for future hBN-based quantum networks in Chapter 9.

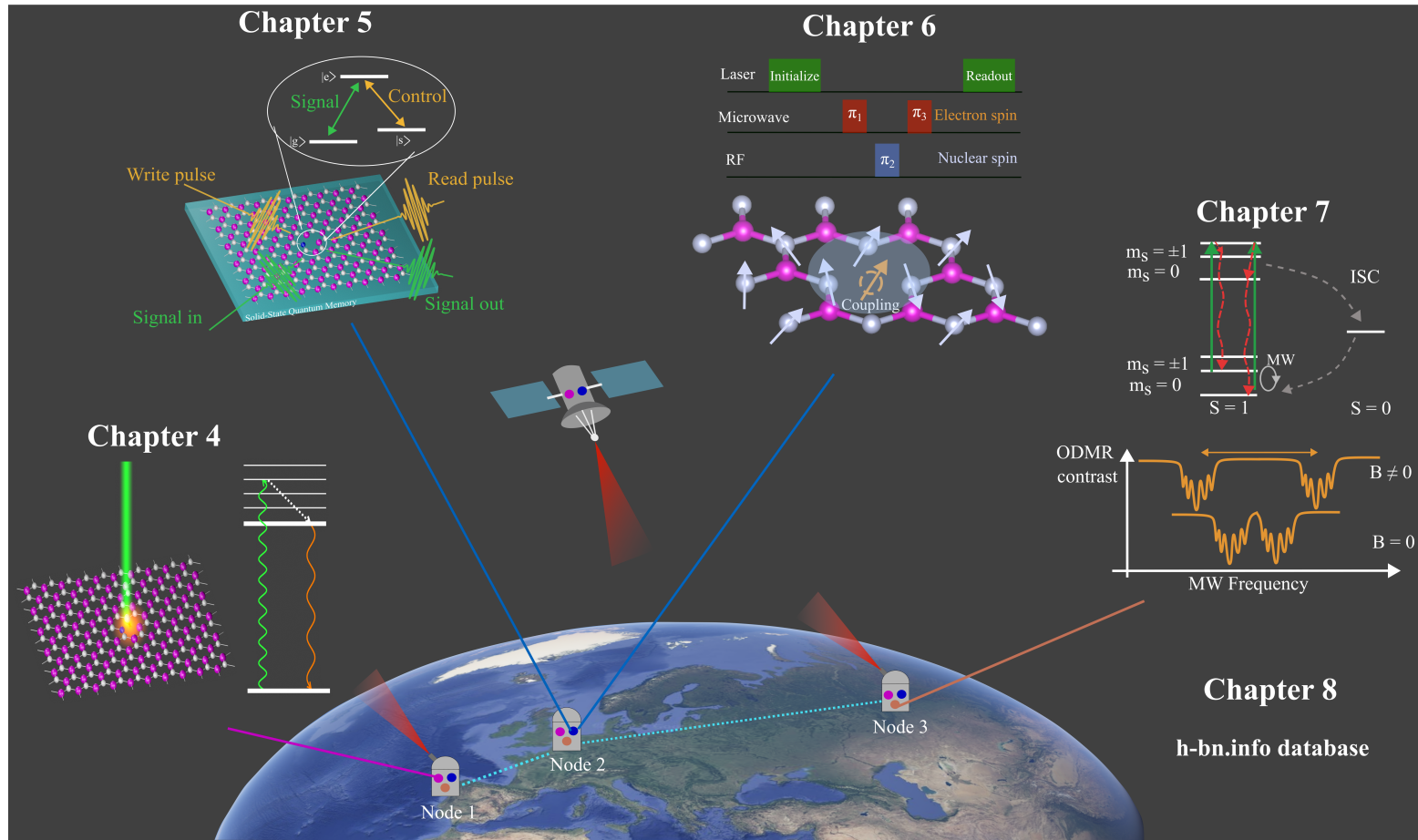


Figure 1.3: Overview of dissertation structure. Each node represents an hBN system containing quantum emitter (pink dot), quantum memory (blue dot), and quantum sensing (orange dot). Chapter 4 focuses on the quantum emitter, while Chapter 5 covers Raman-based quantum memory, and Chapter 6 addresses nuclear-spin-based quantum memory. Chapter 7 discusses quantum sensing, and Chapter 8 introduces the hBN online database. Finally, Chapter 9 is a summary and outlook, which is visualized by this entire image of quantum networks based on hBN color centers.

Chapter 2

Theoretical Schemes for Investigating Solid-State Quantum Systems

This chapter is aimed to provide a comprehensive summary of the theoretical framework and methodology employed in Chapters 4 – 8 of this dissertation, encompassing solid-state physics, density functional theory (DFT), and open quantum systems.

First, fundamental knowledge of 2D materials, electronic structures, and various types of defects is discussed. This section introduces the essential concepts necessary for understanding the behaviors of materials at the atomic level. It covers the basic principles of electronic band structures, the characteristic properties of two-dimensional materials, and the nature and impact of defects within these materials.

Following this, the chapter explains how DFT is used to simulate electronic properties, offering insights into the theoretical basis of DFT, the approximations involved, and the computational techniques employed. The chapter then transitions to post-processing DFT, where the focus is on computing properties relevant to quantum technology applications. This involves techniques used to extract information from raw DFT results, such as optical properties, charge distributions, and other parameters pertinent to the functionality of quantum emitters. This section bridges the gap between raw computational data and practical insights into material properties.

In addition to the electronic and physical properties of the system, the spin qubit properties will be addressed. Therefore, the final section of this chapter introduces the sources of decoherence, methods and approximations to simulate these effects, and the criteria used to evaluate the coherence of spin qubits.

By covering these topics, this chapter ensures that readers gain a solid foundation of the theoretical principles and computational techniques essential for the research conducted in the dissertation. This foundational knowledge sets the stage for a deeper exploration of the results and findings presented in the subsequent chapters.

2.1 Solid-State Physics

This section elucidates the distinction between fundamental and optical bandgaps, which are pertinent for both theoretical calculations and experimental analysis. Subse-

quently, the definition of 2D materials and their defects is provided.

2.1.1 Electronic Band Structures

The electronic band structure is a fundamental concept in solid-state physics that describes the energy dispersion relation of electrons in a crystal. While the mathematical derivation of the band structure is beyond the scope of this dissertation, an overview of the key concepts is provided below.

In theoretical calculations, the band structure is typically determined using several computational methods. These include some simplified models, the tight-binding approximation, and DFT. These methods provide the fundamental bandgap, which is the energy difference between the top of the valence band and the bottom of the conduction band. Mathematically, this bandgap E_g is given by [87]

$$E_g = E_{cbm} - E_{vbm}, \quad (2.1)$$

where E_{cbm} denotes the energy level of the conduction band minimum (CBM), whilst E_{vbm} denotes the energy level of the valence band maximum (VBM). In crystalline materials, VBM and CBM may occur at different locations in the Brillouin zone, the unique primitive cell defined in reciprocal space, leading to classifications of direct and indirect band gaps.

1. Direct band gap: electrons can transition directly from the conduction band to the valence band with the emission of a photon without a change in momentum.
2. Indirect band gap: electrons can transition from the conduction band to the valence band with the emission of a photon with a change in momentum. Photon emission then must be accompanied by a phonon (lattice vibration) to conserve momentum.

In contrast, the experimental bandgap is often determined through techniques such as photoluminescence (PL) spectroscopy. The optical band gap measured experimentally refers to the energy required to generate an exciton, that is, a bound state of an electron and a hole in the material. This bandgap is typically slightly smaller than the fundamental bandgap due to the Coulomb attraction between the electron and the hole, which reduces the energy required for exciton formation. The optical band gap E_{opt} can be expressed as

$$E_{opt} = E_g - E_b, \quad (2.2)$$

where E_b is the binding energy of the exciton, which is the energy required to separate the electron from the hole.

2.1.2 Two-dimensional Materials

2D materials are characterized by a crystal lattice structure where the binding energy within the plane (typically designated as the xy plane), often associated with covalent bonds, is significantly stronger than the binding energy in the perpendicular or z direction, usually governed by the van der Waals force. For many years, the existence of a true 2D material, consisting of only a single atomic layer, remained a theoretical concept. However, the isolation of single-layer graphene was achieved in 2004, a groundbreaking discovery that marked a pivotal moment in materials science [88]. The significance of groundbreaking experiments with graphene, a single layer of carbon atoms arranged in a hexagonal lattice, was further underscored by the awarding of the Nobel Prize in Physics in 2010. This recognition catalyzed an explosion of research in 2D materials, leading to the discovery of numerous other promising materials, such as black phosphorus, TMDs, and hBN. These materials have garnered significant attention for their unique properties and potential applications across various domains of science and technology.

Focusing on applications related to the second-generation quantum technologies, graphene is excluded owing to its lack of a two-level quantum system due to its intrinsic semimetal [89, 90, 91, 92]. The absence of such a system in graphene precludes its use in several key quantum technology applications, including the generation of single photons, the operation of quantum memory through read/write processes, and the support of EPR and ODMR for quantum sensing. As a result, the focus on 2D materials applicable in quantum technologies has shifted towards TMDs and hBN, both of which possess the requisite two-level quantum systems. The following sections will elaborate on the specific properties and advantages of TMDs and hBN in the context of quantum technology applications.

Transition Metal Dichalcogenides

2D TMDs are 2D materials as shown in Fig. 2.1 in the composition of MX_2 where M is transition metals such as Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, and Re whereas X is chalcogens such as S, Se, and Te. These combinations, e.g., MoS_2 , WS_2 , $MoSe_2$, and WSe_2 , have obtained significant attention as promising candidates for SPSs. These materials exhibit a unique combination of direct band gaps, strong spin-orbit coupling, and valley-selective optical selection rules, rendering them highly suitable for applications in optical quantum technologies [51, 52, 53, 54, 55].

In monolayer TMDs, the band gap is direct and lies within the visible to near-infrared wavelength, depending on the specific material [93]. The direct band gap, coupled with the reduced dimensionality of the monolayer, leads to tightly bound excitons with substantial binding energies. As a result, the optical bandgap can be significantly different from the fundamental bandgap.

When a TMD monolayer is subjected to localized strain, defects, or other perturbations, the band structure can be locally bent, resulting in the creation of potential

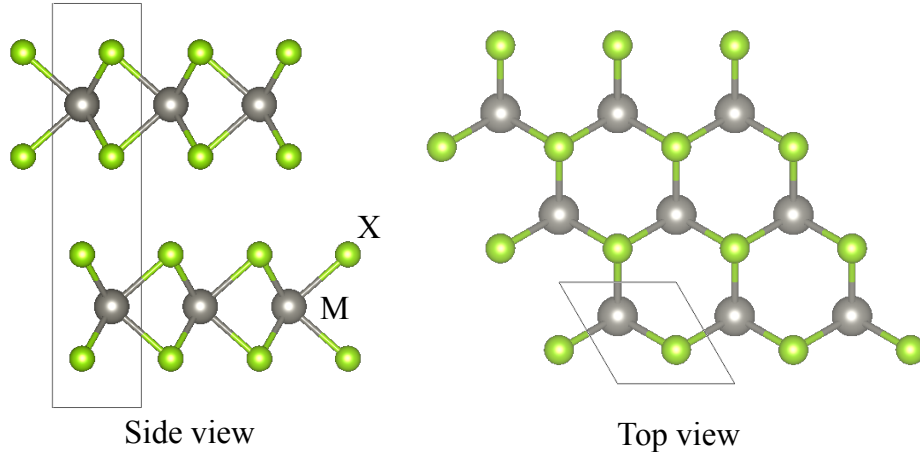


Figure 2.1: Lattice structures of MX_2 TMDs in 2H phase where M denotes transition metals whereas X denotes chalcogens. The side view represents the AB stacking and the top view represents the hexagonal structure. A unit cell consists of three atoms as the sandwiched structure (X-M-X): M at the center and the other two X at the top and bottom of M.

wells capable of trapping excitons or charge carriers. These localized states can function as quantum emitters. Experimental evidence suggests that in WSe_2 , single-photon emission is likely attributable to localized intervalley defect-bound excitons, which are the combination of exciton, defect, and strain [94, 95]. That is, when an excitation laser is applied, an exciton or electron-hole pair can be formed. Normally, this exciton cannot be trapped; however, with the presence of strain, the exciton is trapped to the low-potential strained level. This is the so-called bright exciton localized at the bright band. In WSe_2 , the dark exciton can also exist at energies below the bright one or at the dark band. This is called dark because the transition of the exciton to the dark band is optically forbidden due to the selection rule. Nonetheless, this restriction can be lifted if there is a defect [94, 95]. The defect level breaks the spin-momentum locking of WSe_2 . The dark exciton can then be allowed to relax to the defect level. This forms the so-called intervalley defect excitons, giving rise to a single photon emission where the two-level quantum system is composed of the dark band and the defect level [94, 95]. This finding indicates that TMDs benefit from the presence of both strain and defect.

Hexagonal Boron Nitride

2D hBN crystallizes in a hexagonal lattice structure, much like graphite, with boron (B) and nitrogen (N) atoms alternately occupying the vertices of a honeycomb pattern, as visualized in Fig. 2.2. Each boron atom forms strong covalent bonds with three neighboring nitrogen atoms, and conversely, each nitrogen atom is similarly bonded to

three boron atoms. This robust in-plane bonding gives hBN exceptional mechanical stability and resilience within each layer.

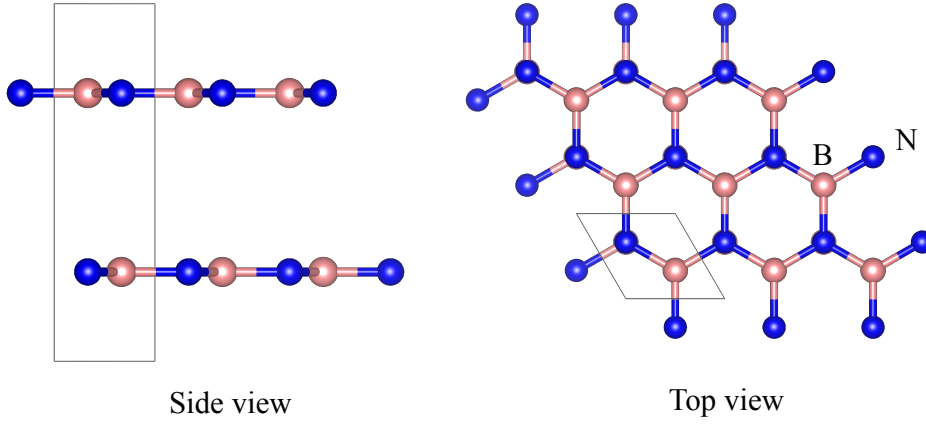


Figure 2.2: Lattice structures of hBN where the side view represents the AB stacking and the top view represents the hexagonal structure. A unit cell consists of two atoms: boron and nitrogen.

Unlike graphene, which is typically black or gray due to its zero bandgap and metallic nature, hBN is visually white. This is because hBN possesses a wide bandgap of approximately 6 eV, which prevents the absorption of visible light, giving it a distinct white appearance. This wide bandgap also contributes to its excellent insulating properties, distinguishing it from the conductive nature of graphene and earning it the nickname “white graphene.”

For quantum technology applications, hBN is particularly noteworthy for its potential as SPS, though with a different mechanism than that of TMDs. While TMDs rely on their excitonic properties and direct band gaps to generate single photons, hBN operates through defect states that form a two-level quantum system. These defect states in hBN can localize excited electrons and facilitate the emission of single photons, making hBN a promising candidate for quantum photonic applications.

Single-photon emission from hBN defects has been demonstrated not only in bulk crystals but also in monolayer forms. As the electronic structure transitions from bulk to monolayer, the bandgap shifts from approximately 6 eV (indirect) in bulk hBN to around 7 eV (direct) in monolayer hBN [96, 97]. Despite this change, the defect states remain crucial in generating single photons. Note that the direct/indirect hBN property is still under debate [96, 98, 99]. Additionally, the hBN monolayer stands out due to its potential to reduce decoherence, thereby enabling more robust spin qubits [100]. This makes the hBN monolayer intriguing in quantum technologies.

2.1.3 Defects

As mentioned in Sec. 2.1.2 regarding the functionality of defects, this section elaborates on the definition and classification of defects in crystalline materials. A defect is an imperfection or impurity that disrupts the perfect symmetry and periodicity of a pristine crystal lattice. Defects in crystals can be categorized according to their dimensionality, as depicted in Fig. 2.3.

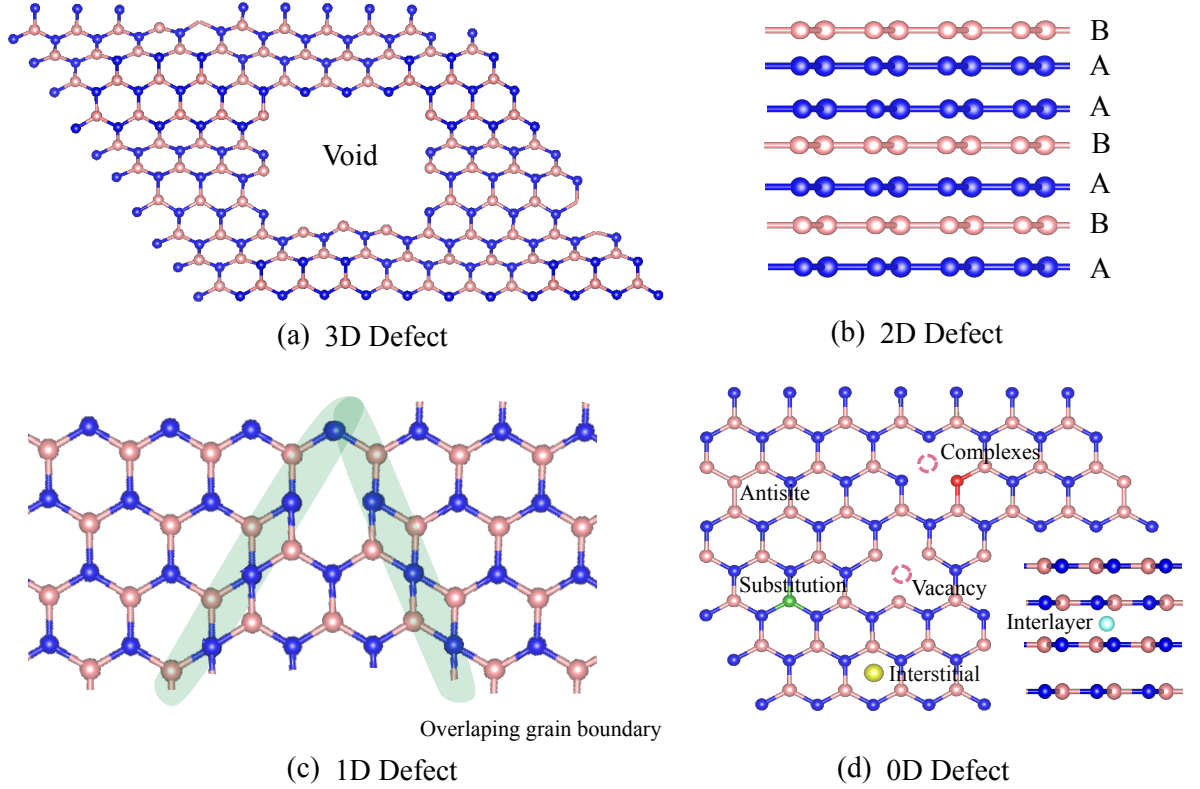


Figure 2.3: Defect classification.

1. In 3D defects, these are large-scale imperfections within the crystal structure. Common examples include step dislocations, where there is a break in the regular atomic layers (often appearing as voids), and screw dislocations, which involve a spiral arrangement of atoms around a dislocation line.
2. In 2D defects, these defects occur within a plane of the crystal and disrupt the regular stacking sequence of atomic layers. An example is a stacking fault, where the typical sequence of atomic layers (e.g., ABCABCABC) is interrupted by an irregular sequence (e.g., ABCABABC). In this case, the missing 'C' layer creates a planar defect.

3. In 1D defects, these are defects along a line within the crystal, often associated with the grain boundaries that form during the crystal growth process. Dislocations are another common type of linear defect, where atoms are misaligned along a line in the crystal.
4. In 0D defects, these can be called point defects. These are localized imperfections that occur at specific lattice sites and include several types.
 - a) Vacancies: these occur when atoms are missing from their regular lattice positions.
 - b) Substitutional defects: in this case, an atom of a different species replaces a host at a lattice site.
 - c) Interstitial defects: these occur when an additional atom occupies a position between the regular lattice points. The additional atom can be the same or different from the host elements.
 - d) Antisite defect: these defects occur in compound crystals (such as hBN) when an atom of one species occupies a lattice site typically occupied by another species.
 - e) Point-like complexes: these are combinations of the aforementioned point defect types, forming more complex defect structures.
 - f) Stone-Wales defect: these involve the rotation of a π -bond in carbon-based materials (e.g., graphene) by 90° , resulting in a reconfiguration of the carbon atoms.
 - g) Interlayer defects: the intercalant (the species that occupies the interlayer space) interacts with the atoms in adjacent layers through various bonding mechanisms, which could include the van der Waals forces, ionic interactions, or even covalent bonds in some cases.

2.2 Density Functional Theory

Addressing problems related to many-body systems necessitates the use of highly efficient computational resources due to the inherently complex and cumbersome nature of the equations involved. Various methodologies exist for tackling these problems, such as the quantum Monte Carlo (QMC) method [101], which applies variational Monte Carlo (VMC) [102] and diffusion Monte Carlo (DMC) [103] techniques. Despite their effectiveness, these approaches are computationally intensive. In contrast, DFT emerges as a more computationally feasible alternative. DFT fundamentally shifts the focus from wave functions to electron charge density, which drastically reduces the number of degrees of freedom involved in the calculations [104, 105, 106]. This reduction in complexity translates to a substantial decrease in computational cost, often by a factor of

approximately one thousand compared to Monte Carlo methods. As a result of its computational efficiency and practical applicability, DFT is used in calculations of material properties throughout this dissertation, and its principles are summarized below.

2.2.1 Many-Body Hamiltonian and Approximations

In solid-state physics and quantum mechanics, a primary objective is to uncover the properties present at the nanoscale that transcend classical regimes. These properties can be determined through the eigenvectors and eigenvalues obtained from the time-independent Schrödinger equation, which accounts for the interactions between nuclei and electrons, as explained below

$$\hat{H}\Psi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E_i\Psi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M). \quad (2.3)$$

This is the stationary Schrödinger equation where Hamiltonian $\hat{H}$ consists of M nuclei and N electrons. The wavefunction Ψ_i is a function of the electron positions ($\vec{r}$) and the nuclei positions ($\vec{R}$). The Hamiltonian can be decomposed into

$$\begin{aligned} \hat{H} = & -\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{e^2}{4\pi\epsilon_0} \sum_i^N \sum_A^M \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \frac{e^2}{8\pi\epsilon_0} \sum_i^N \sum_{j \neq i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \\ & + \frac{e^2}{8\pi\epsilon_0} \sum_A^M \sum_{B \neq A}^M \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|}. \end{aligned} \quad (2.4)$$

The first two terms correspond to the kinetic energy of electrons and nuclei, whereas the remaining terms describe the Coulomb potential energy; that is, the attractive nucleus-electron Coulomb interaction, the repulsive electron-electron Coulomb interaction, and the repulsive nucleus-nucleus Coulomb interaction, respectively.

For the sake of simplifying the complexities associated with fundamental physical constants, atomic units are employed. In this system, length and energy are expressed in terms of the Bohr radius (a_0), and the Hartree energy (E_H). Specifically, the Bohr radius is defined as

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}, \quad (2.5)$$

and the Hartree energy is given by

$$E_H = \frac{\hbar^2}{m_e a_0^2} = \frac{e^2}{4\pi\epsilon_0}. \quad (2.6)$$

Consequently, the Hamiltonian simplifies using the substitutions $\vec{r} = \frac{\vec{r}}{a_0}$ and $\nabla^2 = \frac{\tilde{\nabla}^2}{a_0^2}$ as follows

$$\hat{\tilde{H}} = -\sum_{i=1}^N \frac{1}{2} \tilde{\nabla}_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \tilde{\nabla}_A^2 + \left[-\sum_i^N \sum_A^M \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_A^M \sum_{B \neq A}^M \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \right] \quad (2.7)$$

where the symbol $\sim$ indicates a dimensionless quantity, which can be suppressed subsequently for the sake of simplicity. As a result, the rescaled Schrödinger equation is expressed as follows.

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}, \quad (2.8)$$

$$\hat{H} = T_e + T_n + V_{ne} + V_{ee} + V_{nn}, \quad (2.9)$$

where the indices A and B iterate over the M nuclei, while i and j denote the indices of the N electrons.

Born Oppenheimer Approximation

According to Eq. (2.8), which includes all interactions between nuclei and electrons, the complexity of the equation renders it challenging to solve directly. Therefore, the Born-Oppenheimer approximation was introduced to simplify certain terms in Eq. [107]. Given that the nuclei have significantly greater mass compared to the electron (by a factor of at least 1800), each nucleus moves much more slowly. Hence, it can be considered nearly stationary relative to the electron's motion. Consequently, the nuclei can be treated classically as fixed while the electrons orbit around them. This adiabatic separation of the nuclear and electronic degrees of freedom allows one to neglect some terms in Eq. (2.8). Specifically, the kinetic energy term of the nuclei becomes negligible, and its potential energy term is approximately constant and can be treated as a background energy shift. This simplification results in the reduction of the Hamiltonian to

$$\hat{H}_{\text{electron}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}, \quad (2.10)$$

which describes the energy for electrons only. When the nucleus potential energy is later added, the total energy becomes

$$E_{\text{total}} = E_{\text{electron}} + E_{\text{nucleus}}, \quad (2.11)$$

where

$$E_{\text{nucleus}} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (2.12)$$

Now, the task is to solve the electronic Schrodinger equation, which will be discussed in the next section.

Hartree-Fock Approximation

Eq. (2.10) is incomplete because it does not account for the fact that electrons are fermions, which are indistinguishable particles that obey the Pauli exclusion principle. Consequently, it is necessary to include an additional exchange term, K_{ij} , to the total energy. Before addressing this point, we must first propose a trial solution. Assume that the ground state wave function, Ψ_0 , can be approximated by the Hartree-Fock wave function, $\Psi_{HF}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$. This Ψ_{HF} must be anti-symmetric to ensure that no two electrons can occupy the same quantum state, in accordance with the Pauli exclusion principle. The wave function Ψ_{HF} depends on N electrons, with each electron possessing six degrees of freedom: three for spatial coordinates $\phi(x, y, z)$ and three for spin functions $\sigma(S_x, S_y, S_z)$. Therefore, the appropriate trial wave function should be expressed as a Slater determinant of spin-orbital wave functions, as written in Eq. (2.13).

$$\Psi_0 \approx \Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix} \quad (2.13)$$

where $\psi_i(\vec{r}) = \phi_i(x, y, z)\sigma_+(S_x, S_y, S_z)$ for spin up and $\psi_i(\vec{r}) = \phi_i(x, y, z)\sigma_-(S_x, S_y, S_z)$ for spin down. After that, one can employ the variation method to calculate the energy.

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}),$$

where h_i is the core Hamiltonian containing kinetic energy and electron-nucleus attraction; J_{ij} is the Coulomb term or Hartree term; and K_{ij} is the exchange term.

$$h_i = \int \psi_i^*(\vec{r}) \left[-\frac{1}{2} \nabla^2 - V_{ext}(\vec{r}) \right] \psi_i(\vec{r}) d\vec{r} \quad (2.14)$$

$$J_{ij} = \int \int \psi_i(\vec{r}_1) \psi_i^*(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_j^*(\vec{r}_2) \psi_j(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (2.15)$$

$$K_{ij} = \int \int \psi_i^*(\vec{r}_1) \psi_j(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_i(\vec{r}_2) \psi_j^*(\vec{r}_2) d\vec{r}_1 d\vec{r}_2. \quad (2.16)$$

However, the Hartree-Fock method has a significant limitation due to its neglect of electron correlation effects. This issue is addressed by the Kohn-Sham approach, which enhances the equation by introducing an additional exchange-correlation potential term [105]. The specific details of this method are discussed in the following sections.

Hohenberg-Kohn Theorems

As mentioned earlier, the many-body Schrödinger equation can be solved by several methods. One such method is DFT, which treats electronic wavefunctions in terms of

their probability density of charge distribution. This section explains why it is possible to find the energy functional $E[\rho]$ and the electron charge density $\rho(\vec{r})$ by minimizing $E[\rho]$.

The first Hohenberg-Kohn theorem states [104] that the external potential $V_{ext}(\vec{r})$ is uniquely determined by the ground state density $\rho(\vec{r})$. In other words, $V_{ext}(\vec{r})$ has a one-to-one correspondence with $\rho(\vec{r})$, ensuring that each $V_{ext}(\vec{r})$ generates a unique density $\rho(\vec{r})$. Consequently, the ground state density $\rho(\vec{r})$ can yield all ground state properties. Additionally, the kinetic energy, potential energy, and total energy can be expressed in terms of $\rho(\vec{r})$, denoted as $T[\rho]$, $V[\rho]$, and $E[\rho]$, respectively.

$$\begin{aligned} E[\rho] &= E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] \\ &= E_{Ne}[\rho] + T[\rho] + J[\rho] + E_{xc}[\rho] \end{aligned} \quad (2.17)$$

$$= \int \rho(\vec{r}) V_{Ne}(\vec{r}) d\vec{r} + T[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho], \quad (2.18)$$

The third term of Eq. (2.18) is the classical Coulomb interaction, but the last term, $E_{xc}[\rho]$, includes exchange-correlation effects which are not purely classical. The explicit forms of $T[\rho]$ and $E_{xc}[\rho]$ are generally not known. According to the first theorem and Eq. (2.18), all energies can be expressed as functionals of the electron charge density $\rho(\vec{r})$. Normally, the electron charge density for many-body systems is given by

$$\begin{aligned} \rho(\vec{r}) &= \langle \psi | \rho(\vec{r}) | \Psi \rangle \\ &= \sum_{i=1}^N \int \delta(\vec{r} - \vec{r}_i) |\psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N \\ &= \int |\psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N + \int |\psi(\vec{r}_1, \vec{r}, \vec{r}_3, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_3 \dots d\vec{r}_N + \dots \\ &= N \int |\psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N, \end{aligned} \quad (2.19)$$

where $\vec{r}_i$ is the coordinate of each electron and N is the total number of electrons. The nucleus-electron interaction E_{Ne} is given by

$$\hat{V}_{Ne} = - \sum_i^N \sum_A^M \frac{Z_A}{|\vec{r}_i - \vec{R}_A|}. \quad (2.20)$$

Thus, its expectation value is

$$\begin{aligned}
 E_{Ne} &= \langle \psi(\vec{r}_1, \dots, \vec{r}_N) | \hat{V}_{Ne} | \psi(\vec{r}_1, \dots, \vec{r}_N) \rangle \\
 &= - \sum_i^N \sum_A^M \int \psi^*(\vec{r}_1, \dots, \vec{r}_N) \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} \psi(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N \\
 &= - \sum_A^M \left[\int \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|} |\psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N \right. \\
 &\quad \left. + \int \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} |\psi(\vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N + \dots \right] \\
 &= - \sum_A^M \left[\int \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|} d\vec{r}_1 \int |\psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N \right. \\
 &\quad \left. + \int \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} d\vec{r}_2 \int |\psi(\vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_3 \dots d\vec{r}_N + \dots \right]. \tag{2.21}
 \end{aligned}$$

Given Eq. (2.19), the expectation value becomes

$$\begin{aligned}
 E_{Ne} &= - \frac{1}{N} \sum_A^M \left[\int \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|} \rho(\vec{r}_1) d\vec{r}_1 + \int \frac{Z_A}{|\vec{r}_2 - \vec{R}_A|} \rho(\vec{r}_2) d\vec{r}_2 + \dots \right] \\
 &= - \sum_A^M \left[\int \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} \rho(\vec{r}_i) d\vec{r} \right] \\
 E_{Ne} &= \int \rho(\vec{r}) V_{Ne}(\vec{r}) d\vec{r}. \tag{2.22}
 \end{aligned}$$

For the electron-electron interaction E_{ee} , we have

$$E_{ee} = \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|}. \tag{2.23}$$

However, E_{ee} cannot be expressed solely in terms of the single-particle density and must be formulated based on the two-particle charge density as follows

$$E_{ee} = \frac{1}{2} \int \int d\vec{r}_1 d\vec{r}_2 \frac{\rho^{(2)}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \tag{2.24}$$

Since solving the many-body problem is challenging, the two-particle charge density $\rho^{(2)}(\vec{r}_1, \vec{r}_2)$ is approximated as a combination of one-particle densities and a correction term [106]

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1) \rho(\vec{r}_2) + \Delta \rho^{(2)}(\vec{r}_1, \vec{r}_2). \tag{2.25}$$

As a result, this term eventually becomes

$$E_{ee} = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho], \tag{2.26}$$

where the first term represents the classical Coulomb interaction, while the second term, $E_{xc}[\rho]$, accounts for the exchange-correlation effects that are not included in the Hartree term.

The second Hohenberg-Kohn theorem states that the energy functional $E[\rho]$ achieves its minimum value when the input density is the true ground state density [104]. In other words, $\rho(\vec{r})$ can always be obtained by minimizing $E[\rho]$. This theorem ensures that the derived density is indeed the ground state density, analogous to the variational principle.

Kohn-Sham Approach

To this point, we have expressed all energy terms as functions of the density as shown in Eq. (2.18), except for the kinetic term $T[\rho]$ and the non-classical term $E_{ncl}[\rho]$. The challenge now is to convert these two terms into functions of $\rho(\vec{r})$. In 1965, Kohn and Sham proposed a solution whereby the kinetic energy term can be approximated using a non-interacting reference frame. This involves single-particle orbitals that yield the same density as the actual interacting system

$$\rho_S(\vec{r}) = \sum_i^N \sum_s |\phi_i(\vec{r}, s)|^2 = \rho(\vec{r}) \quad (2.27)$$

$$T_S = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle. \quad (2.28)$$

Here, ϕ_i are the orbitals of the non-interacting system, known as Kohn-Sham orbitals. While T_S is not the true kinetic energy, Kohn and Sham addressed this by defining a functional $F[\rho]$ as

$$F[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho], \quad (2.29)$$

where E_{xc} is the exchange-correlation energy, encompassing all unknown terms, defined as

$$E_{xc}[\rho] \equiv (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]). \quad (2.30)$$

Finally, the total energy can be expressed as

$$E[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] + E_{Ne}[\rho] \quad (2.31)$$

$$= -\frac{1}{2} \sum_i^N \int d\vec{r} \phi_i^* \nabla^2 \phi_i + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \int d\vec{r} \epsilon_{xc}[\rho] \rho(\vec{r}) + \int V_{Ne} \rho(\vec{r}) d\vec{r}. \quad (2.32)$$

When this expression is substituted into the Schrödinger equation, it becomes the Kohn-Sham equation [105].

$$\left(-\frac{1}{2} \nabla^2 + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{|\vec{r}_1 - \vec{r}_A|} \right) \phi_i = \epsilon_i \phi_i \quad (2.33)$$

$$\left(-\frac{1}{2} \nabla^2 + V_S(\vec{r}_1) \right) \phi_i = \epsilon_i \phi_i, \quad (2.34)$$

where $V_S(\vec{r}_1)$ is the Kohn-Sham potential.

$$V_S(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{|\vec{r}_1 - \vec{r}_A|} \quad (2.35)$$

The remaining task is to accurately determine the exchange-correlation term, which will be discussed next.

2.2.2 The Exchange and Correlation Functional

The exchange-correlation functional $E_{xc}[\rho]$ is essential for accurately describing electron interactions that are not captured by the classical Coulomb interactions. Several approximations have been developed to describe $E_{xc}[\rho]$. The most basic approximation is the local density approximation (LDA), which relies on the exchange-correlation energy of a homogeneous electron gas with the same local density. The generalized gradient approximation (GGA) improves upon LDA by including the gradient of the electron charge density in the functional, which provides a better description of systems where the electron charge density varies more rapidly [108]. However, both LDA and GGA significantly underestimate the bandgap for wide band-gap materials, including hBN of our interest, due to the self-interaction errors [109, 110]. This error tends to delocalize the electrons, reducing the effective potential experienced by the electrons. Hence, this delocalization results in a lower conduction band and a higher valence band, thereby underestimating the band gap. Therefore, a hybrid functional is employed for all DFT calculations in this dissertation to achieve more accurate results.

Focusing on hybrid functionals, it incorporates a portion of exact exchange energy from Hartree-Fock (HF) theory with exchange-correlation energies from traditional DFT approximations like LDA and GGA. For hBN in particular, our DFT calculations employed the Heyd-Scuseria-Ernzerhof (HSE06) functional [111], which uses an error-function-screened Coulomb potential to calculate the exchange portion of the energy and can be expressed as

$$E_{xc} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}. \quad (2.36)$$

where $E_x^{\text{HF,SR}}$ denotes the short-range exact exchange from Hartree-Fock theory, whereas $E_x^{\text{PBE,SR}}$ and $E_x^{\text{PBE,LR}}$ are the short and long range interaction from the Perdew-Burke-Ernzerhof (PBE) exchange functional, respectively. E_c^{PBE} represents the correlation energy from PBE functional [112]. Here, α is the fraction of exact exchange (for HSE06, it is set to 0.25), and SR and LR denote short-range and long-range components, respectively. ω is a screening parameter which defines the cutoff distance where the transition from short-range to long-range occurs (typically $\omega = 0.20 \text{ Bohr}^{-1}$).

We note that even using the HSE06 functional for calculations, DFT has only a finite accuracy. The predicted band structures are nevertheless qualitatively correct and

agree well with experiments (and in particular better than functionals in GGA), as recent studies comparing different DFT functionals to calculate quantum emitters in hBN have pointed out, unless a defect includes a multireference character [110, 113, 114].

2.3 Quantum Decoherence in Solid-State Quantum Systems

In contrast to the electronic structure calculations with DFT, this section scopes down to the properties of spin qubits in solid-state quantum systems. Spin qubits in such systems typically involve electron spins and nuclear spins. On one hand, qubits from the spin are advantageous in quantum computing [29], quantum sensing [115], and quantum memory [68, 69]. This addressed spin typically refers to central spin. On the other hand, some nuclear spins that cannot be addressed become environmental nuclear spins, causing quantum decoherence [116]. In this case, increasing the number of nuclear spins tends to enhance quantum decoherence. However, other sources can also induce noise/decoherence, such as lattice vibration from phonons induced by temperature [117, 118], trapped charges induced by paramagnetic defects [119], spin-orbit coupling from the heavy-element materials [120], etc.

To capture quantum decoherence effects, several approaches have been proposed, including a top-down approach, a bottom-up approach, and an approximation such as the cluster expansion [121] and the cluster-correlation expansion (CCE) [122]. The top-down approach involves solving the Lindblad (Markovian) master equation, which assumes that the environment acts as a noisy source [123]. In this framework, the time evolution of the system is resolved by decomposing it into the system's density matrix and the noise's density matrix. This method is particularly useful when the system interacts with its environment in a Markovian manner. In Markovian dynamics, the system's future evolution depends only on its current state and not on its past history [124]. However, this approach has two main limitations: (i) it assumes Markovian dynamics, and (ii) it requires knowledge of the noise behavior of the environment. Markovian assumptions often oversimplify the interactions by ignoring memory effects, and accurately modeling the noise behavior can be challenging. To overcome these limitations, the bottom-up approach, also known as the quantum bath approach, can be employed [124]. This approach involves solving the time evolution of the entire system, which includes both the qubit and its environment, using the Schrödinger equation. In this method, it is essential to know the system Hamiltonian, allowing non-Markovian effects to be considered. This approach does not assume that the environment is a simple noisy source, but rather models it explicitly, capturing the detailed interactions and memory effects. Once the total system's time evolution is determined, the environmental degrees of freedom are traced out to obtain the reduced density matrix, which contains the coherence properties of the system. These coherence properties are found in the

off-diagonal elements of the reduced density matrix.

However, in practical solid-state quantum systems, the Hilbert space dimension of the total Hamiltonian is of the order of 2^N (it can be 3^N if the nuclear spin belongs to a triplet), where N is the number of nuclear spins. For a system with 1000 nuclear spins, this dimension becomes 2^{1000} , which is computationally infeasible to calculate directly. Therefore, approximations are necessary to make the problem tractable. The CCE method offers a structured way to manage this complexity by truncating the expansion at a certain cluster size, making the calculations feasible while retaining essential physics [122]. These approximations and their applications will be discussed in this section.

Before diving into the details of quantum decoherence in a solid-state system, some fundamentals of decoherence [122, 124, 125] are summarized as follows.

2.3.1 Spin-1/2 Decoherence

Considering a quantum system with a spin-1/2 as a central spin under an external magnetic field, the governing Hamiltonian evolves the quantization of the spin according to the magnetic field given by

$$\hat{H}_0 = \hbar\omega_0\hat{S}_z. \quad (2.37)$$

It is important to note that $\hbar$ is set to 1 for simplicity throughout all sections below. The corresponding general solution becomes

$$|\theta, \phi\rangle \equiv \cos\left(\frac{\theta}{2}\right)|\uparrow\rangle + \sin\left(\frac{\theta}{2}\right)e^{i\phi}|\downarrow\rangle, \quad (2.38)$$

where spins up $|\uparrow\rangle$ and down $|\downarrow\rangle$ are the eigenstates of the spin in the z direction ($\hat{S}_z$), whereas θ and ϕ are polar and azimuth angles in the Bloch sphere, as depicted in Fig. 2.4. Being isolated from the environment, quantum coherence is fully preserved, implying that the central spin undergoes the unitary evolution; $|\theta, \phi\rangle \rightarrow e^{i\hat{H}_0 t}|\theta, \phi\rangle = |\theta, \phi + \omega_0 t\rangle$. In contrast, when the system is coupled with the environment, the coherence will be destroyed. The central spin then undergoes the non-unitary evolution to transform a pure state into a mixed state. In order to visualize and quantify such decoherence, the density operator $\hat{\rho} = |\psi\rangle\langle\psi|$ can be implemented. In this case, the density operator can be expressed in terms of a quantization basis as a 2×2 density matrix

$$\hat{\rho} = \begin{bmatrix} \rho_{\uparrow\uparrow} & \rho_{\uparrow\downarrow} \\ \rho_{\downarrow\uparrow} & \rho_{\downarrow\downarrow} \end{bmatrix}, \quad (2.39)$$

where the diagonal terms $\rho_{\uparrow\uparrow}$ and $\rho_{\downarrow\downarrow}$ account for the population of each eigenstate or the net longitudinal magnetization whereas the off-diagonal matrix terms $\rho_{\downarrow\uparrow} = \rho_{\uparrow\downarrow}^*$ account for the phase correlation between each eigenstate or the coherence properties of the ensemble. The central spin can then be visualized through the Bloch vector $\hat{\mathbf{S}}(t)$, defined as

$$2\langle\hat{\mathbf{S}}(t)\rangle \equiv 2\text{Tr}[\hat{\mathbf{S}}\hat{\rho}(t)], \quad (2.40)$$

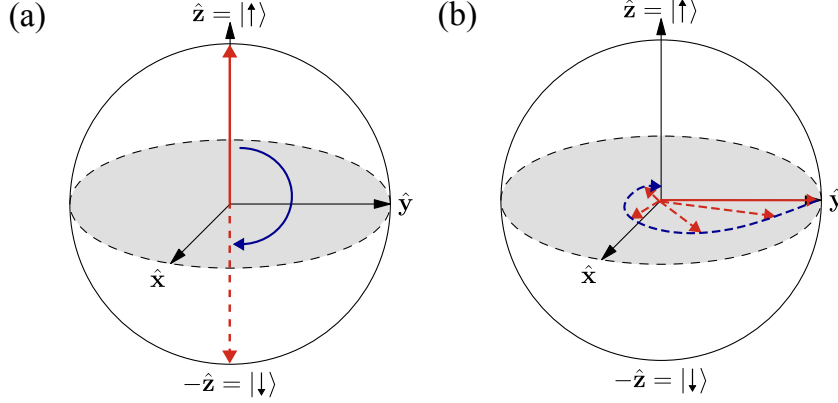


Figure 2.4: Evolution of the central spin represented by the Bloch vector under (a) unitary evolution from spin relaxation process and (b) non-unitary evolution from spin dephasing.

where

$$\hat{\rho}(t) = \frac{\hat{I}}{2} + \langle \hat{\mathbf{S}}(t) \rangle \cdot \hat{\boldsymbol{\sigma}}. \quad (2.41)$$

The identity matrix is denoted by $\hat{I}$ and the Pauli matrices are denoted by $\hat{\boldsymbol{\sigma}} = (\sigma_x, \sigma_y, \sigma_z)^T$. Note that our Bloch vector is expressed in terms of the spin-1/2 operator $\hat{\mathbf{S}}$. Then our expression is slightly different from the standard one, which is $\hat{\rho}(t) = \frac{1}{2} (\hat{I} + \mathbf{r}(t) \cdot \hat{\boldsymbol{\sigma}})$ where $\mathbf{r}(t) = 2 \langle \hat{\mathbf{S}}(t) \rangle$.

Suppose the magnetic field is applied in the z direction; if the length of the Bloch vector is preserved, as visualized in Fig. 2.4(a), this becomes a unitary evolution. This can be explained by the Zeeman Hamiltonian in Eq. (2.37) governing the Bloch vector to precess at the Larmor frequency, which can be mathematically expressed as $\langle \dot{\mathbf{S}}(t) \rangle = \omega_0 \mathbf{e}_z \times \langle \hat{\mathbf{S}}(t) \rangle$ with $\langle \dot{S}_z(t) \rangle = 0$ and $\langle \dot{S}_\pm(t) \rangle = -i\omega_0 \langle \hat{S}_\mp(t) \rangle$, where $S_\pm \equiv S_x \pm iS_y$. This precession thus only transforms a pure state into another pure state. However, if the length of the Bloch vector is shrunk, as depicted in Fig. 2.4(b), this is a so-called non-unitary evolution. In this case, spin decoherence turns a fully coherent pure state into an incoherent mixture of different pure states.

2.3.2 Classification of Decoherence

Decoherence can be introduced by distinct sources, e.g., lattice vibration, trapped charges, spin-orbit coupling, and environmental nuclear spins. The first three noises can be resolved by low-temperature operation [117, 118], device engineering [119], and light-element materials [120], respectively. However, the nuclear spins become a relevant noise source and are not easily resolved. More precisely, the environmental nuclear spins are not properly addressed for qubits. These will form a magnetic environment and consequently decohere the central spins through two different mechanisms: spin

relaxation and spin dephasing [116].

Spin Relaxation

Spin relaxation or the so-called longitudinal relaxation or T_1 process describes the changes in the diagonal populations in the density matrix defined as the longitudinal component of the Bloch vector $r_z = 2\langle\hat{S}_z(t)\rangle$ [124]. Considering the density matrix from Eq. (2.41)

$$\hat{\rho}(t) = \begin{bmatrix} \frac{1}{2} + \langle\hat{S}_z(t)\rangle & \langle\hat{S}_x(t)\rangle - i\langle\hat{S}_y(t)\rangle \\ \langle\hat{S}_x(t)\rangle + i\langle\hat{S}_y(t)\rangle & \frac{1}{2} - \langle\hat{S}_z(t)\rangle \end{bmatrix} = \begin{bmatrix} \rho_{\uparrow\uparrow}(t) & \rho_{\uparrow\downarrow}(t) \\ \rho_{\downarrow\uparrow}(t) & \rho_{\downarrow\downarrow}(t) \end{bmatrix}. \quad (2.42)$$

The longitudinal component $2\langle\hat{S}_z(t)\rangle = \rho_{\uparrow\uparrow}(t) - \rho_{\downarrow\downarrow}(t)$. When the environmental noise induces this decoherence, it can embrace the spin flipping between $|\uparrow\rangle$ and $|\downarrow\rangle$ of the central spin. Then, the central spin energy is changed by an amount of ω_0 from the Hamiltonian in Eq. (2.37) to obey the energy conservation. Focusing only on the memoryless random central spin flip, the noises fluctuate so rapidly that they cannot retain a memory of their past states (Markovian noise). This implies that the central spin flips occur in a manner that only depends on the current state of the spin and not on its history.

Suppose a density operator $\hat{\rho}(t)$ is a pure superposition that can be decomposed to the spin components up and down: $|\psi\rangle \equiv |\psi_\uparrow\rangle + |\psi_\downarrow\rangle$. When the environment absorbs energy ω_0 from the central spin, it can cause a random jump in the spin state. For example, if the central spin is in the state $|\uparrow\rangle$, the environment can absorb energy and induce the spin to flip to the state $|\downarrow\rangle$. This process is known as energy dissipation or relaxation. Assume that this random jump from $|\uparrow\rangle$ to $|\downarrow\rangle$ occurs at a constant rate γ . After the small interval dt , the $|\psi_\uparrow\rangle$ is incoherently jumped to $\hat{S}_-|\psi_\uparrow\rangle = \hat{S}_-|\psi\rangle = |\psi_\downarrow\rangle$ with a probability γdt while the component $|\psi_\downarrow\rangle$ remains intact. The central spin state at the later time $t + dt$ can thus be expressed in terms of the density matrix

$$\hat{\rho}(t + dt) = \hat{M}_1\hat{\rho}(t)\hat{M}_1^\dagger + \hat{M}_0\hat{\rho}(t)\hat{M}_0^\dagger, \quad (2.43)$$

which accounts for the incoherent mixture of the collapsed (spin flip) and non-collapsed (no spin flip) components. In other words, $\hat{M}_1$ is an operator describing the process where a spin flip occurs, whereas $\hat{M}_0$ is an operator describing the process where no spin flip occurs. The former can be written as

$$\hat{M}_1|\psi\rangle \equiv \sqrt{\gamma dt}\hat{S}_-|\psi\rangle, \quad (2.44)$$

where $\hat{S}_-$ is the spin lowering operator ($\hat{S}_-|\uparrow\rangle = |\downarrow\rangle$ and $\hat{S}_-|\downarrow\rangle = 0$) whereas the latter can be expressed as

$$\hat{M}_0|\psi\rangle \equiv |\psi_\downarrow\rangle + \sqrt{1 - \gamma dt}|\psi_\uparrow\rangle \approx e^{-(\gamma dt/2)\hat{S}_-^\dagger\hat{S}_-}|\psi\rangle. \quad (2.45)$$

This evolution represents a weak measurement of the central spin induced by the environment, resulting in two feasible outcomes (which are not known to an observer); that is, the central spin collapses to either $\hat{M}_1 |\psi\rangle$ or $\hat{M}_0 |\psi\rangle$. The time evolution of $\hat{\rho}(t)$ due to this random spin-flip process can be derived by substituting $\hat{M}_0 \approx I - \frac{\gamma dt}{2} S_-^\dagger S_-$ and $\hat{M}_1 = \sqrt{\gamma dt} S_-$ in Eq. (2.43).

$$\hat{\rho}(t + dt) = \gamma dt S_- \rho(t) S_-^\dagger + (I - \frac{\gamma dt}{2} S_-^\dagger S_-) \rho(t) (I - \frac{\gamma dt}{2} S_-^\dagger S_-). \quad (2.46)$$

By neglecting higher-order terms in dt since dt is infinitesimally small, we get

$$\begin{aligned} \hat{\rho}(t + dt) &= \gamma dt S_- \rho(t) S_-^\dagger + \rho(t) - \frac{\gamma dt}{2} (S_-^\dagger S_- \rho(t) + \rho(t) S_-^\dagger S_-) \\ \hat{\rho}(t + dt) - \rho(t) &= \gamma dt S_- \rho(t) S_-^\dagger - \frac{\gamma dt}{2} (S_-^\dagger S_- \rho(t) + \rho(t) S_-^\dagger S_-) \\ \frac{\hat{\rho}(t + dt) - \rho(t)}{dt} &= \gamma S_- \rho(t) S_-^\dagger - \frac{\gamma}{2} (S_-^\dagger S_- \rho(t) + \rho(t) S_-^\dagger S_-) \\ \dot{\rho}(t)_{|\uparrow\rangle \rightarrow |\downarrow\rangle} &= \gamma \left[S_- \rho(t) S_-^\dagger - \frac{1}{2} (S_-^\dagger S_- \rho(t) + \rho(t) S_-^\dagger S_-) \right] \end{aligned} \quad (2.47)$$

This can then be rewritten as

$$[\dot{\rho}(t)]_{|\uparrow\rangle \rightarrow |\downarrow\rangle} \equiv \frac{\hat{\rho}(t + dt) - \hat{\rho}(t)}{dt} = \gamma \mathcal{D} [\hat{S}_-] \hat{\rho}(t), \quad (2.48)$$

where $\mathcal{D}[\hat{L}] \hat{\rho} \equiv \hat{L} \hat{\rho} \hat{L}^\dagger - \{\hat{L}^\dagger \hat{L}, \hat{\rho}\} / 2$ is the standard Lindblad form for dissipation.

While the environment absorbing energy from the central spin can induce the random jump, the environment can also deliver energy to the central spin, causing a reverse spin flip from $|\downarrow\rangle$ to $|\uparrow\rangle$. This process requires the environment to provide the energy ω_0 necessary for the spin flip. However, when the system is in thermal equilibrium, the probability of the absorbing and delivering energy occurring is not equal. The reverse process, where the environment delivers energy to the central spin, occurs less frequently than the process where the environment absorbs energy. The difference in the rates of these processes is determined by a Boltzmann factor, $e^{-\beta \omega_0}$. Here, β is defined as $\beta \equiv \frac{1}{k_B T_{\text{env}}}$, where k_B is the Boltzmann constant, and T_{env} is the temperature of the environment. For instance, at absolute zero temperature ($T_{\text{env}} = 0$), the environment lacks the energy to provide ω_0 for the spin-flip from $|\downarrow\rangle$ to $|\uparrow\rangle$ as it is in the ground state. As a result, this reverse process is effectively blocked at zero temperature because the environment cannot supply the necessary energy. Combining these two spin-flipping processes ($|\uparrow\rangle$ to $|\downarrow\rangle$ and $|\downarrow\rangle$ to $|\uparrow\rangle$), the evolution of central spin induced by the environment is described by

$$[\dot{\rho}(t)]_{T_1} = \gamma \left(\mathcal{D} [\hat{S}_-] + e^{-\beta \omega_0} \mathcal{D} [\hat{S}_+] \right) \hat{\rho}(t) = \begin{bmatrix} -\frac{\rho_{\uparrow\uparrow}(t) - \rho_{\uparrow\uparrow}^{\text{eq}}}{T_1} & -\frac{\rho_{\uparrow\downarrow}(t)}{2T_1} \\ -\frac{\rho_{\downarrow\uparrow}(t)}{2T_1} & -\frac{\rho_{\downarrow\downarrow}(t) - \rho_{\downarrow\downarrow}^{\text{eq}}}{T_1} \end{bmatrix}, \quad (2.49)$$

where $T_1 \equiv [(1 + e^{\beta\omega_0})\gamma]^{-1}$ is denoted as the spin relaxation time, which governs the central spin into thermal equilibrium with the environment. The thermal equilibrium is written by

$$\hat{\rho}^{eq} \equiv \frac{e^{-\beta\hat{H}_0}}{\text{Tr}e^{-\beta\hat{H}_0}} = \begin{bmatrix} \frac{1}{1+e^{\beta\omega_0}} & 0 \\ 0 & \frac{e^{\beta\omega_0}}{1+e^{\beta\omega_0}} \end{bmatrix}. \quad (2.50)$$

During the spin relaxation process, the population or the diagonal elements and the off-diagonal elements decay exponentially to their respective thermal equilibrium values. However, the off-diagonal coherence decays at a rate that is only half the rate of the population decay, which introduces the so-called spin dephasing. Therefore, spin relaxation (T_1 process) is invariably associated with spin dephasing (T_2 process), which is explained below.

Spin dephasing

Spin dephasing indicates the decay of the off-diagonal coherence in the density matrix or the so-called transverse relaxation, corresponding to the transverse components of the Bloch vector: $\langle \hat{S}_x(t) \rangle = \text{Re}\{\rho_{\uparrow\downarrow}(t)\}$ and $\langle \hat{S}_y(t) \rangle = -\text{Im}\{\rho_{\uparrow\downarrow}(t)\}$ [124]. In principle, the pure dephasing (without spin relaxation) can be classified into two types: (1) true decoherence (T_ϕ process) and (2) inhomogeneous dephasing (T_2^* process) [125].

First, T_ϕ process is induced by the random jumps of the relative phase between eigenstates $|\uparrow\rangle$ and $|\downarrow\rangle$ of the central spin. Assuming that the noises lost memory much more rapidly than the spin dephasing, the evolution of central spin becomes memoryless. This leads to the same assumption where the random phase induced by the environment is jumped from $|\psi\rangle$ to $\hat{\sigma}_z|\psi\rangle$ at a constant rate γ_ϕ . At the short time later, the central spin state becomes an incoherent mixture explained by the density matrix

$$\hat{\rho}(t + dt) = \hat{M}_c \hat{\rho}(t) \hat{M}_c^\dagger + \hat{M}_{nc} \hat{\rho}(t) \hat{M}_{nc}^\dagger, \quad (2.51)$$

which accounts for the mixing of the collapsed (phase flip) and non-collapsed (no phase flip) components. In other words, $\hat{M}_c$ is an operator describing the process where a phase flip occurs, whereas $\hat{M}_{nc}$ is an operator describing the process where no phase flip occurs. The former is written as

$$\hat{M}_c |\psi\rangle \equiv \sqrt{\gamma_\phi dt} \hat{\sigma}_z |\psi\rangle, \quad (2.52)$$

while the latter is

$$\hat{M}_{nc} |\psi\rangle \equiv \sqrt{1 - \gamma_\phi dt} |\psi\rangle \approx e^{-(\gamma_\phi dt/2) \hat{\sigma}_z^\dagger \hat{\sigma}_z} |\psi\rangle. \quad (2.53)$$

This incoherent collapse again corresponds to the binary-outcome weak measurement. The central spin evolution can thus be expressed in the standard Lindblad form

$$[\dot{\rho}(t)]_{T_\phi} = \gamma_\phi \mathcal{D}[\hat{\sigma}_z] \hat{\rho}(t) = \begin{bmatrix} 0 & -\frac{\rho_{\uparrow\downarrow}(t)}{T_\phi} \\ -\frac{\rho_{\downarrow\uparrow}(t)}{T_\phi} & 0 \end{bmatrix}, \quad (2.54)$$

where $T_\phi \equiv 1/(2\gamma_\phi)$ is denoted as the pure dephasing time. This implies that, over a timescale T_ϕ , the longitudinal component or the diagonal element of the Bloch vector stays constant. In contrast, the magnitude of the transverse components or the off-diagonal terms decays exponentially during this true decoherence.

Second, T_2^* process originates from the inhomogeneity in an ensemble expressed by the static noises. When subject to static noise, the central spin is evolved under the Hamiltonian $\hat{H}_b = H_0 + \mathbf{b} \cdot \hat{\mathbf{S}}$. Here, the local field $\mathbf{b}$ stays invariant for each individual sample but varies across different samples, following a probability distribution $P(\mathbf{b})$. For any given sample with local field $\mathbf{b}$, the central spin evolves unitarily as $\hat{\rho}_b(t) = e^{-i\hat{H}_b t} \hat{\rho}(0) e^{i\hat{H}_b t}$ (the length is preserved). The Bloch vector, defined as $\langle \hat{\mathbf{S}} \rangle_t = \text{Tr}[\hat{\mathbf{S}} \hat{\rho}_b(t)]$, experiences coherent precession described by

$$\frac{d}{dt} \langle \hat{\mathbf{S}}(t) \rangle_{\mathbf{b}} = (\omega_0 \mathbf{e}_z + \mathbf{b}) \times \langle \hat{\mathbf{S}}(t) \rangle_{\mathbf{b}}. \quad (2.55)$$

The density matrix $\hat{\rho}(t)$ of the ensemble can be written as an average over all samples:

$$\hat{\rho}(t) = \int \hat{\rho}_b(t) P(\mathbf{b}) d\mathbf{b}, \quad (2.56)$$

and the Bloch vector is:

$$\langle \hat{\mathbf{S}}(t) \rangle = \int \langle \hat{\mathbf{S}}(t) \rangle_b P(\mathbf{b}) d\mathbf{b}. \quad (2.57)$$

In theory, the inhomogeneous local field distribution can give rise to both spin relaxation and spin dephasing. Nonetheless, only pure dephasing by the longitudinal noise $\tilde{b}_z$ can also take place in the case that the noise field is much weaker than the external field. Then, the transverse noise components $\tilde{b}_{x,y}$ hardly affect the precession axis from the z -axis because the large energy splitting ω_0 between the spin-up $|\uparrow\rangle$ and spin-down $|\downarrow\rangle$ states suppresses the longitudinal spin relaxation. Different precession frequencies for different samples cause their azimuthal angles $\phi_j(t) = \omega_0 t + b_j t$ to spread out, which causes the transverse Bloch vector components $\langle \hat{S}_\pm(t) \rangle$ to decay. The off-diagonal coherence of inhomogeneous distribution ($L_{\text{inh}}(t)$), with the phase factor $e^{-i\omega_0 t}$ removed, yields

$$L_{\text{inh}}(t) = \int P_{\text{inh}}(b) e^{-ib_z t} db. \quad (2.58)$$

This means that the coherence decays over a timescale $\sim T_2^*$, which is the inverse of the width of the static noise distribution $P_{\text{inh}}(b)$. This type of decay, caused by averaging over static noise, is called T_2^* process. Typically, the noise distribution behaves like a Gaussian function provided by

$$P_{\text{inh}}(b) = \frac{1}{\sqrt{2\pi} b_{\text{rms}}} e^{-\frac{b^2}{2b_{\text{rms}}^2}}. \quad (2.59)$$

The spin coherence of the inhomogeneous dephasing, in turn, decays as

$$L_{\text{inh}}(t) = e^{-(t/T_2^*)^2}, \quad (2.60)$$

with

$$T_2^* = \frac{\sqrt{2}}{b_{\text{rms}}}. \quad (2.61)$$

When considering all sources of decoherence, including unitary evolution, T_1 processes (spin relaxation), and T_ϕ processes (pure dephasing), we assume that the environmental noises fluctuate so rapidly that they lose their memory much faster than the central spin can decohere [124]. Under this assumption, the time evolution of the density matrix $\hat{\rho}_b(t)$ of the central spin is expressed by

$$\dot{\rho}_b(t) = -i[\hat{H}_0 + b\hat{S}_z, \hat{\rho}_b(t)] - \begin{bmatrix} \frac{[\hat{\rho}_b(t)]_{\uparrow\uparrow} - \rho_{\uparrow\uparrow}^{eq}}{T_1} & \frac{[\hat{\rho}_b(t)]_{\uparrow\downarrow}}{T_2} \\ \frac{[\hat{\rho}_b(t)]_{\downarrow\uparrow}}{T_2} & \frac{[\hat{\rho}_b(t)]_{\downarrow\downarrow} - \rho_{\downarrow\downarrow}^{eq}}{T_1} \end{bmatrix}, \quad (2.62)$$

Here, $\hat{H}_0$ is the Hamiltonian of the central spin without any perturbations, and $b\hat{S}_z$ represents the coupling to an external field or noise parameter b , with $\hat{S}_z$ being the spin operator in the z -direction. In this equation, T_1 is the spin relaxation time, which describes the time scale when the central spin relaxes to its equilibrium state ρ^{eq} by exchanging energy with its environment. T_2 is the spin dephasing time, which characterizes the loss of coherence in the off-diagonal terms in the density matrix written as

$$\dot{\rho}_{\uparrow\downarrow}(t) = \frac{-\rho_{\uparrow\downarrow}}{T_2}. \quad (2.63)$$

Hence, T_2 can be correlated with T_1 and T_ϕ by considering with the off-diagonal component of Eqs (2.49) and (2.54); that is,

$$\dot{\rho}_{\uparrow\downarrow}(t)_{\text{total}} = \dot{\rho}_{\uparrow\downarrow}(t)_{T_1} + \dot{\rho}_{\uparrow\downarrow}(t)_{T_\phi} = -\left(\frac{1}{2T_1} + \frac{1}{T_\phi}\right) \rho_{\uparrow\downarrow}(t). \quad (2.64)$$

Mapping Eqs. (2.63) and (2.64), the relation among T_2 , T_1 , and T_ϕ become

$$T_2 = [1/(2T_1) + 1/T_\phi]^{-1} \leq 2T_1, \quad (2.65)$$

where T_ϕ is the pure dephasing time, representing dephasing processes that do not involve energy exchange with the environment. The inequality $T_2 \leq 2T_1$ indicates that dephasing can never be slower than twice the relaxation time [124, 125]. It is worth noting that the simplified formula in Eq. (2.65) aims to elucidate the primary mechanisms affecting coherence decay, particularly those associated with pure dephasing (T_ϕ), while setting aside additional complexities introduced by T_2^* , which encompasses broader environmental influences such as magnetic field inhomogeneities. Thus, the exclusion of T_2^* from this relation allows for a clearer theoretical exploration of the fundamental limits and interactions between relaxation mechanisms and pure dephasing phenomena.

Considering the presence of inhomogeneous broadening, which results from variations in the local environment of the spins, the observed density matrix $\hat{\rho}(t)$ must be

obtained by averaging the density matrix $\hat{\rho}_b(t)$ over the distribution of the noise parameter b . This averaging accounts for the variations in the local fields that different spins experience. It is essential to recognize that while spin relaxation theoretically limits the spin dephasing time with the relation (via the relation $T_2 \leq 2T_1$), in practice, the T_2 of the central spin is often much shorter than T_1 . This discrepancy arises because T_2 is also limited by pure dephasing processes (denoted by T_ϕ and T_2^*), which are typically more significant than the relaxation processes. T_ϕ contributes to the decay of coherence without energy relaxation, and T_2^* represents the additional inhomogeneous broadening effects that further shorten the observable coherence time.

2.3.3 Spin Hamiltonian

In the previous section, the difference between T_1 and T_2 and extracting them from the density matrix are elaborated. In this section, we formulate an actual physical system for a solid-state spin qubit in hBN host material. Unlike the spin-1/2 system, hBN defects should have a spin-1 state (triplet state) to be applicable to a wider range of quantum technologies. The reason pertains to the coherent control explained in Sec. 3.2.2 in Chapter 3.

Fig. 2.5 exemplifies the feasible interactions that can exist in V_B^{-1} defect, and this can be described by the following spin Hamiltonian

$$H = H_{\text{central}} + H_{\text{interaction}} + H_{\text{bath}}, \quad (2.66)$$

where H_{central} represents the Hamiltonian for the central spin; $H_{\text{interaction}}$ represents the Hamiltonian for the interactions between the central spin and the bath spins; and H_{bath} represents the Hamiltonian for the bath spins. This total Hamiltonian can be further expanded to

$$\hat{H} = \mu_B \mathbf{B} \cdot g \mathbf{S} + \mathbf{S} \cdot D \mathbf{S} + \sum_n \mathbf{S} \cdot A_n \mathbf{I}_n + \sum_n \gamma_n \mathbf{B} \cdot \mathbf{I}_n + \sum_{i < j} \mathbf{I}_i \cdot J_{ij} \mathbf{I}_j + \sum_n \mathbf{I}_n \cdot P_n \mathbf{I}_n, \quad (2.67)$$

where $\mathbf{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ and $\mathbf{I} = (\hat{I}_x, \hat{I}_y, \hat{I}_z)$ denote the central spin and bath spin operators, respectively. The vector $\mathbf{B} = (B_x, B_y, B_z)$ represents the external magnetic field. In the subsequent discussion, each interaction in the spin Hamiltonian will be explained in detail.

Electron Zeeman interaction

The electron Zeeman interaction describes the interaction between the magnetic moment of an electron (in this case, it is a central spin) and an external magnetic field. This interaction can be expressed by

$$\hat{H}_Z = \mu_B \mathbf{B} \cdot g \mathbf{S}, \quad (2.68)$$

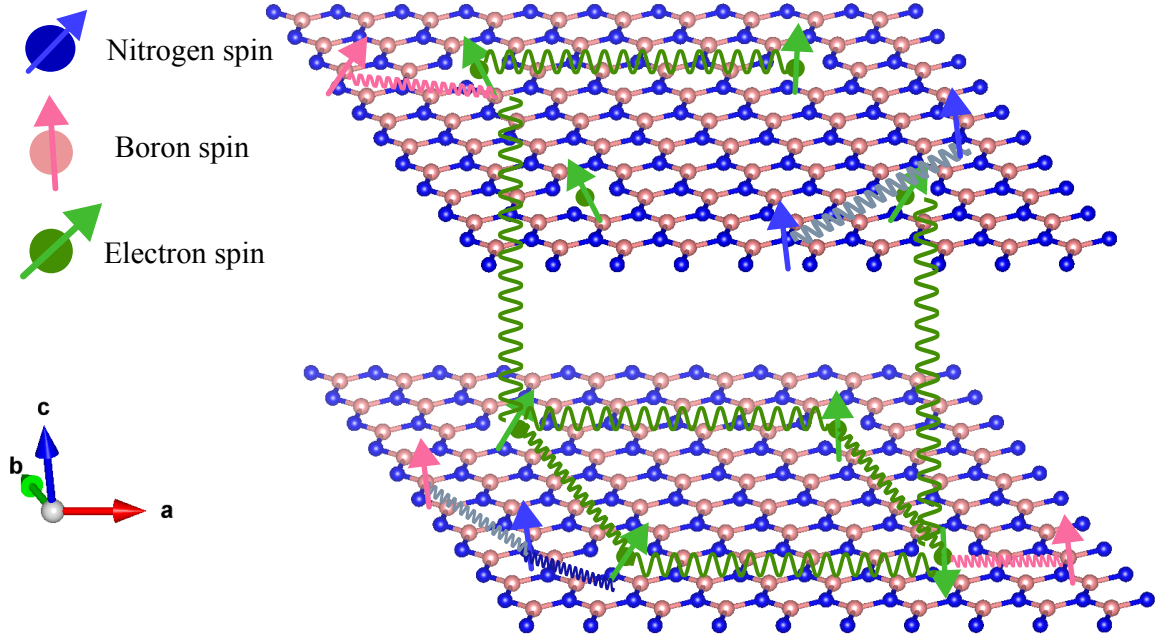


Figure 2.5: Possible interactions in a V_B^{-1} defect in hBN, consisting of electron-electron spin interaction shown by the green wavy line (the first two terms in Eq. (2.67)), the electron-nuclear spin interactions shown by the blue and pink wavy line (the third term in Eq. (2.67)), and the nuclear-nuclear spin interaction between the nitrogen nuclear spin and boron nuclear spin and themselves shown by the gray wavy line (the remaining terms in Eq. (2.67)).

where μ_B is Bohr magneton representing the magnitude of the magnetic moment of an electron due to its spin $\mu_B = e\hbar/(2m_e)$. g is a dimensionless tensor that accounts for the anisotropic nature of the interaction between the electron spin and the magnetic field. It has contributions from both the electron spin and orbital angular momentum interactions with the magnetic field. In isotropic cases, g can be taken as a scalar, typically close to 2 for a free electron. $\mathbf{S}$ is the spin operator for a central spin.

Electron zero field splitting

This term arises when the spin Hamiltonian does not commute with the spin operator $\mathbf{S}$, causing energy splitting even in the absence of an external magnetic field.

$$\hat{H}_{ZFS} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}. \quad (2.69)$$

The tensor $\mathbf{D}$ characterizes the zero-field splitting (ZFS), which can be represented as a 3×3 matrix. Since the tensor is symmetric (meaning $D_{ij} = D_{ji}$) and traceless, the

ZFS Hamiltonian can be simplified to

$$\hat{H}_{ZFS} = D \left(S_z^2 - \frac{S(S+1)}{3} \right) + E(S_x^2 - S_y^2). \quad (2.70)$$

The D term represents the axial (or uniaxial) component of the zero field splitting and is associated with the difference in energy between $m_s = \pm 1$ and $m_s = 0$ spin states. The E term represents the transverse component of the ZFS and is associated with anisotropic effects that lead to additional splitting of the energy levels.

Hyperfine interaction

It describes the interaction between the magnetic moment of the electron (due to its spin; $\mathbf{S}$) and the magnetic moment of the nucleus (due to n -th nuclear spin; $\mathbf{I}_n$), implying the coupling between electron and nuclear spins. In fact, this interaction always takes place in a solid-state system. Also, the nearest neighboring nuclear spin is always the most influenced due to the highest hyperfine coupling. The far nuclear spins from an electron spin normally have a weak hyperfine interaction. This becomes one of the criteria for determining the structure size to attain the hyperfine tensors from DFT. To understand its physical meaning, the Hamiltonian is expressed as

$$\hat{H}_{HFI} = \sum_n \mathbf{S} \cdot A_n \mathbf{I}_n. \quad (2.71)$$

The hyperfine coupling tensor A_n accounts for three different interactions. First, the isotropic (contact) part represents scalar interaction that is independent of direction and arises due to the Fermi contact interaction between the electron and the nucleus (an overlap between electron and nuclear wavefunctions at the nucleus).

$$(A_n^{iso})_{ab} = -\delta_{ab} \frac{\mu_0 \gamma_e \gamma_n \hbar^2}{3S} n_s(\mathbf{R}_n). \quad (2.72)$$

Second, the anisotropic (dipolar) part describes the anisotropic interaction between the electron and nuclear spins due to their relative orientations and distances. It originates from the dipole-dipole interaction between the magnetic moments of the electron and the nucleus.

$$(A_n^{dip})_{ab} = \frac{\mu_0 \gamma_e \gamma_n \hbar^2}{2S 4\pi} \int \left[\frac{|\mathbf{r} - \mathbf{R}_n| \delta_{ab} - 3(\mathbf{r} - \mathbf{R}_n)_a (\mathbf{r} - \mathbf{R}_n)_b}{|\mathbf{r} - \mathbf{R}_n|^5} \right] n_s(\mathbf{r}) d\mathbf{r}, \quad (2.73)$$

where γ_e and γ_n are the gyromagnetic ratios of the central spin and bath spin; n_s is the spin density; S is the spin quantum number; μ_0 is the permeability of free space; and $\mathbf{R}_n$ denotes the position of the n -th nucleus.

Last, the spin-orbit coupling part represents the spin-orbit coupling contribution to the hyperfine interaction. This component arises from the interaction between the

electron spin and the magnetic field generated by the nuclear spin's orbital motion.

Considering the components in the hyperfine coupling tensor A_n , the longitudinal component ($A_{\parallel}$) is the component that interacts parallel to the external magnetic field. This component primarily affects the splitting of energy levels along the z axis. Experimentally, this can be measured and observed in electron paramagnetic resonance (EPR), especially the number of EPR peaks and linewidth. Turning to the transverse hyperfine coupling component ($A_{\perp}$), this influences the transitions between different spin states and can also be observed in the EPR spectrum.

Nuclear Zeeman interaction

This describes the interaction between the nuclear magnetic moment $\mathbf{I}_n$ and the external magnetic field $\mathbf{B}$, underlying the splitting of nuclear energy levels. It is governed by

$$\hat{H}_{NZ} = \gamma_n \mathbf{B} \cdot \mathbf{I}_n, \quad (2.74)$$

where γ_n is the gyromagnetic ratio of the n -th nucleus, which determines how strongly its magnetic moment responds to an applied magnetic field.

J-coupling and dipolar coupling

The J-coupling (scalar coupling) interaction between pairs of nuclei i and j arises due to the magnetic dipole-dipole interaction between the nuclei with non-zero spins ($\mathbf{I}_i$ and $\mathbf{I}_j$) in close proximity and is governed by

$$\hat{H}_{nn} = \mathbf{I}_i \cdot J_{ij} \mathbf{I}_j, \quad (2.75)$$

The term J_{ij} represents the coupling interaction between nuclei i and j , which depends on their relative positions and their chemical environment. It consists primarily of two components: (1) dipolar coupling for both electron and nuclear spin baths, and (2) nuclear spin bath alone.

The direct dipolar coupling, which models interactions between two bath spins as point dipoles, is expressed as:

$$\hat{H}_{dd} = \frac{\mu_0}{4\pi} \gamma_i \gamma_j \frac{\hbar^2}{r_{ij}^3} \left[\frac{I_i I_j}{2} - \frac{3(\mathbf{I}_i \cdot \mathbf{r}_{ij})(\mathbf{I}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right],$$

where γ_i and γ_j are the gyromagnetic ratios of nuclei i and j ; μ_0 is the permeability of free space; $\mathbf{r}_{ij}$ is the vector connecting nuclei i and j ; and I_i, I_j are the spin operators.

Quadrupole interaction

Quadrupole interaction refers to the electrostatic interaction between a nuclear quadrupole moment and the electric field gradient generated by surrounding charges

or mass distributions. Unlike a dipole moment, which involves a simple separation of charges leading to a vector interaction, a quadrupole moment arises from the distribution of charges or mass that results in a more complex spatial arrangement. The Hamiltonian describing the quadrupole interaction $\hat{H}_Q$ can be expressed as

$$\hat{H}_Q = \mathbf{I}_n \cdot P_n \mathbf{I}_n = \frac{eQ}{6I(2I-1)} \sum_{a,b \in \{x,y,z\}} V_{ab} \left[\frac{3}{2}(I_a I_b + I_b I_a) - \delta_{ab} I(I+1) \right]$$

where Q denotes the nuclear quadrupole moment; e the elementary charge; I the nuclear spin quantum number; V_{ab} the second derivative of the electrostatic potential at the nucleus with respect to the coordinates a and b ; I_a and I_b the components of the nuclear spin operator.

2.3.4 Cluster Correlation Expansion

As discussed earlier, the coherence of a qubit is often characterized by two key timescales: T_1 and T_2 . To calculate these coherence times, the spin Hamiltonian needs to be constructed. From the spin Hamiltonians in Eq. (2.67), exact solutions are often infeasible due to the exponential growth of the state space with the number of spins involved. For instance, within 5 nm from a defect in a solid-state system like SiC, NV⁻, and hBN, it contains greater than 1000 nuclear spins [126]. Then, the dimension of the Hilbert space of the Hamiltonian is increased up to 2^{1000} for the nuclear spin-1/2. It can be even larger if the nucleus belongs to spin-1 or others. The Hamiltonian is difficult to be diagonalized exactly. This is a direct consequence of the high-dimensional nature of quantum systems, which makes the exact treatment of interactions computationally prohibitive. Some approximation methods are therefore needed.

The CCE method is one of the approximation approaches to simulate the quantum decoherence dynamics in a finite spin bath [122, 127, 128]. This approximation method involves truncating the system into clusters of spins and considering only the correlations within each cluster up to a certain size. The key idea is to capture the most significant correlations without dealing with the full complexity of the entire system. Some regimes are indicated as follows.

Pure dephasing regime $T_1 \gg T_2$

In this regime, the T_1 is so long that it is independent of T_2 . Thus, the decoherence can be determined by the off-diagonal elements of the qubit's density matrix [129]. Assume that the initial state of a qubit is $|\psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle + e^{i\phi}|1\rangle)$, the coherence can be quantified by the coherence function ($L(t)$), which computes the loss of the relative phase between the $|0\rangle$ and $|1\rangle$ states with the following equation

$$L(t) = \frac{\langle 1 | \hat{\rho}_S(t) | 0 \rangle}{\langle 1 | \hat{\rho}_S(0) | 0 \rangle} = \frac{\langle \hat{\sigma}_-(t) \rangle}{\langle \hat{\sigma}_-(0) \rangle}, \quad (2.76)$$

where $\hat{\rho}_S(t)$ denotes the central-spin density matrix, and $|0\rangle$ and $|1\rangle$ are its qubit levels. In a solid-state quantum system, the qubit can be the coupled states between electron and nuclear spins such as $|m_s = 0, m_I = 1/2\rangle$ and $|m_s = 0, m_I = -1/2\rangle$ if the electron spin is from a defect with the triplet and the nuclear spin belongs to spin-1/2. Instead of solving the Schrödinger equation by diagonalizing the total spin Hamiltonian and tracing out the degrees of freedom from the bath, the CCE approach can be applied here to factorize the spin-bath decoherence into a set of clusters which still reflect the same interaction as that in the total Hamiltonian but reduce the complexity and dimension significantly. Then the coherence function becomes [122, 127, 128]

$$L(t) = \prod_C \tilde{L}_C = \prod_i \tilde{L}_{\{i\}} \prod_{i < j} \tilde{L}_{\{ij\}} \cdots, \quad (2.77)$$

where $\tilde{L}_{\{C\}}$ is the coherence function of the qubit influenced by the interaction with the bath spin in an indicated cluster C . This coherence function can be factorized by the order of cluster approximation. For instance, the first-order correlation cluster expansion (CCE-1) accounts for the contribution of a single bath spin i to the central spin, which is computed by

$$\tilde{L}_{\{i\}} = \frac{L_{\{i\}}}{\tilde{L}_{\{0\}}}, \quad (2.78)$$

where $\tilde{L}_{\{i\}}$ is the contribution from the single bath spin i ; and $\tilde{L}_{\{0\}} = L_{\{0\}}$ is the phase factor of the free evolution of the central spin. This implies that there is interaction between the nuclear spins and the central electron spin, but direct interactions between nuclear spins (nuclear-nuclear interactions) are not explicitly included.

In the CCE-2 approximation, each cluster contains two nuclear spins, allowing for the additional influence of nuclear-nuclear spin interaction $L_{\{ij\}}$ to be included. In other words, the interaction between the nuclear spins and the central electron spin as well as the direct interaction between nuclear spins are explicitly included. Its coherence function is written as

$$\tilde{L}_{\{ij\}} = \frac{L_{\{ij\}}}{\tilde{L}_{\{0\}} \tilde{L}_{\{i\}} \tilde{L}_{\{j\}}}, \quad (2.79)$$

where $\tilde{L}_{\{ij\}}$ is the irreducible contribution from the spin pair i, j . In the CCE-3 approximation, in addition to the aforementioned interaction, the nuclear-nuclear interaction of up to three nuclear spins is taken into account.

Next, the coherence function can be obtained by the two following techniques: conventional CCE [122] and generalized CCE (gCCE) [130]. The conventional CCE simplifies the modeling of decoherence by projecting the total Hamiltonian of the system onto the qubit's basis states. This results in two effective Hamiltonians that describe the bath's dynamics conditioned on the qubit being in either of its basis states, typically $|0\rangle$ and $|1\rangle$. The total Hamiltonian is expressed as

$$H_{\text{total}} = |0\rangle \langle 0| \otimes H_{\text{eff}}^{(0)} + |1\rangle \langle 1| \otimes H_{\text{eff}}^{(1)}, \quad (2.80)$$

where $H_{\text{eff}}^{(0)}$ and $H_{\text{eff}}^{(1)}$ are the effective Hamiltonians of Eq. (2.67) acting on the bath when the qubit is in the states $|0\rangle$ and $|1\rangle$. This consequently contains an approximation based on the perturbation theory. The system's evolution is then computed separately for these states, and the coherence function is determined by

$$L_C(t) = \text{Tr} \left[U_C^{(0)}(t) \hat{\rho}_C U_C^{(1)\dagger}(t) \right], \quad (2.81)$$

where $U_C^{(0/1)}(t) = e^{-iH_{\text{eff}}^{(0/1)}t}$ are the time propagators for the clusters in the presence of the qubit states and $\hat{\rho}_C$ denotes the density matrix of an initial state in the bath spin cluster C . While this approach is computationally efficient and captures the leading-order effects of decoherence, it has limitations in accurately describing complex interactions. Specifically, it may miss higher-order correlations and entanglement between the qubit and the bath since it treats the qubit-bath interactions indirectly [122, 124, 129].

In contrast, gCCE method includes the central spin (qubit) directly within each cluster's Hamiltonian. This means that instead of projecting the Hamiltonian onto qubit states, the qubit's degrees of freedom are explicitly modeled within the same framework as the bath spins. The combined Hamiltonian H follows Eq. (2.67). This comprehensive approach allows for the full joint evolution of the qubit and bath, capturing detailed dynamics such as entanglement, non-Markovian effects, and higher-order correlations. The coherence function of the cluster C is given by

$$L_C(t) = \text{Tr}_{bc} \left[U_C(t) \rho_{bc} U_C^\dagger(t) \right], \quad (2.82)$$

where $U_C(t) = e^{-iHt}$ is the time propagator for the combined cluster, and ρ_{bc} is the initial density matrix of both the bath spin and the central spin. As a result, gCCE can more accurately represent the decoherence process, particularly in systems where complex interactions between the qubit and the environment are significant [122, 124, 129].

Chapter 3

Mechanisms of hBN Color Centers for Quantum Technologies

In contrast to the theoretical schemes discussed in Chapter 2, this chapter focuses on the mechanisms of hexagonal boron nitride (hBN) color centers for quantum technologies. The chapter is structured to provide a comprehensive understanding of the practical implementations and applications of these color centers.

First, the working principles of quantum emitters are detailed. This begins with an explanation of the mechanisms underlying the emission processes in hBN color centers, including the role of electronic transitions and the specific properties of the defects that facilitate these transitions. Important parameters such as emission wavelength, photoluminescence (PL) intensity, and lifetime are discussed to provide a thorough understanding of what makes these emitters suitable for quantum applications.

Second, this chapter explores the working principles of quantum memory and the protocols for storing quantum information, including both Raman and nuclear-spin techniques. The Raman protocol is explained with an emphasis on its ability to manipulate and read out the quantum states using control fields. The nuclear-spin protocol is also discussed, emphasizing the advantages of longer coherence times and the methods for coupling between nuclear spins and electron spins for efficient information storage and retrieval.

Finally, quantum sensing is examined through electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) spectra. The chapter details how these spectroscopic techniques are used to probe the local environment of the hBN color centers. EPR and ODMR provide insights into the magnetic and electric fields, temperature, and strain around the defects. The sensitivity of these methods and their application in high-precision sensing technologies are thoroughly discussed, emphasizing the practical benefits and potential advancements they bring to quantum sensing.

By addressing these topics, this chapter bridges theoretical concepts with practical applications, offering readers a comprehensive understanding of the mechanisms and applications of hBN color centers in quantum technologies. This foundational knowledge is essential before deepening into the results presented in Chapters. 4 - 8 of this

dissertation.

3.1 Quantum Emitter

A quantum emitter is a crucial component for optical quantum technologies as it can generate a reliable single photon, which can be utilized in various applications. As discussed in Chapter 1, hBN color center is chosen, so its mechanisms are summarized below.

3.1.1 Photon Emission Mechanisms

Solid-state single photons can originate from two main mechanisms, namely the defect and the charge ionization. While all of the calculations throughout this dissertation rely on the defect mechanism, the charge-ionization one is also discussed in this section.

Single Photons from Defect States

Solid-state quantum emitters often arise from local alterations in the electronic structure of crystalline materials. Simple instances include point-like defects that create new energy levels within the crystal's bandgap or strains that induce band bending [90, 92, 94, 95]. Focusing specifically on hBN quantum emitters, a single photon emission stems from the states of a point-like defect. Given that hBN has a wide band gap of approximately 6 eV, defect states can be localized in the region between the valence and conduction bands. Ultimately, two defect states, occupied and unoccupied, are favored, forming what is known as a two-level system. The occupied state refers to the defect state where electrons are present, while the unoccupied state corresponds to the absence of electrons. Then, the single photon emission will take place between these occupied and unoccupied states, as illustrated in Fig. 3.1(a). It is worth noting that the charge of a defect remains unchanged throughout this process, and the transition must conserve spin polarizations; for instance, the transition is allowed only from spin-up to spin-up states or from spin-down to spin-down states.

Despite the desired two-level systems in Fig. 3.1(a), there are two additional cases where the transition can also take place, as depicted in Figs. 3.1(b) and (c). The former is the case when the electron is excited to the conduction band, while the latter is the case when the excited electron relaxes to the valence band. In principle, both cases can still emit a single photon if the gap between the defect state and the bands is excitable by an excitation laser [92]. Nonetheless, in practice, both transitions normally fail to produce a single photon with high quantum efficiency as the excited electron likely becomes mobile at the conduction band, whereas exciting only one electron at the valence band is challenging [89, 92].

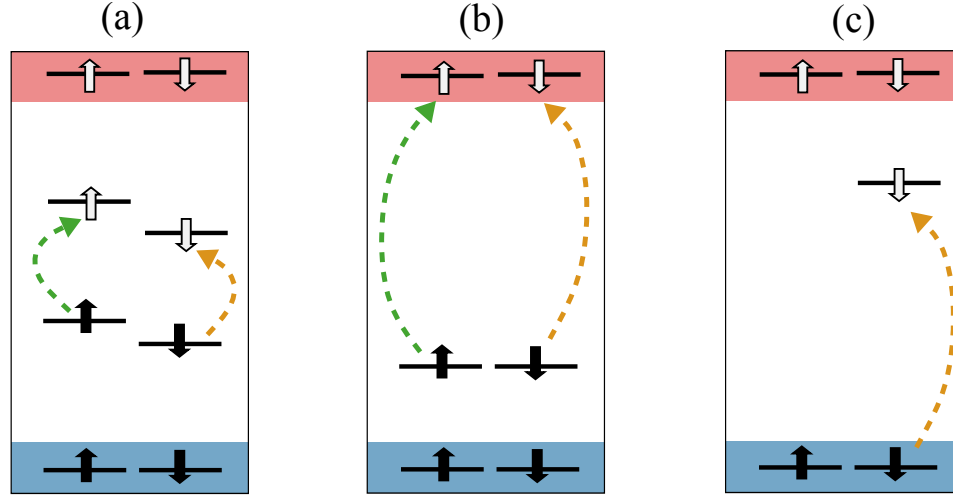


Figure 3.1: Single photon emission from defect states where it takes place at (a) between the occupied and unoccupied defect states, (b) between the conduction band and the occupied defect state, and (c) between the unoccupied defect state and the valence band. The up and down arrows represent the spin up and down polarizations; and the filled and unfilled arrows represent the occupied and unoccupied defect states. The states present in the bandgap region come from defect states. The dashed green and orange curves represent the electronic transition of spin-up and spin-down channels, respectively.

Single Photons from Charge Ionization

Instead of the two-level quantum system, single photons can also be induced by the charge ionization [131]. Fig. 3.2(a) depicts the charge transition level of a defect. Here, a single photon emits a wavelength equal to the energy of the charge transition. In this case, the transition takes place from the negative to neutral charges via the hole capture process $A^{-1} + h^{+} \rightarrow A^0$, as illustrated in Fig. 3.2(b). This is different from the defect mechanism because of the changes in the system's charge.

3.1.2 Zero-Phonon-Line Calculation

A single dominant peak observed in the PL experiment is related to the ZPL, which is defined as the transition without phonons involved. As such, this can be computed from the total energy difference between the ground and excited configurations. However, if a defect features a two-level quantum system in both spin-up and down directions, as depicted in Fig. 3.1(a), the ZPL should be considered separately due to the different total energy of excited configurations between spin up and spin down. This, in turn, yields two different ZPL values for both transitions. It is worth noting that while the ZPL excludes the phonon contribution, the zero-point energy (ZPE) can still exist. For

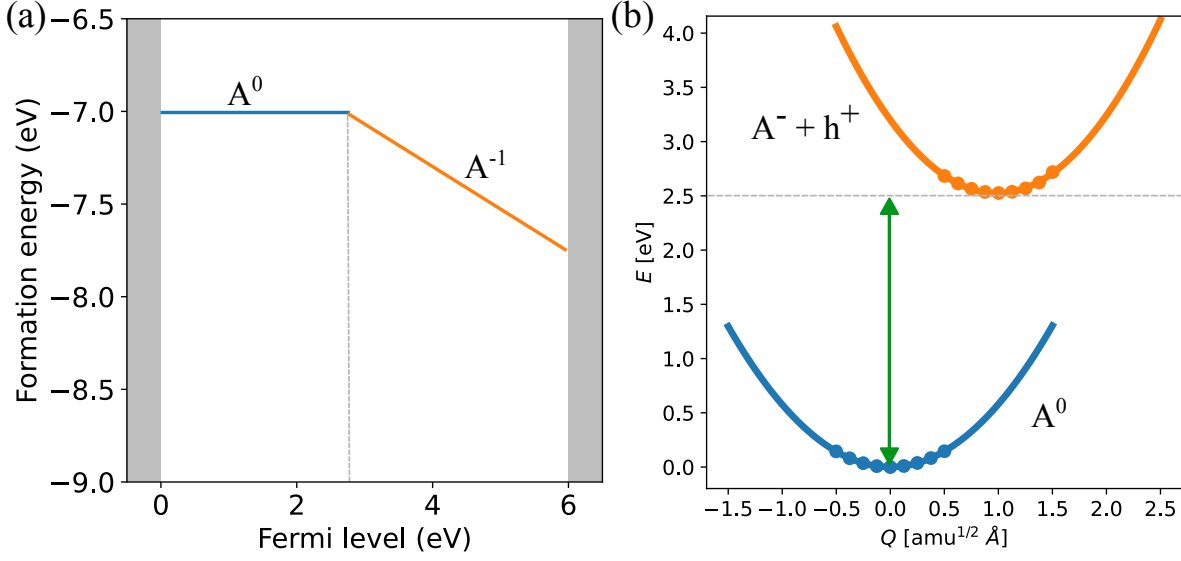


Figure 3.2: Single photon emission from the charge-ionization process ($A^{-1} + h^+ \rightarrow A^0$), where the charge transition level is shown in (a) the defect formation energy and (b) the configuration coordinate diagrams. Note that the charge transition level in (a) corresponds to the zero-phonon line (ZPL) energy represented by the green arrow in (b).

instance, the ZPE difference between ground and excited states in hBN defects is varied from around 1 meV to 0.1 eV, depending on a defect [132, 133]. Our calculations assume that the ZPE between ground and excited states is canceled out when computing the ZPL.

3.1.3 Defect Formation Energy

Then, defect formation energy, denoted by $E^f[D^q]$, is a parameter that can determine the existence possibility of a defect. This can be calculated using the following equation

$$E^f[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{hBN}] - \sum_i n_i \mu_i + q(\epsilon_{\text{vbm}} + \epsilon_{\text{fermi}}) + E_{\text{corr}}(q), \quad (3.1)$$

where $E_{\text{tot}}[D^q]$ is the total energy of hBN with a defect; $E_{\text{tot}}[\text{hBN}]$ is the total energy of pristine hBN; n_i is the number of removing or adding defects; μ_i is a chemical potential of an isolated element; q is the charge of a defect; ϵ_{Fermi} is the Fermi level, representing the chemical potential of the electron reservoir, referenced to the VBM of a pristine hBN, denoted as ϵ_{vbm} ; and $E_{\text{corr}}(q)$ is a correction term accounting for electrostatic interactions due to periodic boundary conditions in charged supercells [134]. If the

defect formation energy yields a negative value, that defect is likely thermodynamically stable. It is important to note that, although the correction term can significantly affect the properties of charged defects, it is not considered in this dissertation since the proposed defects are neutral. As a result, the corresponding optical properties remain unaffected.

3.1.4 Transition Dipole Moments and Polarization

For the defect-defect transition, we consider two dipoles involved in the excitation and emission processes, as depicted in Fig. 3.3: the excitation dipole and the emission dipole. Although both dipoles can be inferred from the group symmetry of each defect, many defects, especially defect complexes, exhibit broken structural symmetry, complicating their classification through group theory. Therefore, it is essential to examine the dipoles explicitly for each individual defect.

The transition dipole moment (TDM) $\boldsymbol{\mu}$ is computed using the wavefunctions of the initial and final states, ψ_i and ψ_f , respectively, as [135]

$$\boldsymbol{\mu} = \frac{i\hbar}{(E_f - E_i)m} \langle \psi_f | \mathbf{p} | \psi_i \rangle, \quad (3.2)$$

where E_i and E_f represent the eigenenergies of the initial and final orbitals, respectively, m denotes the electron mass, and $\mathbf{p}$ is the momentum operator. For the excitation TDM, ψ_i is defined as the wavefunction corresponding to the most stable ground-state configuration, indicated by the lowest total energy of the blue curve in Fig. 3.3, while ψ_f corresponds to the most stable excited-state configuration, represented by the lowest total energy of the red curve in Fig. 3.3. In contrast, for the emission TDM, the roles of ψ_i and ψ_f are reversed and then would yield different values. It is crucial to recognize that ψ_f from the excitation TDM and ψ_i from the emission TDM are typically not the same due to local environment of the defect [135].

As the experiment usually reports the polarizations obtained from the polarization-resolved PL measurements rather than dipole axes, the calculation needs to map the dipole axes to the polarization to ensure the compatibility. To do so, the coordinate system is aligned such that the xy -plane represents the hBN crystal plane. Given that the excitation and emission polarizations are perpendicular to their respective dipoles, we first rotate both dipoles by 90° and then adjust by taking modulo 60° to find the angle relative to the nearest crystal axis. The hexagonal crystal lattice has symmetry with 120° intervals; thus, angles beyond 180° are effectively equivalent. Finally, both dipoles are projected onto the xy -plane to determine the in-plane polarization visibility.

3.1.5 Photoluminescence

For the luminescence calculation [137], it is necessary to determine how atoms in the excited state are displaced relative to their positions in the ground state by calculating

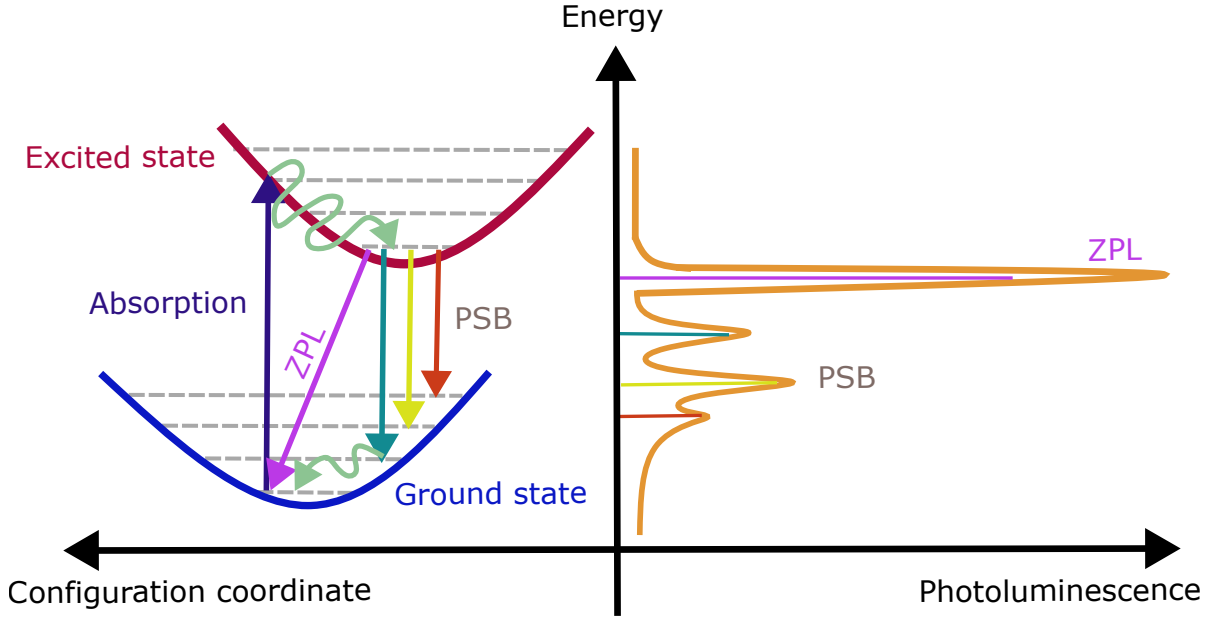


Figure 3.3: A schematic comparison between energy surfaces of occupied (ground) and unoccupied (excited) defect states and the resulting photoluminescence. The (off-resonant) excitation is represented by the absorption (purple) arrow. Then, the radiative transition takes place to relax the excited electron through the ZPL and PSB paths, and meanwhile, the non-radiative transition can also take place via phonon scattering shown by the wavy light green arrows. This figure is adapted with permission from Ref. [136]. Copyright 2023, American Chemical Society.

the configuration coordinate (q_k) defined as

$$q_k = \sum_{\alpha, i \in x, y, z} \sqrt{m_\alpha} (R_{e, \alpha i} - R_{g, \alpha i}) \Delta r_{k, \alpha i}, \quad (3.3)$$

where α and i index the atomic species and spatial coordinates (x, y, z), respectively. Here, m_α denotes the mass of atom species α ; $R_{g, \alpha i}$ and $R_{e, \alpha i}$ represent the stable atomic positions in the ground and excited states, respectively; and $\Delta r_{k, \alpha i}$ is the displacement vector of the atom α in the phonon mode k between the ground and excited states. Subsequently, for a given phonon mode k , the partial Huang-Rhys (HR) factor s_k is determined as

$$s_k = \frac{\omega_k q_k^2}{2\hbar}, \quad (3.4)$$

where ω_k is the frequency of the phonon mode k . This partial HR factor contributes to the total HR factor (S), which can now quantify the electron-phonon coupling, expressed

as

$$S(\hbar\omega) = \sum_k s_k \delta(\hbar\omega - \hbar\omega_k). \quad (3.5)$$

To obtain the PL spectrum, the time-dependent spectral function is computed as

$$S(t) = \int_0^\infty S(\hbar\omega) \exp(-i\omega t) d(\hbar\omega). \quad (3.6)$$

Finally, the PL intensity is derived from

$$L(\hbar\omega) = C\omega^3 A(\hbar\omega), \quad (3.7)$$

where C is a normalization constant, and $A(\hbar\omega)$ is the optical spectral function calculated by

$$A(E_{ZPL} - \hbar\omega) = \frac{1}{2\pi} \int_{-\infty}^\infty G(t) \exp(-i\omega t - \gamma|t|) dt. \quad (3.8)$$

Here, $G(t)$ is the generating function defined as $G(t) = \exp(S(t) - S(0))$, and γ is a fitting parameter, which can be fitted with the experimental PL.

3.1.6 Radiative and Non-radiative Transitions

The radiative transition rate serves as an estimator of the decay pathway with the conserved spin. This quantity can be computed from [138]

$$\Gamma_R = \frac{n_D e^2}{3\pi\epsilon_0 \hbar^4 c^3} E_0^3 \mu_{e-h}^2, \quad (3.9)$$

where e is the electron charge; ϵ_0 is the vacuum permittivity; E_0 is the transition energy defined as the energy difference between the ground and excited states; n_D is the refractive index of the host crystal (for hBN bulk, this is 2.22 and 1.61 for ordinary and extraordinary ray, respectively [139]. As the value strongly depends on the experimental conditions, the refractive index of 1.85 is used for hBN throughout this dissertation [140]); and μ_{e-h}^2 is the modulus square of the dipole moment obtained from Eq. (3.2). Although the refractive index of 1.85 is derived from bulk hBN, it can also be applied to the monolayer, supported by a linear relationship between the optical path length (OPL) and hBN thickness observed from the rigorous coupled-wave analysis simulation [140]. This suggests that the refractive index remains constant across different thicknesses, including bulk and monolayer. Nonetheless, we acknowledge that the refractive index can be sensitive to sample variations and may exhibit some degree of variability.

It is crucial to recognize that in most experimental setups, hBN layers are mounted on a substrate, typically SiO₂. This substrate can appear as the state or possess the charge traps, which may then open additional decay channels. These influence the density of states and also the decay rate of the emitter. Hence, these interactions can

modify the dipole emission pattern and impact the emitter's lifetime (and thus the radiative transition rate) due to the Purcell effect [140]. While direct calculation of this effect is not feasible with DFT, the lifetime predictions obtained from DFT can be adjusted using the Purcell factor derived from alternative methods, such as finite-difference time-domain (FDTD) simulations with Lumerical software, to account for the effects of the surrounding dielectric environment. These results are demonstrated in Appendix C.2.

In addition to the radiative decay pathway, the excitation can also relax non-radiatively to the ground state through phonon-assisted recombination. The rate of this process is computed using the Nonrad Python code [137, 141], developed based on Fermi's golden rule formalism

$$\Gamma_{\text{NR}} = \frac{2\pi}{\hbar} g \sum_{n,m} p_{in} \left| \langle fm | H^{\text{e-ph}} | in \rangle \right|^2 \delta(E_{fm} - E_{in}), \quad (3.10)$$

where Γ_{NR} is the non-radiative transition rate between the electron state i in phonon state n and the electron state f in phonon state m , g is the degeneracy factor, p_{in} is the thermal probability distribution of state $|in\rangle$ following the Boltzmann distribution, and $H^{\text{e-ph}}$ is the electron-phonon coupling Hamiltonian.

In practice, Eq. (3.10) can be simplified using the static coupling approximation and the one-dimensional phonon approximation, resulting in

$$\Gamma_{\text{NR}} = \frac{2\pi}{\hbar} g |W_{if}|^2 X_{if}(T), \quad (3.11)$$

$$W_{if} = \left\langle \psi_i(\mathbf{r}, \mathbf{R}) \left| \frac{\partial H}{\partial Q} \right| \psi_f(\mathbf{r}, \mathbf{R}) \right\rangle \Big|_{\mathbf{R}=\mathbf{R}_a}, \quad (3.12)$$

$$X_{if} = \sum_{n,m} p_{in} |\langle \phi_{fm}(\mathbf{R}) | Q - Q_a | \phi_{in}(\mathbf{R}) \rangle|^2 \delta(m\hbar\omega_f - n\hbar\omega_i + \Delta E_{if}), \quad (3.13)$$

where the phonon term X_{if} and the electronic term W_{if} become separated. More details can be found in the work of Turiansky *et al.* [141].

3.1.7 Quantum Efficiency

Considering both radiative and non-radiative transitions, the quantum efficiency η of an emitter can be estimated. Quantum efficiency is a crucial parameter that quantifies the efficiency of the emission process, defined as the ratio of the radiative transition rate to the total transition rate. The total transition rate includes contributions from both the radiative and non-radiative processes. The quantum efficiency η is given by

$$\eta = \frac{\Gamma_{\text{R}}}{\Gamma_{\text{R}} + \Gamma_{\text{NR}}}, \quad (3.14)$$

where Γ_{R} is the radiative transition rate, and Γ_{NR} is the non-radiative transition rate. A high quantum efficiency indicates that the emitter predominantly relaxes via radiative transitions. Conversely, a low quantum efficiency signifies significant losses through non-radiative channels, which can degrade the emitter's performance.

3.1.8 Zero Field Splitting

In principle, a high-spin system, i.e., a system with the total spin greater than triplet ($S \geq 1$), typically exhibits energy splitting of the spin sublevels m_s even in the absence of an external magnetic field because of the magnetic dipolar coupling between unpaired electrons in a solid-state defect. This phenomenon is referred to as zero-field splitting (ZFS), and its ZFS tensor ($\mathbf{D}$) is attained by

$$\mathbf{D}^{SS} = \frac{\mathbf{d}}{S(S - 1/2)}, \quad (3.15)$$

where $\mathbf{d}$ is the traceless 3×3 matrix of magnetic dipolar interaction between all the pairs of occupied Kohn-Sham states. Further details are referred to Ref. [142]. However, an overestimation of ZFS often occurs in high-spin states. This overestimation can be attributed to the fact that the spin-up and spin-down orbitals can occupy different spatial regions and exhibit different shapes. This spatial discrepancy leads to a situation where the overall wave function no longer accurately represents a pure spin state but rather contains a mixture of states with different total spin values. Consequently, the system is not in a true eigenstate of the total spin-squared operator S^2 . To address this inherent issue, the correction approach proposed by Ref. [142] involves averaging the contributions from the $m_s = S$ and $m_s = S - 1$ spin states to isolate and remove the spin contamination error. This method is summarized in the following equation

$$\tilde{\mathbf{D}}^{SS} = \frac{\mathbf{d}(m_s = S) - \mathbf{d}(m_s = S - 1)}{2S - 1}, \quad (3.16)$$

where $\tilde{\mathbf{D}}^{SS}$ represents the corrected ZFS tensor. This correction scheme leverages the fact that the physical part of the dipolar coupling is symmetric and should be unaffected by spin contamination. The contamination errors cancel out when the difference is taken and averaged, as described in Eq. (3.16). As a consequence, the calculation of ZFS for the high-spin system should take into account the ZFS from the low-spin system as well.

3.2 Quantum Memory

A quantum memory, a crucial element in photonic quantum technologies, denotes a system with the ability to reliably store quantum states, preserving them for a certain period of time, and transmitting them to successive communication nodes. This potentially gives rise to possible large-scale quantum technologies, not only for quantum communication [143, 144], but also for quantum computing [145]. So far, extensive efforts have been dedicated to investigating many distinct physical systems with different quantum memory mechanisms with the goal of finding the most suitable long-lived quantum memory. Typically, the quantum memory performance is evaluated based on fidelity, efficiency, storage time, bandwidth, and on-demand operation etc. Below, two mechanisms in quantum memory are summarized.

3.2.1 Raman Quantum Memory

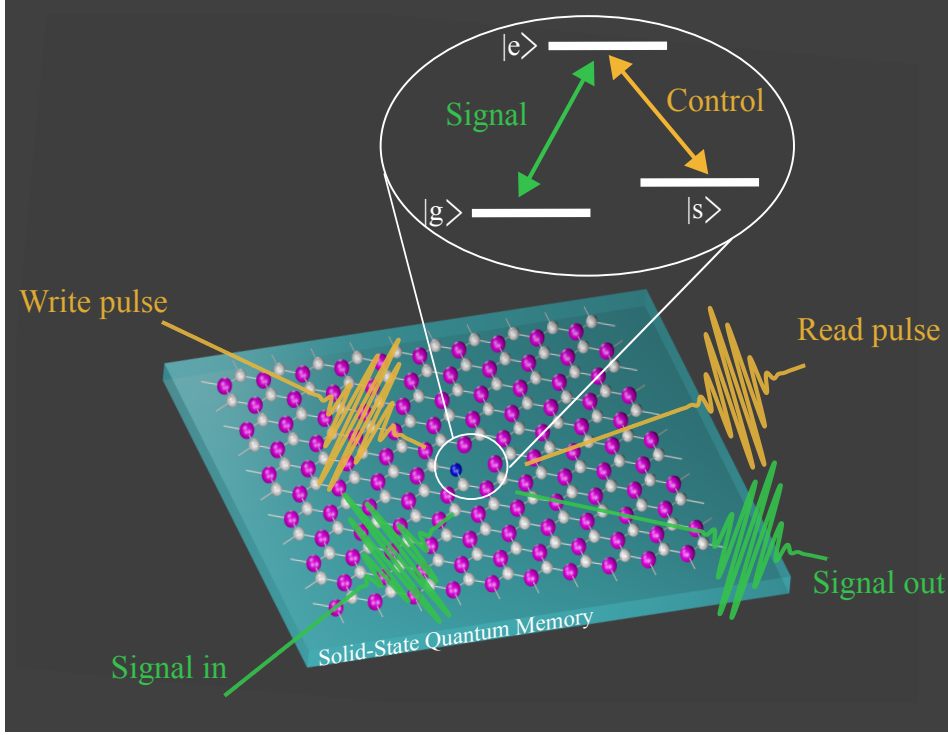


Figure 3.4: Schematics of solid-state Raman quantum memory, whose electronic structure contains the Λ type, namely the ground state ($|g\rangle$), the excited state ($|e\rangle$), and the meta-stable state ($|s\rangle$). Two pulses are applied during the operation. The figure is adapted from Ref. [146] available under a [CC-BY 4.0 license](#). Copyright 2024 Nateeboon *et al.*

In this protocol, a solid-state system should, in principle, feature the Λ electronic structures, consisting of a ground state $|g\rangle$, an excited state $|e\rangle$, and a meta-stable or spin state $|s\rangle$, as shown in Fig. 3.4 [147, 148, 149]. This can be the intersystem crossing between triplet ($S = 1$) and singlet ($S = 0$) states or the magnetic sub-spin levels in the triplet state only ($m_s = +1, 0, -1$). More precisely, the former means $m_s = +1$ state at the ground state of the triplet ($S = 1$) acts as $|g\rangle$ while $m_s = +1$ at the excited state of $S=1$ acts as $|e\rangle$. Then, $m_s = 0$ of the singlet state ($S = 0$) acts as $|s\rangle$. We refer to Fig. 3.6(a) for the sake of visualization. For the other possible Λ structure, the $|g\rangle$ and $|e\rangle$ states remain belonged to $m_s = +1$ state of the triplet ground and excited states, respectively, but the $|s\rangle$ is changed to $m_s = -1$ state of the triplet ground state [148, 149]. This Λ structure type therefore does not need the transition via intersystem crossing.

Turning to the working principle, the Raman quantum memory normally needs to embed a quantum memory in a cavity to enhance the coupling with photons [147], so it becomes a spin-photon interface. The writing (storage) process involves coherently

transferring the quantum state of an incoming photon (signal pulse) into the $|s\rangle$ state without populating the $|e\rangle$ state, thereby avoiding losses due to spontaneous emission. To achieve this, the incoming photon interacts with the atomic ensemble via the transition between the $|g\rangle$ state and the $|e\rangle$ state. Simultaneously, a strong control pulse is applied to couple between $|s\rangle$ and $|e\rangle$ states. By adiabatically turning on the control pulse, the system exploits the adiabatic evolution of the dark state, which is a coherent superposition of $|g\rangle$ and $|s\rangle$. This evolution leads to the coherent transfer of the atomic population from $|g\rangle$ to $|s\rangle$, while the photon is absorbed. Consequently, the photon's quantum information is effectively stored as a collective excitation in the $|s\rangle$ state of the atomic ensemble [147, 148, 149]. Throughout this adiabatic process, the system remains in the dark state, ensuring that the $|e\rangle$ state remains unpopulated, thus preserving coherence and minimizing loss. The reading (retrieval) process can be reversed. Note that the dark state is the state decoupled from the $|e\rangle$ state, so there will be no unwanted photon emission from the spontaneous emission. Of course, in experiment, this emission might still exist, but it is assumed that the transition rate is very low.

3.2.2 Nuclear-Spin Quantum Memory

Unlike Raman quantum memory, where information is typically stored in collective excitations of atomic ensembles (electronic states), nuclear-spin quantum memory stores information in the nuclear spin states. This information transfer is mediated by the hyperfine interaction that couples electron and nuclear spins. Thus, the information initially received by the electron spin can be transferred to the nuclear spin for storage [68, 79]. The primary advantage of this mechanism lies in the inherently long coherence time of a nuclear spin compared to that of an electron spin [79]. To thoroughly understand this mechanism, it is essential to explore the concepts of electron-nuclear coupling and coherence control. These aspects are crucial for the efficient transfer and preservation of quantum information in nuclear-spin systems. In this dissertation, a negatively charged boron vacancy (V_B^{-1}) in hBN is exemplified.

Electron-nuclear coupling

For the non-zero nuclear spin isotopes, electron and nuclear spins can always be coupled through the hyperfine interaction. Specifically, V_B^{-1} in hBN is surrounded by three nitrogen nuclei. Intrinsically, the nitrogen nuclei have spin-1 and spin-1/2 for ^{14}N and ^{15}N isotopes, respectively. These three nearest neighboring non-zero nuclear spins can couple with the V_B^{-1} electron spin with the following hyperfine interaction.

$$H_{\text{hf}} = \sum_{i=1}^3 \mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i. \quad (3.17)$$

Considering each parameter, the spin-1 operators for the V_B^{-1} can be written as

$$S_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}, S_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, S_y = \frac{1}{\sqrt{2}i} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}. \quad (3.18)$$

Alternatively, all operators can also be written in terms of the spin raising and lowering operators as follows

$$S_+ = \sqrt{2} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} = S_x + iS_y, \quad S_- = \sqrt{2} \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} = S_x - iS_y. \quad (3.19)$$

Combining Eqs. (3.18) and (3.19) results in

$$S_x = \frac{S_+ + S_-}{2}, \quad S_y = \frac{S_+ - S_-}{2i}. \quad (3.20)$$

When considering the nuclear spins, their operator I can be written differently depending on the nitrogen isotope considered. Now, as the experiment found that ^{15}N isotope has the longest coherence time [79], this work focuses on this isotope. Then, the nuclear spin operator for $1/2$ - ^{15}N is written as

$$I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad I_y = \frac{1}{2i} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}. \quad (3.21)$$

and spin ladder operators

$$I_+ = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = I_x + iI_y, \quad I_- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = I_x - iI_y, \quad (3.22)$$

Similarly, ^{15}N nuclear spin operators can be rewritten as

$$I_x = \frac{I_+ + I_-}{2}, \quad I_y = \frac{I_+ - I_-}{2i}. \quad (3.23)$$

The last remaining term refers to the hyperfine coupling tensor for the i -th nitrogen nucleus, which can be expressed in the following form

$$\mathbf{A} = \begin{bmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{bmatrix} = \begin{bmatrix} A_{xx} & A_{xy} & 0 \\ A_{yx} & A_{yy} & 0 \\ 0 & 0 & A_{zz} \end{bmatrix}. \quad (3.24)$$

It is worth noting that the terms A_{xz} , A_{yz} , A_{zx} , and A_{zy} in Eq. (3.24) are zero due to the mirror symmetry of V_B^{-1} with respect to the $\hat{x} - \hat{y}$ plane where the $\hat{z}$ -axis is aligned along

the c-axis of hBN. Consequently, the complete form of hyperfine interaction Hamiltonian can be expanded to

$$\begin{aligned}
 \sum_{j=1}^3 \mathbf{S} \mathbf{A}^j \mathbf{I}^j &= \sum_{j=1}^3 \left(A_{zz}^j S_z I_z^j + A_{xx}^j S_x I_x^j + A_{yy}^j S_y I_y^j + A_{xy}^j S_x I_y^j + A_{yx}^j S_y I_x^j \right) \\
 &= \sum_{j=1}^3 \left[A_{zz}^j S_z I_z^j + \frac{1}{4} A_{xx}^j (S_+ + S_-) (I_+^j + I_-^j) - \frac{1}{4i} A_{yy}^j (S_+ - S_-) (I_+^j - I_-^j) \right. \\
 &\quad \left. + \frac{1}{4i} A_{xy}^j (S_+ + S_-) (I_+^j - I_-^j) + \frac{1}{4i} A_{yx}^j (S_+ - S_-) (I_+^j + I_-^j) \right] \\
 &= \sum_{j=1}^3 \left[A_{zz}^j S_z I_z^j + \frac{A_{xx} + A_{yy}}{4} (S_+ I_-^j + S_- I_+^j) \right. \\
 &\quad \left. + \left(\frac{A_{xx} - A_{yy}}{4} + \frac{A_{xy}}{2i} \right) S_+ I_+^j + \left(\frac{A_{xx} - A_{yy}}{4} - \frac{A_{xy}}{2i} \right) S_- I_-^j \right].
 \end{aligned} \tag{3.25}$$

Last, we utilize the symmetry property that $A_{xy} = A_{yx}$. Additionally, exploiting the relations $(S_+ I_-^j)^\dagger = (S_- I_+^j)$ and $(S_- I_-^j)^\dagger = (S_+ I_+^j)$, we can further simplify the expression to the following form

$$\sum_{j=1}^3 \mathbf{S} \mathbf{A}^j \mathbf{I}^j = \sum_{j=1}^3 \left[A_{zz}^j S_z I_z^j + (A_1^j S_+ I_-^j + \text{h.c.}) + (A_2^j S_+ I_+^j + \text{h.c.}) \right], \tag{3.26}$$

where we define $A_1^j = \frac{1}{4} (A_{xx}^j + A_{yy}^j)$ and $A_2^j = \frac{1}{4} (A_{xx}^j - A_{yy}^j) + \frac{1}{2i} A_{xy}^j$.

Level Anticrossing

Level anticrossing is a phenomenon in quantum mechanics where two energy levels come very close to each other as a function of an external parameter, such as a magnetic field, and then repel each other instead of crossing. This interaction occurs due to a coupling or interaction between the states that causes their energies to avoid crossing and instead undergo a sharp change in their energy levels, leading to a characteristic “anticrossing” behavior.

For an hBN defect system in particular, level anticrossing plays a crucial role in coherently controlling the nuclear spins, as this is where the electron spin states cross with the nuclear spin states. To derive this behavior, we start from the spin Hamiltonian

$$\begin{aligned}
 \hat{H} &= \hat{H}_{\text{ZFS}} + \hat{H}_{\text{e,Zeeman}} + \hat{H}_{\text{n,Zeeman}} + \hat{H}_{\text{HF}}, \\
 &= D \left(S_z^2 - \frac{S(S+1)}{3} \right) + \frac{E}{2} (S_+^2 + S_-^2) + \mu_B \mathbf{B} \cdot g \mathbf{S} + \sum_n \gamma_n \mathbf{B} \cdot \mathbf{I}_n + \sum_n \mathbf{S} \cdot A_n \mathbf{I}_n.
 \end{aligned} \tag{3.27}$$

The first two terms of $\hat{H}$ in Eq. (3.27) belong to the ZFS. Then, in the third term, the electron Zeeman term is considered, and it depends on the applied magnetic field

strength. The fourth term comes from nuclear spins. The nuclear Zeeman interaction is also contributed by the magnetic field; nonetheless, this needs to take into account the three nearest neighboring nitrogen nuclei. Last, the hyperfine coupling between electron and nuclear spins is included according to Eq. (3.26).

By solving the governing Hamiltonian Eq. (3.27) for its eigenvalues and eigenstates, we can identify certain crossing points where the eigenenergies of specific spin states become nearly degenerate. This is the so-called ground-state level anticrossing (GSLAC) and excited-state level anticrossing (ESLAC). For instance, the energy levels of the eigenstates $m_s = 0$ and $m_s = -1$ approach each other closely at particular values of the applied magnetic field. At these near-degeneracy points, the interaction between electron and nuclear spins is strong because the wavefunctions of the electron spin states mix significantly with those of the nuclear spin states. More detailed analysis can be found in Sec. 6.2.2 of Chapter. 6. This interaction enables the electronic and nuclear spins to exchange spin angular momentum efficiently. A key mechanism facilitating this exchange is the flip-flop process, wherein the electronic spin undergoes a flip while the nuclear spin simultaneously flops in the opposite direction. Consequently, this process leads to the transfer of spin polarization from the electronic spin to the nuclear spins, as elaborated in the following section. The calculation details and results are also demonstrated in Chapter 6.

This polarization transfer between the electron spin and the nuclear spin is crucial for applications in quantum information processing, as it can perform quantum memory and qubit operations. The mechanism of the coherent spin control is described in the next section.

Mechanism for Coherent Nuclear Spin Control

A nuclear spin can technically be controlled by any arbitrary magnetic field strength. However, specific magnetic field intensities, particularly those corresponding to the GSLAC and ESLAC, facilitate stronger coupling between electron and nuclear spins. Recently, several mechanisms for nuclear spin control have been demonstrated. For instance, some protocols apply the B field at ESLAC, while others apply at GSLAC [79, 150, 151]. They claimed that the laser for spin control at GSLAC requires less power than that of ESLAC [151]. Below is an example of coherently controlling nuclear spins of three ^{15}N nuclei in hBN.

The step-by-step procedure following Fig. 3.5 is as follows.

1. Optical pumping by excitation laser

The laser selectively excites the electron spins in the V_B^{-1} center. When these excited electrons relax back to the ground state, they preferentially populate the $|m_s = 0\rangle$ state due to spin-dependent relaxation processes. This step effectively initializes the electron spin state to $|m_s = 0\rangle$, which is crucial for subsequent coherent control.

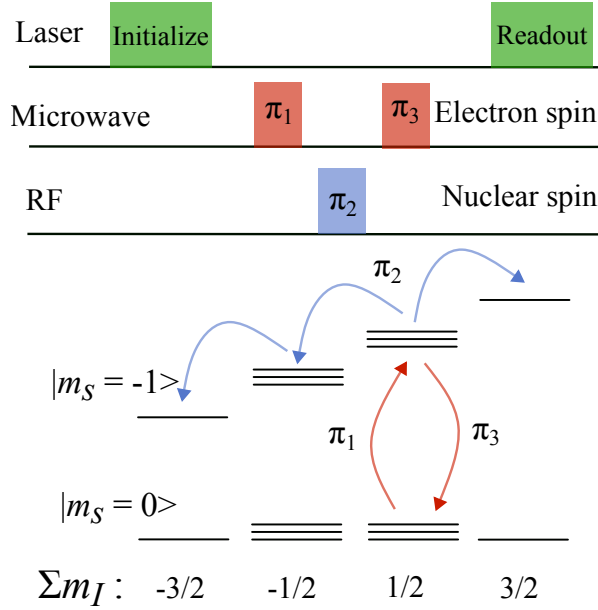


Figure 3.5: A schematic procedure of coherent control in nuclear spins ^{15}N of a V_B^{-1} in hBN. The numbers specified in the π pulse indicate the order of the pulse applied. The total spins of $\sum m_I = \pm 1/2$ have degenerate states, as elaborated in Sec. 6.2.1.

2. Electron population transfer by a nuclear spin selective microwave pulse

A microwave (π_1 pulse) pulse is used to change/flip the electron spin state from $|m_s = 0\rangle$ to $|m_s = -1\rangle$ while selectively addressing the nuclear spin configuration where the total nuclear spin projection $\sum m_I = 1/2$. In other words, the nuclear spin state remains unchanged. This selective transition allows for coherent control over the nuclear spins, creating a specific superposition or entangled state between the electron and nuclear spins. The transition rate for this process is governed by the Fermi's golden rule, which ensures that the perturbation (the MW pulse) efficiently induces the desired transition. It is important to emphasize that, at this step, information can be stored during spin transfer to the nuclear spin [75].

3. Driving nuclear spin states by a radiofrequency (RF) pulse (π_2)

The RF pulse specifically targets the nuclear spins, flipping their states (for instance, from $|m_s = -1, \sum m_I = 1/2\rangle$ to $|m_s = -1, \sum m_I = -1/2\rangle$). Rabi oscillations, which are periodic oscillations of the spin state populations, can be observed as the nuclear spins undergo coherent transitions. These oscillations provide a clear signature of coherent control as the spins oscillate between different states in a predictable manner under the influence of the RF field. The transition rate between nuclear spin states, induced by the RF pulse, is also determined by the Fermi's golden rule.

4. Nuclear-spin detection

This step reverses the initial microwave pulse with the π_3 pulse, bringing the system back to the $|m_s = 0\rangle$ state. By doing so, the state of the nuclear spins (now $\sum m_I = 1/2$) can be read out optically. The fluorescence intensity associated with the $|m_s = 0\rangle$ state will differ depending on the nuclear spin configuration, allowing for the detection of the nuclear spin states. The transition rate for this final microwave-induced transition is once again determined by the Fermi's golden rule, ensuring efficient population transfer. This step is also referred to as the retrieval process in quantum memory.

It is important to stress that nuclear spin control in hBN remains an ongoing research field nowadays.

3.3 Quantum Sensing

Turning to quantum sensing applications, solid-state quantum systems can significantly advance the field by offering higher accuracy, sensitivity, stability, and resolution, thus overcoming the limitations of classical approaches. These advancements are primarily achieved through the mechanisms involving the spin-selective channels of the electronic structures, which allow for the alteration of optical signals, such as PL.

In practice, various protocols are utilized for quantum sensing applications. For example, spin relaxometry is a technique that can detect rapidly fluctuating signals in the range of MHz to GHz. This method works by comparing the T_1 of isolated spin defects to that in the presence of target fluctuating fields [152, 153]. Another technique is the continuous wave ODMR protocol. This is widely favored due to its straightforward implementation for practical sensing tasks. In this method, the resonant frequencies within the spectrum are monitored, and shifts are observed when external fields are applied [85, 154]. In this dissertation, only the latter protocol is in the scope of the research and its principles are explained in detail as follows.

3.3.1 Electron Paramagnetic Resonance

EPR is a technique used to study point defects in materials that have unpaired electrons, such as those in doublet ($S = 1/2$) or triplet ($S = 1$) states [132, 155, 156]. These defects exhibit magnetic properties due to the spins of their electrons. The governing Hamiltonian for EPR is the same as the spin Hamiltonian described in Eq. (2.67), and it can be used to understand the behavior of these systems under various conditions.

When a microwave of a specific frequency is applied, transitions between the split energy levels are induced. The absorption of energy during these transitions produces a signal, which appears as a peak in the EPR spectrum when plotted against the microwave frequency [132, 155, 156]. Additionally, if nearby atoms in the material possess spin (such as nitrogen atoms in certain defect systems), their interaction with the spins of

the defect's electrons can cause further splitting of the energy levels. This phenomenon is known as hyperfine splitting and results in multiple peaks in the EPR spectrum. The number of these peaks follows a specific mathematical pattern, reflecting the nature and strength of the hyperfine interactions.

Therefore, such aforementioned splittings can be used for defect identification, which will be discussed in Chapter 7.

3.3.2 Optically Detected Magnetic Resonance

Similar to EPR, ODMR is also based on the resonance between the spin states of unpaired electrons (paramagnetic centers) in a material, e.g., $m_s = 0, \pm 1$ for a triplet ($S=1$). The working principle of ODMR is as follows.

Suppose the system comprises a triplet ground state, a triplet excited state, and a metastable singlet manifold, as illustrated in Fig. 3.6(a). Under continuous off-resonant optical excitation (e.g. a 532 nm laser for the NV center in diamond), population in the m_s ground sublevels is promoted to the m_s excited sublevels with the spin conserving; that is, $m_s = 0$ to $m_s = 0$, $m_s = -1$ to $m_s = -1$, and $m_s = 1$ to $m_s = 1$. Then the electron from $m_s = 0$ decays radiatively back to $m_s = 0$, producing the characteristic bright PL background, while $m_s = \pm 1$ can have two decay pathways: radiative or non-radiative paths. When an MW field is applied on resonance with the $m_s = 0 \rightarrow -1$ transition, spins are flipped into the $m_s = -1$ ground sublevel. These spins are then excited by the laser into the $m_s = -1$ excited state, from which two relaxation pathways compete: direct radiative decay to $m_s = -1$ (emitting a photon) or non-radiative ISC into the singlet. Because the ISC probability far exceeds that of the radiative channel, most population enters the dark singlet and subsequently decays into $m_s = 0$ of the ground triplet without photon emission, thereby suppressing the steady-state PL and creating one dip in the ODMR spectrum. As shown in Fig. 3.6(b), a second dip arises when the MW drives the $m_s = 0 \rightarrow +1$ transition: the same sequence, which is laser excitation of $m_s = +1$, preferential ISC into the singlet, and decay into $m_s = 0$, again depletes the bright cycle and produces a second PL reduction. These spin-dependent shelving pathways thus give rise to the two characteristic dips in the ODMR contrast.

Considering the ODMR characteristics for a triplet, there are typically two dips, corresponding to the transition between $m_s = 0$ and $m_s = -1$, and that between $m_s = 0$ and $m_s = +1$ of ground states, as shown in Fig. 3.6(b). It is worth noting that the transition between $m_s = 0$ and $m_s = -1$, and that between $m_s = 0$ and $m_s = +1$ of excited states can also take place and hence cause the other two different dips. Such a ODMR contrast is beneficial for sensing various physical parameters such as magnetic field, temperature, strain, and pressure [157, 158, 159, 160, 161, 162]. That is, for the magnetometry, the separation between these two dips increases with an increasing external magnetic field due to the Zeeman interaction. The Zeeman effect causes a shift in the energy levels of the $m_s = \pm 1$ states, resulting in a measurable change in the separation of the ODMR dips. This relationship enables accurate sensing of the

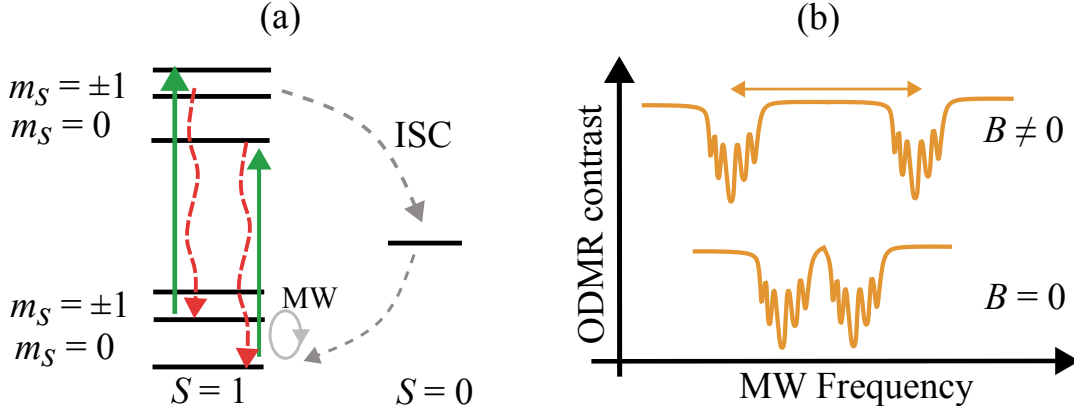


Figure 3.6: Schematics of the relation between electronic structures and ODMR spectrum. (a) Electronic structure of a defect inheriting triplet and singlet configurations. The green arrows represent an excitation, i.e., by a laser. The red dot arrows represent radiative decay while the gray dot arrows represent non-radiative decay, interfacing ISC to change from $S = 1$ to $S = 0$ spin states. The MW signifies the microwave pulse driving the transition between $m_s = 0$ and $m_s = \pm 1$. Note that $m_s = \pm 1$ states are degenerate unless the magnetic field is applied. (b) ODMR spectrum with and without magnetic fields. The dips observed contain two dips, corresponding to the transition between $m_s = 0$ and $m_s = \pm 1$ of the ground state. Note that the transition between $m_s = 0$ and $m_s = \pm 1$ of the excited state is also possible, but it is not shown in this diagram. The middle point of two dips for the zero magnetic field corresponds to ZFS.

magnetic field by precisely measuring the separation between the two dips in the ODMR spectrum. For sensing temperature, strain, and pressure, the ZFS with the case of zero magnetic field can be adopted by analyzing the shifting of the ZFS position according to sensing.

It is important to remark that the small oscillation in each dip can be justified by the hyperfine coupling. This will be explained in details in Chapters 6 and 7.

Chapter 4

Comprehensive Properties of hBN Quantum Emitters

In this chapter, the comprehensive properties of hBN quantum emitters are characterized. While various quantum emitters have been realized so far, as discussed in Sec. 3.1, the identification and characterization of these fluorescent defects are vital for advancements in quantum technologies, as the precise manipulation of their photophysical properties can improve sensing ability and communication performance, etc.

For example, in optical quantum computing, two-level states of a defect serve as qubits that can be manipulated to perform logic operations [29, 30, 163, 164, 165]. Quantum key distribution benefits from specific wavelengths, such as those in the telecom band for fiber-based communication [166] or particular visible wavelengths for free-space links [66]. Similarly, quantum sensing requires defects with desirable characteristics like triplet and doublet spin states, which facilitate optically detected magnetic resonance (ODMR) for applications in magnetometry [167]. The future of quantum technology envisions not only isolated quantum computers and direct quantum communication but also extensive quantum networks featuring distributed remote capabilities. Quantum networks will demand quantum memory components that can efficiently interface with quantum emitters [9]. Additionally, emitters intended for memory applications must possess specific energy level structures, such as a three-level Λ configuration [168, 169]. Thus, designing defect emitters requires comprehensive consideration of their photophysical properties to ensure their suitability for desired quantum applications.

A prevalent technique for identifying single-photon emitters (SPEs) involves comparing the zero-phonon line (ZPL) energies and photoluminescence (PL) spectra obtained experimentally with those predicted by first-principles calculations, often using DFT [114, 115, 170, 171, 172]. Recently, a defect emitting at around 2 eV has been attributed to the $C_B V_N$ configuration by correlating its electronic transitions with observed PL spectra [173]. Similarly, carbon-based defects, including structures up to tetramers, have been analyzed by examining their phonon side-bands (PSBs) rather than their ZPLs [174]. This analysis indicated that the $C_B C_N C_N$ defect shows comparable PL features to experimental data, although a substantial redshift in the ZPL is required for precise alignment. Another study using DFT further examined the Huang-Rhys (HR)

factor and the lifetime of the second electronic transition for the $C_B C_N C_N$ defect [175]. These methodologies have also been applied to predict the emission wavelengths of other hBN emitters [63] and to provide insights into their electronic structures [176, 177, 178].

Various DFT studies have confirmed that while some parameters agree excellently with experimental results, others can show discrepancies [174, 175]. These inconsistencies can be attributed to many factors, such as (i) the local strain within the crystal, which can drastically influence photophysical properties, especially in 2D crystals as opposed to 3D ones; (ii) complex coupling interactions associated with the defects, which simulations may not accurately capture; and (iii) potential misidentification of the defect, confusing it with another defect that exhibits similar optical characteristics. To address these issues, recent research has suggested using electron paramagnetic resonance (EPR) as an additional method for defect identification, demonstrating a better agreement between DFT calculations and experimental data [155, 177]. This indicates the necessity of considering a comprehensive optical fingerprint, rather than relying on a single property, for accurate defect identification. By employing a multifaceted approach, we can overcome the possible pitfalls of one method and increase confidence in emitter identification.

In this chapter, we first conduct extensive calculations of numerous defect complexes to elucidate their radiative transitions using spin-polarized DFT with the HSE06 functional. Our comprehensive analysis covers the electronic structures of 267 defect complexes, including substitutional atoms from periodic main groups III through VI, transition metals, and multi-defect complexes. For a selected subset of defects, we also examine the influence of their charge states (neutral and ± 1). We establish criteria for identifying promising defects based on the nature of their transitions (radiative/non-radiative), localization (deep/shallow), and transition energies. Using these criteria, we can select emitters with emission wavelengths that are relevant to quantum technologies and apply strain-tuning to tailor their emission wavelengths.

The second objective of this chapter is to demonstrate a method for calculating the complete fingerprint of hBN quantum emitters. The proposed identification technique relies solely on commonly measured experimental properties, which can be obtained using standard photoluminescence microscopy. We illustrate this methodology with examples, such as the $C_B C_N C_B C_N$ defect, which aligns with our previous experimental results [61, 179], as well as the $C_B C_N C_N$ defect, previously proposed [174, 175]. Additionally, we apply this method to predict the complete fingerprint of Al_N and $P_N V_B$ defects. The potential applications of these defects are also explored in this chapter.

The results from this chapter have been published in Refs. [61, 90, 136, 179].

4.1 Photophysical Property Calculation

4.1.1 DFT Computational Details

DFT calculations were performed using two DFT packages, depending on the photophysical properties. First, QuantumATK [180] was used to calculate transition energy and explore the tailoring mechanisms to achieve the first objectives with the following details. In QuantumATK, a numerical linear combination of atomic orbitals (LCAO) double ζ polarized basis sets is selected, as it was benchmarked by an earlier work [181]. The pseudopotentials and basis sets (which influence the accuracy of DFT calculations) are internally constructed by our DFT calculator from a frequently benchmarked and reviewed database for all elements to provide the most accurate results. Since this work mainly focuses on the electronic band structure and optical transitions, we employed the HSE06 functional [111] to avoid underestimating the energy band gap. Thanks to the implemented basis set, it enables geometry relaxation using a $5 \times 5 \times 1$ Monkhorst–Pack reciprocal space grid [182]. Also, for electronic band structures, a dense $11 \times 11 \times 1$ k -point centered at the Γ point was implemented to capture all possible states.

The rest of the calculations in this chapter were achieved by implementing DFT using the Vienna Ab initio Simulation Package (VASP) employing a plane wave basis set [183, 184] and the projector augmented wave (PAW) method for the pseudopotentials [185, 186]. All geometry relaxations were performed with an energy cutoff at 500 eV. While the HSE06 functional was also employed for all calculations, only the single Γ -point scheme was applied due to expensive computational cost demand. However, it is important to note that the convergence test was made and found that the total energy was already well converged within 1 meV/atom by this setting. Furthermore, both occupied and unoccupied defects states show flat bands throughout all high-symmetry k points. For the excited-state properties, the Δ SCF method was employed to manually occupy electrons for the excited-state configuration [187]. Note that the total energy of both ground and excited state configurations was compared among singlet, doublet, and triplet states. Only the most stable configuration was selected for further analysis.

For both DFT packages, point-like defects were created at the center of a $7 \times 7 \times 1$ supercell containing 98 atoms (pristine), as illustrated in Fig. 4.1, which was proven to be sufficiently large to exclude any defect–defect interaction of neighboring cells. In all simulations, the hBN structure was assumed to be a monolayer; hence, a 15 Å vacuum layer was added to isolate this layer from the neighboring ones. Both the supercell size and vacuum layer were validated by convergence tests of the electronic structure characteristics. All structures were optimized until all forces were below $0.01 \text{ eV} \cdot \text{\AA}^{-1}$ and the total energy convergence reached 10^{-4} eV . All calculations include spin polarizations to ensure spin conservation in the transitions.

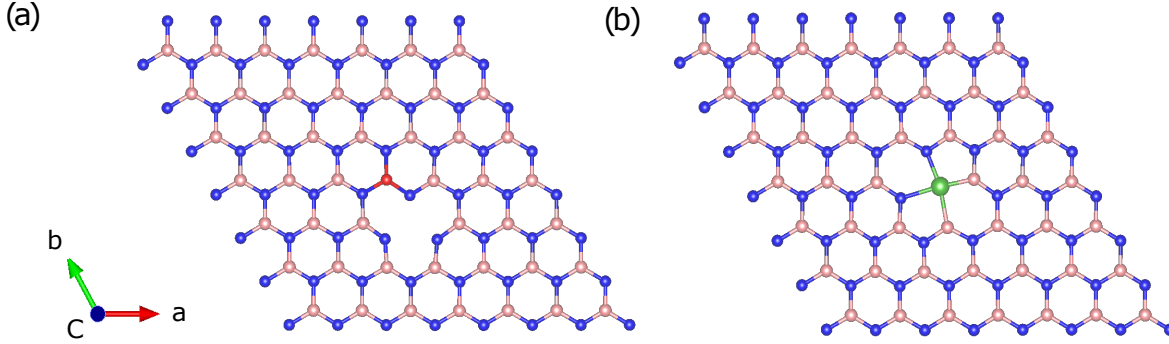


Figure 4.1: A lattice structure of a supercell size $7 \times 7 \times 1$ comprising boron (pink), nitrogen (blue), oxygen (red), and silicon (green). The a and b directions are in-plane. (a) $O_B V_B$ defect, where an O atom substitutes a boron atom next to a boron vacancy. (b) Si_{BN} where a Si atom is located in the middle of a bi-vacancy V_{BN} . The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

4.1.2 Transition Dipole Moment Calculation

As explained in Sec. 3.1.4, the initial and final wavefunctions for each transition were required. Then, the PyVaspwfc Python code was utilized to extract the wave functions [188], while a modified version of this code was employed to handle wave functions from both ground and excited states [135]. The transition dipole moment can be equivalently expressed as:

$$\boldsymbol{\mu} = |\mu_x|\hat{x} + |\mu_y|\hat{y} + |\mu_z|\hat{z}, \quad (4.1)$$

where $\mu_z = 0$ indicates a purely *in-plane* dipole; otherwise, it has an *out-of-plane* contribution.

4.1.3 Photoluminescence Simulation

Based on the theory explained in Sec. 3.1.5, the PL is implemented using the PyPhotonics workflow [189]. This can be done by first considering the lattice structure difference between ground and excited states. Then, the phonon calculation using Phonopy is utilized to find the phonon frequencies of the ground-state configuration [190, 191]. It should be noted that the phonon modes of the excited-state configuration are assumed to remain unchanged significantly from the ground-state one. Finally, the PL spectrum is generated. It is worth noting that all investigated defects were tested for the PL convergence by varying the supercell size, as explained in Appendix C.

4.1.4 Lifetime and Quantum Efficiency Calculations

According to Sec. 3.1.6, radiative and non-radiative lifetimes can be computed from the radiative and non-radiative rates, respectively. The radiative rate and lifetime were implemented by the code from Ref. [135] while the non-radiative ones were computed by the open-source NONRAD python code [141, 137]. Note that the lifetime from DFT can be deviated from that from the experiment. We, therefore, include the Purcell effect in the calculation. Quantum efficiency (QE) based on the theory explained in Sec. 3.1.7 can subsequently be calculated.

4.1.5 Criteria for Promising High Quality Defects

In principle, the photophysical properties of any quantum emitter should feature desired ZPL, low HR factor, high Debye-Waller (DW) factor, high QE, and appropriate excited-state lifetime (short lifetime ideal for quantum communication). While these properties will be calculated later in this chapter, there are some simpler criteria that can screen preliminarily a large number of defects. These are based on electronic structures, which can be computed much faster than other properties. Therefore, in this section, these simple criteria are discussed and demonstrated as the first objectives of this chapter.

To recognize qualified defects for quantum technologies among plenty of investigated complexes, we define the following criteria.

1. Electronic transition type: the defect should introduce a two-level system, where it is preferred that the highest occupied and the lowest unoccupied defect states have the same spin polarization. Then the radiative transition exists from the spin up to up transition and from the spin down to down transition.
2. Transition energy: the emitter should possess an optical emission wavelength that is useful for quantum technology applications. This is inferred from the energy difference between the ground (highest occupied) and excited (lowest unoccupied) states, corresponding to the characteristic peak in the absorption spectrum. Note that this is valid only the case that the two-level system is ideal. Otherwise, the transition energy needs to be calculated through the ZPL calculation, which is discussed in Sec. 3.1.2.
3. Localization in the band structure: defects can introduce additional states anywhere in the in-gap region. The ideal defect state should be localized in the deep-lying states isolated from the band edges. Also, such states should not interact with other states, which is reflected by a flat line in both the density of states and the electronic band structure. This implies every high symmetry point has the same energy.

It is crucial to note that this study focuses solely on first-order transitions between the highest occupied state and the lowest unoccupied state. Although higher-order optically allowed transitions may occur, such excitations would result in multiple decay channels, thereby reducing the quantum efficiency of the transition. Additionally, based on the first-order electronic transition, half of all defects are classified as non-radiative. In the second objective of this chapter, the Δ SCF method is employed to elucidate the allowed optical transition pathways of these defects from the ZPL.

4.1.6 Strain Tuning

Sometimes, the ZPL of a defect slightly shifts from the value applicable to some quantum applications. Hence, a fine-tuning mechanism is required. One of the tailoring mechanisms is strain tuning. In this chapter, the bi-axial strain was applied to the crystal structures by isotropically elongating and compressing them along both the a and b directions (see Fig. 4.1 for the definition of the axial directions). The strain in the crystal lattice was generated using the built-in pressure function in QuantumATK. This pressure is applied through a 3×3 stress tensor, where identical values are assigned to the xx and yy components while all other components are set to zero, thereby simulating bi-axial strain. Subsequently, the geometry is relaxed, and the applied strain s is calculated using the initial length of the unstrained lattice parameter L_0 and the length difference of the strained lattice parameter ΔL , with the strain given by $s = \frac{\Delta L}{L_0}$.

4.2 Distribution of Emission Wavelengths

4.2.1 Transition Energies

Initially, we validate the electronic structure of a pristine hBN monolayer by comparing our results with those available in the literature. Our calculated lattice parameters, energy band gap, and atomic orbital contributions to the electronic band structure are in good agreement with previously reported values. More specifically, using the HSE06 functional, we obtain a direct electronic band gap of $E_g = 5.99$ eV, which agree well with experimental findings [99] and with calculations performed using the G_0W_0 quasiparticle approximation [192], which reported values around 6 eV.

Subsequently, the electronic band structures of various defect complexes were computed and categorized based on the previously outlined criteria in Sec. 4.1.5. Fig. 4.2 illustrates the distribution of transition energies or emission wavelengths for 92 identified radiative defects. The histogram inset depicts that the majority of fluorescent defects in hBN exhibit transition energies between 1.6 and 2.6 eV, whereas a significant portion are not optically active. Notably, transitions below 0.75 eV and above 3.25 eV primarily exhibit radiative transitions or transitions between degenerate states, which can also be considered radiative. It is evident that the transition energy does not correlate with the

periodic main groups of a dopant. Specifically, despite defects potentially having the same number of valence electrons due to their periodic group, the interaction between the specific element and the host hBN can vary significantly, depending on how the spin polarization of the electrons is minimized. However, it was observed that impurities from groups III to VI generally contribute to transition energies ranging from 1 to 4 eV, while transition energies below 1.5 eV predominantly originate from transition metals as dopants, with the exception of $O_N S_N$.

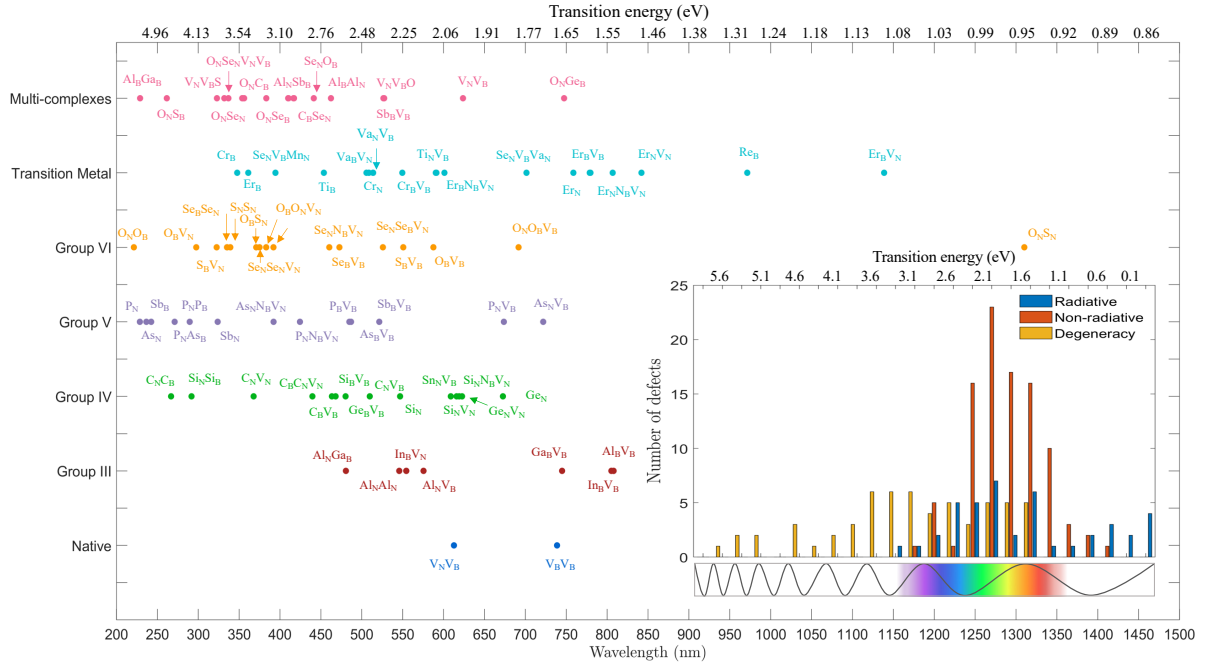


Figure 4.2: Distribution of emission wavelengths in neutral-charge hBN color centers resulting from radiative transitions. The defects are categorized based on the position of the impurity within the periodic table. The inset shows a histogram with a bin width of 0.25 eV, summarizing all 205 examined neutral defects, categorized by their transition type (radiative, non-radiative, and degenerate). It is important to note that, in this chapter, V denotes a vacancy, while the symbol Va is used for the chemical element vanadium. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

4.2.2 Group III Dopants

We now proceed to a detailed analysis of the defect complexes, focusing initially on group III impurities, specifically Al, In, and Ga, substituted at boron or nitrogen lattice

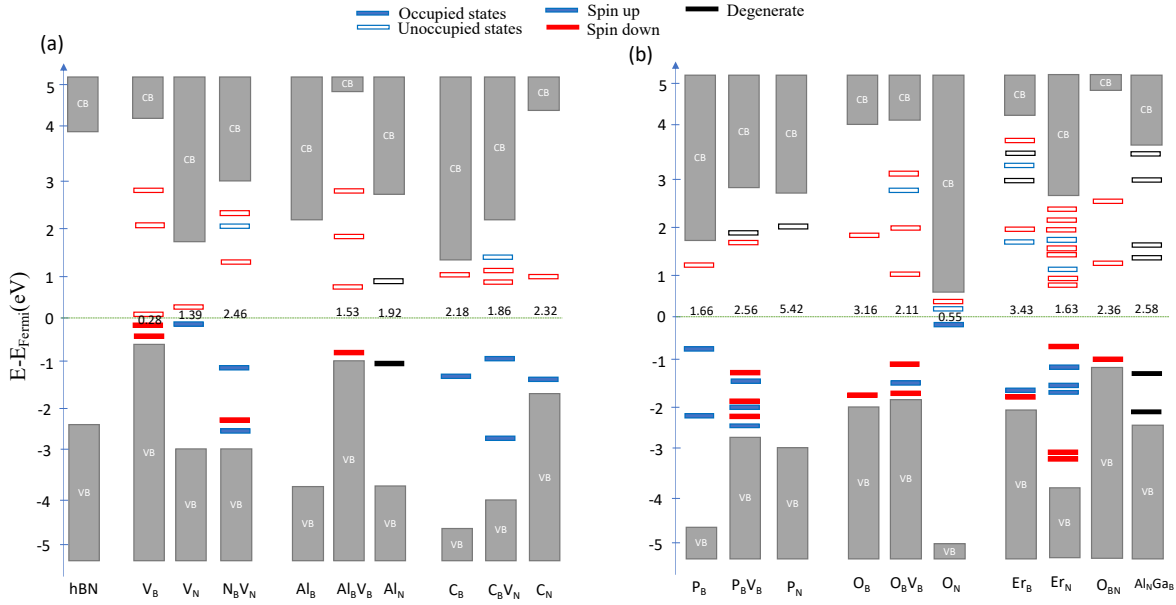


Figure 4.3: Modified electronic band structures showing defect states and transition energies for selected dopant representatives from periodic groups III, IV, V, VI, transition metals, and multi-defect complexes. The gray bars represent the states in the valence and conduction bands. Filled and unfilled bars indicate occupied and unoccupied defect states, respectively. Blue, red, and black bars depict defect states occupied by spin-up, spin-down, and degenerate electrons, respectively. Transition energies between two-level systems are shown near the Fermi level. O_{BN} denotes an interstitial oxygen atom located at the center of a bi-vacancy. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

sites. Fig. 4.3 (see also Appendix A) demonstrates that the large band gap is preserved for all dopants, including those outside group III, although the Fermi energy is shifted. This indicates that intrinsic quantum emission at room temperature is generally feasible, regardless of the specific dopant.

The Al_B and Ga_B centers do not introduce any states between the valence band (VB) and the conduction band (CB) due to their equal number of valence electrons compared to boron, which means there are no additional free charge carriers to occupy new states. However, the In_B center generates a new, deep, but unoccupied state. For Al-based defects, only the Al_BV_B , Al_N , and Al_NV_B defects exhibit radiative transitions around 2 eV. In contrast, the In-based defects show possible transitions for the In_BV_B , In_BV_N , and In_NV_B centers. No first-order transitions were identified for Ga-based defects.

4.2.3 Group IV Dopants

For potential defect complexes, we selected elements from group IV, specifically C, Si, Ge, and Sn (refer to Figs. A.3 and A.4 in Appendix A). Our investigation into C-based defects revealed a wide variety of optically active defects, including the $C_B V_B$, $C_N V_B$, $C_N V_N$, $C_B C_N$, $C_B C_N V_B$, and $C_B C_N V_N$ centers. These findings align with previous studies on C-based quantum emitters [63, 115, 174, 193]. For instance, the C_B defect features one occupied and one unoccupied defect state, indicating an extra free electron from carbon. Similarly, the C_N defect also contributes an additional free electron, creating one unoccupied defect state. Both defects exhibit electronic structures with one spin-up occupied defect state and one spin-down unoccupied defect state, as found earlier by spin-polarized DFT calculations [115, 194, 195]. Notably, bi-carbon defects such as $C_B C_N$ display degenerate defect states, consistent with prior research [174]. Our calculated transition energies of 2 and 4 eV correspond well with other ZPL calculations [63, 115, 174], thereby validating our approach. Conversely, for Si-, Ge-, and Sn-based defects, we identified first-order transitions of deep-level defects with energies ranging from 1.8 to 2.8 eV.

4.2.4 Group V Dopants

From group V, we selected P, As, and Sb for potential defect complexes (see Fig. A.5 in Appendix A). Phosphorus doping results in an optical transition only for the $P_B V_B$ center, observed at 2.56 eV. Arsenic doping, on the other hand, generates a diverse range of transition energies: 5.24 eV (As_N), 1.72 eV ($As_N V_B$), and 3.16 eV ($As_N N_B V_N$). For Sb-based defects, the $Sb_B V_B$ center emerged as the only significant defect for quantum emission applications. These findings suggest that first-order transitions in group V-based defects are predominantly non-radiative. We hypothesize that this behavior arises from the interaction of unpaired electrons within the structures, which can lower the system's energy by flipping spins, thus achieving a state of minimal total energy.

4.2.5 Group VI Dopants

For group-VI dopants (refer to Fig. A.6 in Appendix A), we identified a wide range of allowed transition energies, particularly for oxygen-based complexes, with the exception of $O_N V_N$, aligning with experimental studies [57, 196]. It is important to note that the O_N and $O_N V_B$ defect states are situated near the band edges (i.e., shallow defects), thus not fulfilling our criteria for optimal quantum emitters. Additionally, previous DFT calculations did not report transitions for the $O_N V_B$ and $O_B V_N$ defects [181], whereas our calculations, using the HSE06 functional, identified transitions at 0.34 eV and 4.17 eV, respectively. This discrepancy can be attributed to the use of different functionals; it has been noted that non-hybrid functionals tend to underestimate the band gap [110, 113]. For sulfur- and selenium-based defects, we did not find any defects that meet all our

criteria.

4.2.6 Transition Metal Dopants

Doping transition metals into the hBN lattice introduces a high density of localized states, attributable to the significant hybridization of transition metals (see Fig. A.7 in Appendix A). Among the defects studied, those based on erbium (Er) align well with our selection criteria, as they all exhibit radiative transitions with energies ranging from 1.09 to 3.43 eV. In contrast, none of the vanadium (Va) based defects display radiative transitions. Note that the symbol Va is used throughout this dissertation to distinguish vanadium from vacancies, which are labeled as V. For Ti and Re-based defects, both radiative and non-radiative transitions were observed, covering a spectrum of different transition energies.

4.2.7 Multi-Defect Complexes

Our investigation now extends to multi-defect complexes composed of at least two impurities from different periodic groups (e.g., $\text{Al}_\text{N}\text{Sb}_\text{B}$, see Figs. A.8, A.9, and A.10 in Appendix A). These complexes exhibit a broader spectrum of possible transition energies, ranging from 0.58 to 5.60 eV, thus nearly spanning the entire band gap of hBN. However, from experimental perspectives, fabricating such defects remains challenging, as it requires the precise implantation of different atomic species at adjacent lattice sites rather than random distribution.

4.3 Defects for Quantum Technology Applications

Our findings so far demonstrate that hBN defects cover a broad range of optical transition lines within the visible spectrum and extend into the near-infrared region. This raises the question about their suitability for quantum technology applications. To investigate this, we selected several key wavelengths relevant to quantum technology. For solid-state quantum emitters and qubits, we considered color centers in diamond (NV and group IV centers [197]) and silicon carbide (silicon vacancy [198]). Quantum memories were represented by rare-earth ion-doped crystals (such as $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ and $\text{Tm}^{3+}:\text{Y}_2\text{SiO}_5$ [199]) and alkali vapor-based memories (e.g., sodium, rubidium, and cesium using D1 or D2 transitions [199]). For long-distance quantum communication, the telecom windows are essential, specifically the first window at 850 nm (commonly used in free-space communications) and the telecom O- and C-bands at 1330 and 1550 nm, respectively.

In nearly all these applications, we identified suitable hBN quantum emitters that meet our selection criteria and have transitions near the specific wavelengths of other quantum systems, suggesting efficient coupling potential (see Tab. 4.1). In some cases,

Table 4.1: Summary of defects inheriting emission wavelengths matching with quantum technology applications. This table is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

Wavelength for Quantum Technology (nm)	Other systems in quantum technology	Compatible hBN defects	Defect transition energy (eV) / wavelength (nm)
552	PbV ⁻ (diamond)	S _B V _B	2.252 / 550.7
		In _B V _N	2.237 / 554.4
		In _N V _B	2.236 / 554.5
589	Na-D2	O _B V _B	2.110 / 587.6
590	Na-D1	Ti _N V _B	2.100 / 590.5
		V _N V _B Ti	2.097 / 591.3
602	GeV ⁻ (diamond)	Er _B N _B V _N	2.063 / 601.1
606	Pr ³⁺ :Y ₂ SiO ₅	* Sn _B V _B	2.037 / 608.8
620	SnV ⁻ (diamond)	V _N V _B	2.024 / 612.7
637	NV ⁻ (diamond)	** Al _N	1.918 / 646.6
738	SiV ⁻ (diamond)	V _B V _B	1.678 / 738.8
780	Rb-D2	Er _B V _B	1.592 / 778.7
		Er _N V _B	1.590 / 779.6
793	Tm ³⁺ :Y ₂ SiO ₅	In _B V _B	1.540 / 805.2
795	Rb-D1	Er _N N _B V _N	1.537 / 806.8
		Al _B V _B	1.535 / 807.9
850	Telecom-1	Er _N V _N	1.473 / 842.0
852	Cs-D2		
862	V _{Si} ⁻ (silicon carbide)	Er _B V _N ⁻	1.427 / 869.0
894	Cs-D1	* Er _B V _B ⁺	1.398 / 886.9
1330	Telecom O-band	O _N S _N	0.946 / 1310.2
1550	Telecom C-band	* Er _B ⁺	0.789 / 1572.3

* Transition between VB or degenerate (ground) state and an unoccupied non-degenerate (excited) state.

** Transition between double-occupied (degenerate) ground and unoccupied degenerate excited state.

multiple hBN defects are viable, or a single defect may be applicable to more than one use case. It is noteworthy that for certain applications, suitable transitions were found only in charged defects, which will be discussed in Sec. 4.4.2. Moreover, defects such as Sn_BV_B, Er_BV_B⁺, and Er_B⁺ exhibit transitions between the valence band or a degenerate ground state and an unoccupied excited state. Although these do not technically meet

our criteria for deep defect states, the excited states are not degenerate and can only be excited once due to the Pauli exclusion principle. Thus, these defects can potentially act as single-photon emitters.

4.4 Tailoring the Transition Wavelength for Quantum Technology Applications

Despite identifying hBN defects that align with various quantum technology applications, precise matching between hBN emission wavelengths and quantum applications remains unsuccessful. In the case of narrow transitions (e.g., the Rb-D2 emission line), this can substantially limit the coupling efficiency to the other quantum system. Therefore, this section proposes two fine-tuning mechanisms, strain and charge, to tailor an emitter wavelength to match the target one.

4.4.1 Strain Tuning

The principle behind strain tuning is shifting of the energy levels from the symmetry breaking due to local structure modification [200]. Experimentally, applying strain was successful shortly after their initial discovery [201] to tune the emission wavelength. While we are aware that DFT has a finite accuracy, the result can still be used to predict the tendency.

In Fig. 4.4, we showcase strain tuning for some selected defects to tailor their emission to match the specific wavelengths (for complete band structures, see Figs. A.11, A.12, and A.13 in Appendix A). For instance, to tune the $S_B V_B$ defect into resonance with the PbV^- center in diamond at 552 nm, a strain of 0.10% is needed. Predicting the required strain is challenging because different local defect structures react variably to the same amount of strain. Additionally, strain can break the C_{2v} symmetry of the defects. Our findings indicate that lattice deformation can be classified into in-plane (e.g., $In_B V_N$, Al_N , and $On_S N_N$) and out-of-plane deformations (the remaining defects in Fig. 4.4). As expected, the out-of-plane deformations cause larger wavelength shifts, ranging from 50 to 250 nm, whereas the in-plane deformations result in narrower shifts of 30 to 40 nm. This aligns with the fact that the out-of-plane deformation more significantly alters the symmetry of local structures compared to in-plane deformation.

Many defects exhibit a linear relationship between strain and transition energy, although some show nonlinear behavior (see Fig. 4.4). This effect depends on the interplay between symmetry, initial strain, and defect configuration, such as location and size [202]. Generally, the strain Hamiltonian can be expressed as $H = \sum_{ij} B_{ij} \epsilon_{ij}$, where B_{ij} are the electronic operators and ϵ_{ij} are the strain tensor components. When a quantum emitter is embedded in hBN, the system's strain principal axes can shift due to defect-induced symmetry breaking. Depending on the direction and magnitude of the applied strain, ϵ_{ij} can be a nonlinear function of the strain s , causing the eigenvalues

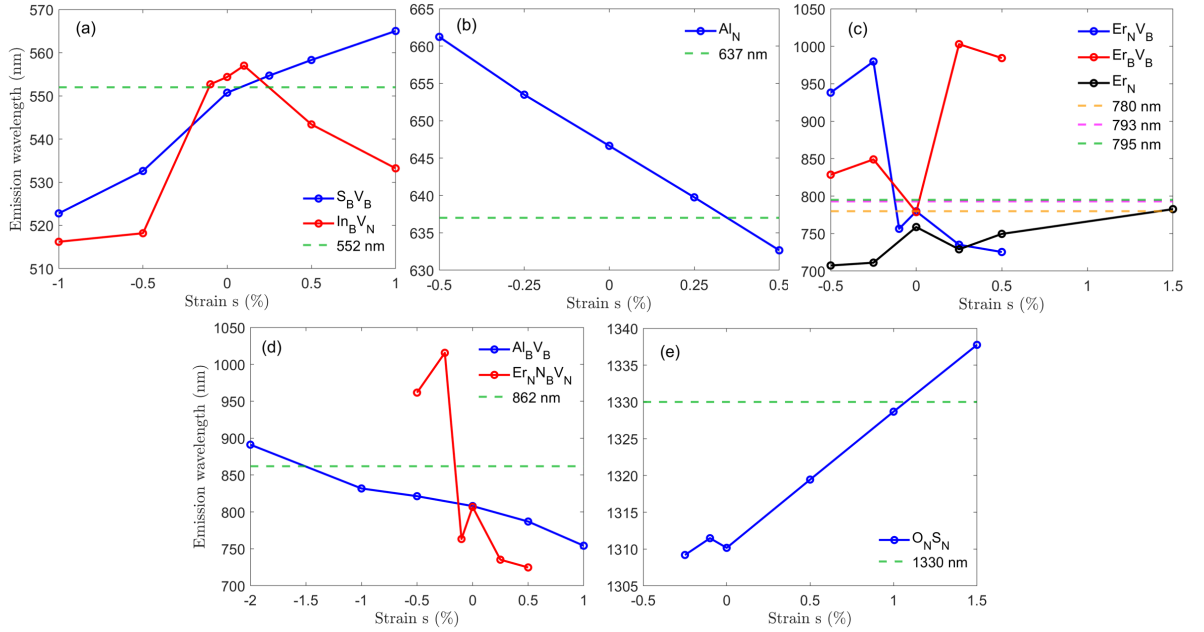


Figure 4.4: Changes of emission wavelength affected by bi-axial strain whose negative and positive signs imply compressive and tensile strains. Dashed lines indicate the target wavelength, while solid lines represent the emission wavelengths of defects at specific values: (a) 552 nm (PbV^- in diamond), (b) 637 nm (NV^- in diamond), (c) 780 nm (Rb-D2), 793 nm ($\text{Tm}^{3+}:\text{Y}_2\text{SiO}_5$), and 795 nm (Rb-D1), (d) 862 nm (VSi^- in silicon carbide), and (e) 1330 nm (telecom O-band). This figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

of H to also nonlinearly depend on s . Even with the hybrid HSE06 functional, DFT maintains finite accuracy, suggesting that the linear trend observed for the $\text{S}_\text{B}\text{V}_\text{B}$ defect in Fig. 4.4(a) may not be purely linear. The more pronounced nonlinear effects, such as those observed for the $\text{In}_\text{B}\text{V}_\text{N}$ defect in Fig. 4.4(a), exceed this accuracy, indicating that the observed nonlinear strain-wavelength relationship is genuine. Nonlinear strain dynamics have been previously reported [200, 201], speculated by initial conditions of the host crystal flakes, including wrinkles, cracks, and lattice mismatches from sample fabrication, leading to different local bond lengths and unpredictable Stokes shifts.

It is also noteworthy that strain can activate quantum emitters in hBN [203]. The donor-acceptor pair (DAP) model qualitatively describes this phenomenon. According to the DAP pair [115, 204], there is an optimal bond length between donor and acceptor sites for strong photoluminescence. When the local structure is strained, the bond length between the active donor and acceptor may adjust to a distance where the structure becomes optically active, even if this is not the most stable configuration

(i.e., the zero-strain relaxed structure). Consequently, optically inactive defects, previously discounted based on our selection criteria, could potentially be activated by strain. However, a comprehensive study of this effect is beyond the scope of the present work.

4.4.2 Charge-State Manipulation

Thus far, our focus has been on neutral charge states. In this section, we extend our study to include charged defects, specifically singly positive and negative charges. The defects listed in Tab. A.1 are categorized based on whether they exhibit radiative or non-radiative first-order transitions. Introducing a single charge to a defect (i.e., adding or removing one electron) naturally shifts the Fermi energy due to the occupation or depopulation of an additional state. A positive charge can depopulate the top-most occupied state, while a negative charge can populate the bottom-most unoccupied state. In many instances, the transition type is preserved, meaning an optically active transition remains active upon charging. However, the level structure may also undergo significant changes, as observed in Fig. 4.5 below and Figs. A.14, A.15, and A.16 in Appendix A for other defects and another previous DFT calculation [115].

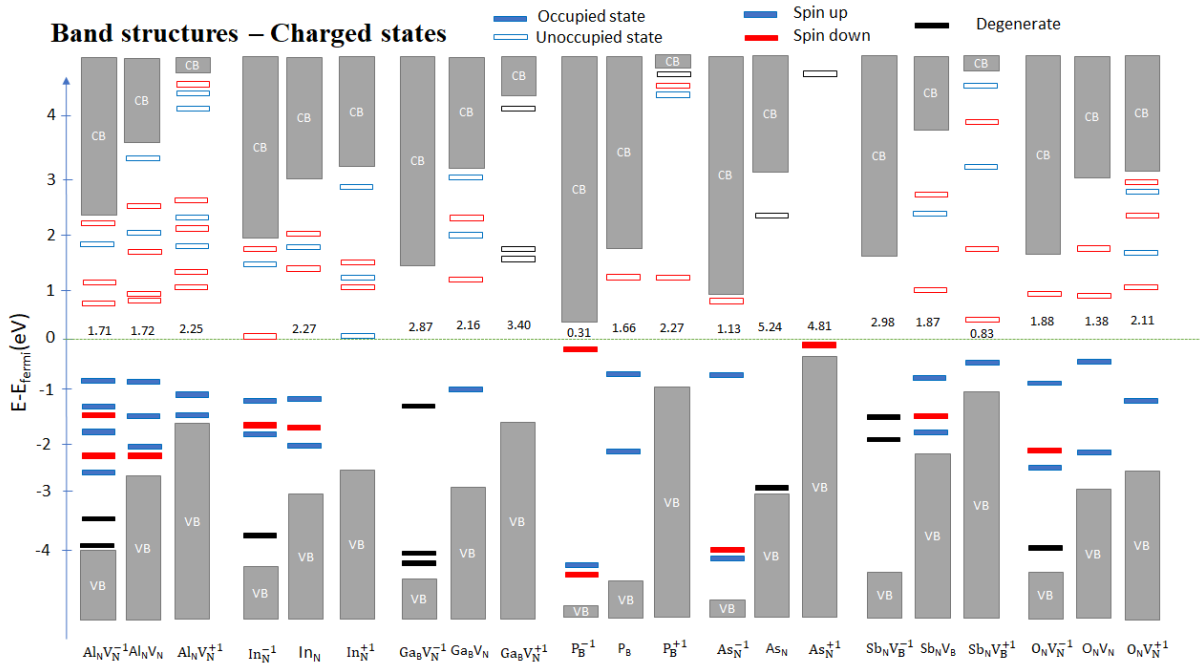


Figure 4.5: Modified electronic band structures for charged-state defects hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

Among our calculations of charged states, we have identified emitters compatible with quantum technologies. For instance, the $\text{Er}_\text{B}\text{V}_\text{N}^-$ defect exhibits a first-order transition near that of the V_{Si}^- center in silicon carbide. The $\text{Er}_\text{B}\text{V}_\text{B}^+$ defect can match to the Cs-D1 transition, while the Er_B^+ defect emits in the telecom C-band, making it suitable for long-distance quantum communication.

4.5 Thorough Comparison with Experimental Findings

Here, we move to the second objective of this chapter: providing a comprehensive fingerprint of hBN quantum emitters, which is compatible with simple experimental measurements. The clues from our own experiment will be first discussed. Then, it will be followed by comprehensive computational properties to match the experimental observations. Finally, we will use such comprehensive properties to propose a few defects for quantum communication. It is important to note that all experimental works were conducted by Anand Kumar and Tjorben Matthes, while this dissertation only performed the calculations.

4.5.1 Experimental Clues for Yellow Quantum Emitters

In a recent experiment conducted by Anand Kumar and Tjorben Matthes in our research group [61, 179], hBN emitter arrays were fabricated using electron beam irradiation using a standard scanning electron microscope with deep sub-micron lateral precision, as shown in the PL map in Fig. 4.6(a). PL characterization, performed with a 530 nm excitation laser, revealed a prominent peak at 575 nm. The second-order correlation function $g^2(\tau)$ was measured across 63 emitters on the same flake, as depicted in Figs. 4.6(d) and (e). The majority had $g^2(0) < 0.5$, indicative of single photon emission, as this threshold proves an existing projection onto the single-photon Fock state [205]. Additionally, the lifetime of all emitters was measured, yielding a mean value of 3.8(5) ns.

In addition to examining the properties of these emitters, our experiment investigated their polarization characteristics [61]. By measuring the angles of excitation and emission dipoles relative to the crystal axes, as illustrated in Figs. 4.6(b) and (c), we discovered that the excitation polarization clusters around the crystal axes (see Fig. 4.6(d)), while the emission polarization clusters between the crystal axes (see Fig. 4.6(d)). This results in the difference of two polarization axes, or the so-called a polarization misalignment, of approximately $18.9(100)^\circ$, as displayed in Fig. 4.6(f). This indicates that the two dipoles are not aligned and that the polarization is not symmetrically distributed by 60° around the crystal axis, as one would expect from a hexagonal lattice (See also Fig. 4.6(g)).

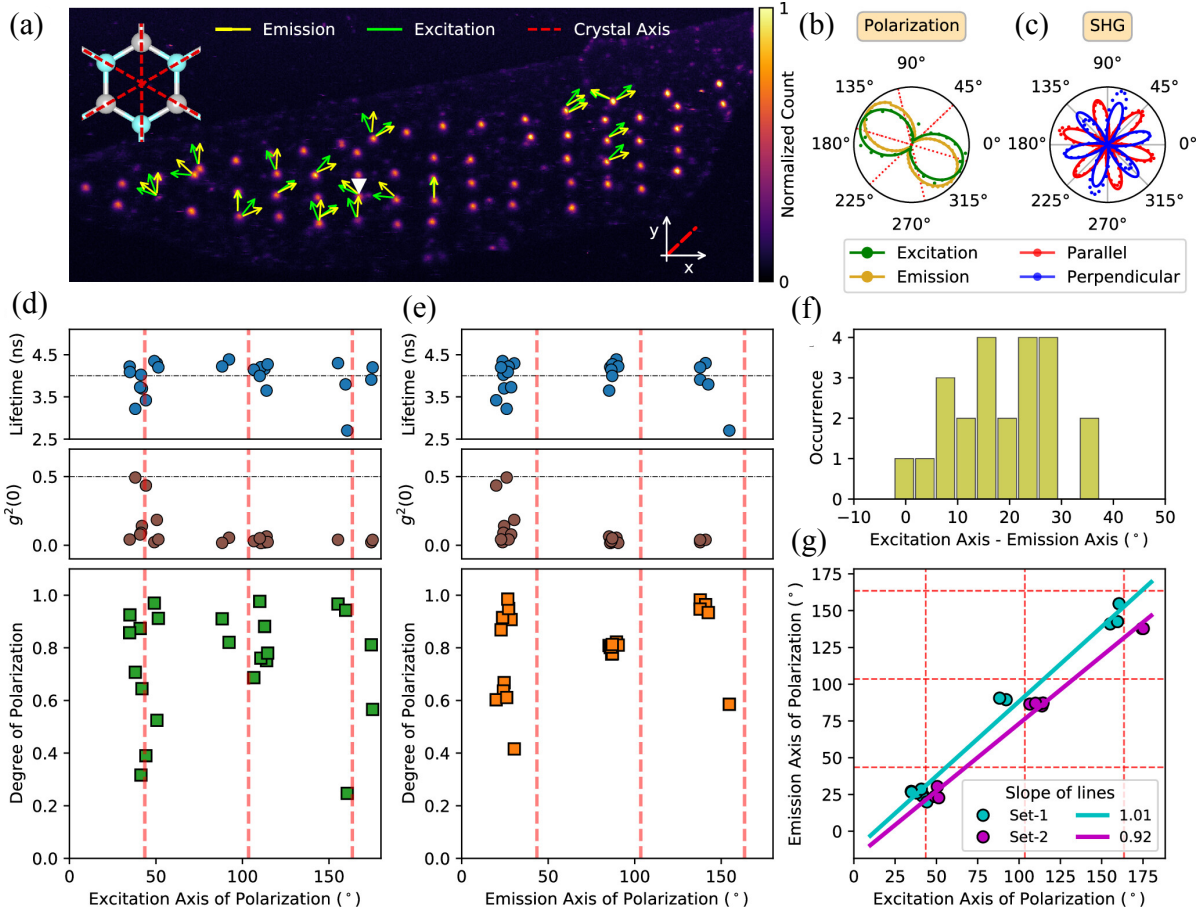


Figure 4.6: Experimental optical properties of hBN yellow emitters. (a) PL map of the entire flake. The emission and excitation axes are represented by arrows. (b) A polar plot of emission and excitation axis at the spot marked with a white ‘▼’ symbol. A cosine-squared fit with 98.01% (emission) and 96.67% (excitation) is used to extract the angle of polarization. Red grid lines represent the crystal axes. (c) A polar plot of crystal axes from the polarization-resolved second-harmonic generation (SHG) measurement. The six-fold symmetry is observed and marked in all other subfigures. (d) and (e) Scatter plots of the polarization axes against the degree of polarization with the corresponding $g^2(\tau = 0)$ and lifetimes of emitters. (f) The histogram of misalignment between excitation and emission axes of polarization. The mean value yields $18.9(100)^\circ$. (g) Relationship between excitation and emission axes across two different emitter sets, namely ‘Set-1’ and ‘Set-2’. Note that this dissertation did not perform this experiment. This figure is adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

Additionally, temporal polarization dynamics were observed, characterized by a significant increase in linear polarization visibility within the first three nanoseconds, as exhibited in Fig. 4.7. Alongside this visibility change, most emitters exhibit a rotation in the polarization axis over the decay time, whereas the polarization of others remains stable. We speculate that these effects are due to photo-induced modifications in the local charge environment surrounding the emitter. Specifically, laser pulses may excite nearby optically inactive emitters or charge states, generating an induced electric field around the emitter. Such electric field fluctuations can temporarily shift the dipole axis of the emitters, leading to a reduction in observed polarization visibility.

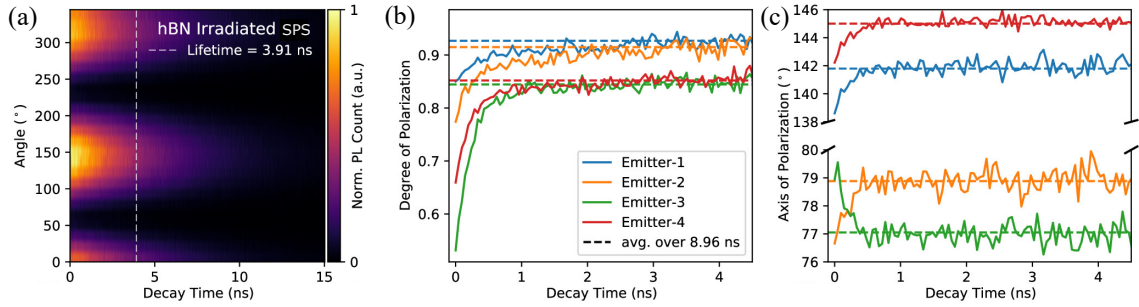


Figure 4.7: Experimental polarization properties of hBN yellow emitters. (a) PL intensity measured with respect to time after excited by the laser pulse as a function of the polarizer rotation angle. (b) The temporal dynamics of the linear degree of polarization. (c) The temporal dynamics of the polarization axis. The dashed lines indicate the time-averaged visibility and polarization axis obtained by integrating over an extended time period. Measurements were obtained with a pulsed excitation of 530 nm at 10 MHz repetition rate. Note that this dissertation did not perform the experiment. This figure is adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

4.5.2 Comprehensive Computational Investigation

This section aims to address the following questions: (Q1) What is the most promising defect candidate for the 575-nm ZPL? (Q2) Why do the excitation and emission dipoles misalign? (Q3) How are the dipoles oriented with respect to the crystal axes? (Q4) Are the dipoles distributed by 60° around the crystal axis corresponding to a hexagonal lattice? (Q5) What is the cause of temporal polarization dynamics? We address these questions utilizing spin-polarized DFT under the HSE06 functional. Our study focuses on the most probable candidates, including intrinsic defects and complexes involving oxygen and carbon impurities in neutral or ± 1 charge states. Carbon complexes, which could form during the SEM irradiation process, are considered consistent

with previous DFT calculations that have identified 2 eV quantum emitters in hBN [90, 115, 193].

Identifying ZPL of Defects for Yellow Emitters

To trace back possible defect candidates responsible for the yellow emission, we considered the possibility that carbon contaminants seem to bond to the surface during SEM imaging, causing the characteristic dark frames. This suggests that carbon may be involved in the defect formation.

The theoretical investigation proceeds as follows. Initially, 27 different carbon-related defects, including neutral and singly charged states (both positive and negative), were characterized based on their ZPL (see Tab. 4.2). Subsequently, only those defects emitting in the yellow region were further analyzed for charge-state stability and PL properties.

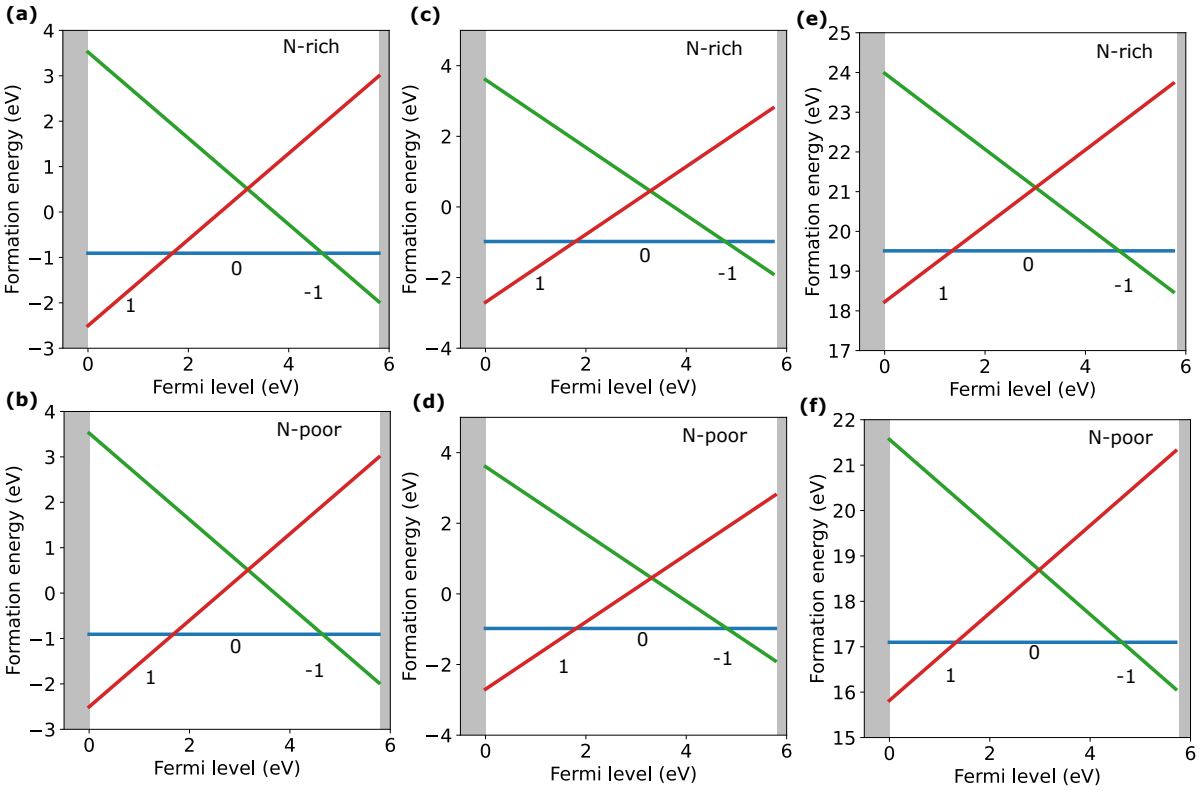


Figure 4.8: Defect formation energy for various defect configurations: (a) and (b) correspond to $C_B C_N C_B C_N$ -5, (c) and (d) to $C_B C_N C_B C_N$ -3, and (e) and (f) to $C_N V_N$. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

Table 4.2: Emission properties of various carbon defects, with the most favorable electronic configuration selected based on total energy comparisons among singlet, doublet, and triplet states. The electronic transition is considered from the transition in a two-level quantum system: occupied and unoccupied states. Note that N/A indicates that the defect does not exhibit a two-level system with the same spin polarization between the occupied and unoccupied defect states. $C_B C_N C_B C_N$ -number refers to different structural configurations, as depicted in Appendix B. The table is adapted from Ref. [179] available under a [CC-BY 4.0 license](#). Copyright 2023 Kumar *et al.*

Defects	Most preferred electronic configuration	Electronic transition	Zero phonon line (eV)	Emission wavelength (nm)
C_B^{-1}	Singlet	up - up	2.62	472.53
C_B	N/A	N/A	N/A	N/A
C_B^{+1}	Singlet	up - up	4.13	300.15
C_N^{-1}	Singlet	up - up	2.96	419.33
C_N	N/A	N/A	N/A	N/A
C_N^{+1}	Singlet	up - up	0.60	2079.84
$C_B V_N^{-1}$	Doublet	up - up	0.80	1553.53
$C_B V_N$	Triplet	up - up	1.89	655.04
$C_B V_N^{+1}$	Doublet	up - up	2.39	22.32
$C_B V_B^{-1}$	Doublet	up - up	2.64	470.53
$C_B V_B$	N/A	N/A	N/A	N/A
$C_B V_B^{+1}$	Doublet	up - up	0.67	1846.86
$C_N V_N^{-1}$	Doublet	up - up	1.02	1218.08
$C_N V_N$	Singlet	down - down	2.36	525.17
$C_N V_N^{+1}$	Doublet	up - up	3.48	356.22
$C_N V_B^{-1}$	Doublet	up - up	2.32	532.99
$C_N V_B$	Triplet	up - up	2.79	444.03
$C_N V_B^{+1}$	Doublet	up - up	0.54	2318.71
$C_B C_N C_B$	Doublet	up - up	4.09	303.49
$C_B C_N C_N$	Doublet	down - down	1.64	754.16
$C_B C_N C_B C_N$ -1	Singlet	down - down	2.87	432.55
$C_B C_N C_B C_N$ -2	Singlet	down - down	1.94	639.85
$C_B C_N C_B C_N$ -3	Singlet	down - down	2.17	572.68
$C_B C_N C_B C_N$ -4	Singlet	down - down	1.95	635.50
$C_B C_N C_B C_N$ -5	Singlet	down - down	2.21	562.15
$C_B C_N C_N C_N$	Triplet	up - up	4.42	280.67
$C_N C_B C_B C_B$	Triplet	up - up	1.08	1145.04

From the 27-carbon-based exploration, Tab. 4.2 reveals that some defects, such as C_B and C_N , can be immediately excluded as candidates since they do not exhibit a two-level system, consistent with previous studies [90, 181]. Among all the defects studied,

only the $C_N V_N$ and $C_B C_N C_B C_N$ configurations show emission wavelengths peaking in the yellow spectral region, similar to experimental observations. Given that four-carbon complexes can have various structural configurations, we varied them randomly, as illustrated in Fig. B.1 in Appendix B. The results indicate that all configurations studied exhibit a ZPL around 2 eV, suggesting that the structural configuration has less effect on the ZPL compared to the defect type. However, only the configurations with ZPLs closest to experimental values (highlighted in Tab. 4.2) were further analyzed for charge stability and complete PL lineshapes. Charge stability was evaluated based on the defect formation energy. As shown in Fig. 4.8, the three proposed promising neutral-charged defects are stable under thermodynamic equilibrium. Next, the PL lineshapes of these defects are characterized.

As depicted in Fig. 4.9, the complete PL lineshapes for $C_B C_N C_B C_N$ and $C_N V_N$ complexes are characterized with structural configurations shown in Fig. 4.9(a-c), as potential candidates for carbon-related emitters with the ZPL in the yellow region. In addition to the ZPL, we calculated the PSB to obtain the complete PL spectrum (see Fig. 4.9(d-f)). The peaks were identified by analyzing the spectral function of the electron-phonon coupling or HR factor, as depicted in Fig. 4.9(g-i). The PSB peaks, ranging from 100 meV to 175 meV, align with typical values for hBN quantum emitters. Notably, the PL spectrum of the $C_N V_N$ defect exhibits a broad peak at 380 meV from the ZPL. This can be attributed to the fact that these modes have higher energy (> 200 meV) than the zone-center longitudinal optical phonon mode ($LO(\Gamma)$) [206]. Due to the Fröhlich interaction, the electron-phonon matrix element diverges at this point, leading to broad PL. The HR factor further clarifies the ZPL assignment, yielding values of 1.033, 1.372, and 4.795, corresponding to configuration coordinate shifts of $0.456 \text{ amu}^{1/2} \text{ \AA}$, $0.435 \text{ amu}^{1/2} \text{ \AA}$, and $0.994 \text{ amu}^{1/2} \text{ \AA}$, respectively, for the defect complexes shown in Fig. 4.9(a-c). This indicates that the $C_B C_N C_B C_N$ configurations exhibit weak phonon coupling, while the $C_N V_N$ defect shows strong phonon coupling. Consequently, our DFT calculations suggest that $C_B C_N C_B C_N$ is a likely candidate for this emission range, whereas $C_N V_N$ is less probable due to the mismatch of its PSB with experimental observations. This result has addressed the first question Q1.

Moreover, when comparing singlet, doublet, and triplet spin configurations of $C_B C_N C_B C_N$, the singlet configuration is favored, suggesting the absence of a metastable triplet state. This implies that $C_B C_N C_B C_N$ is unlikely to exhibit any ODMR signature, consistent with experimental results. Although our DFT calculations have narrowed down the possible defect candidates with ZPL relevant to the yellow region, additional photophysical properties are still required for validation.

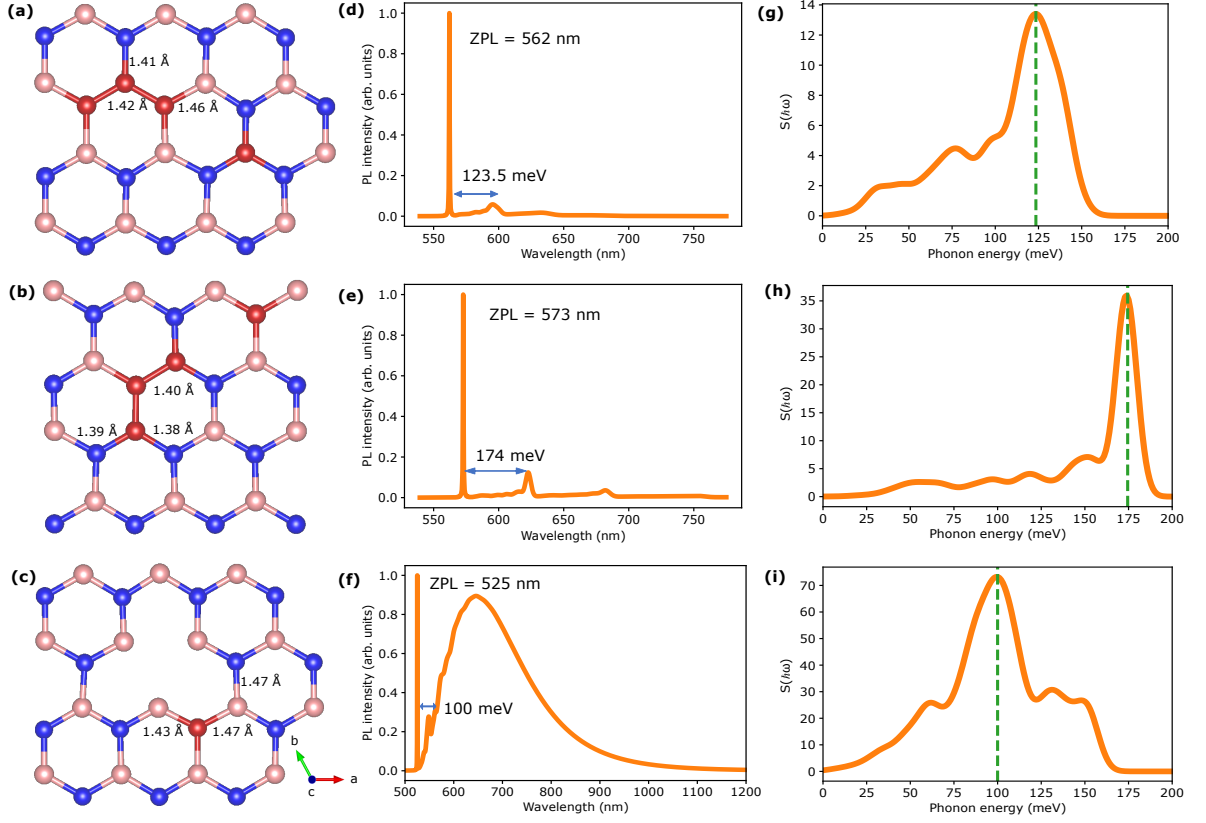


Figure 4.9: Computational investigations of PL resulted from different defect structures. (a, b) Defect structures of the $C_B C_N C_B C_N$ defect in two configurations, and (c) the $C_N V_N$ defect. Boron atoms are shown in pink, nitrogen in blue, and carbon in red, with a and b directions in the plane. (d-f) Simulated PL corresponds to the defect structures in (a-c), where the first peak represents the zero-phonon line (ZPL), and the second peak corresponds to the phonon sideband (PSB). (g-i) Huang-Rhys factors indicate the contributions of specific phonon modes to the PL spectra. The dashed line marks the PSB peak. The broad PL emission in the near-infrared shown in (f) is further discussed in the main text. This figure is adapted from Ref. [179] available under a [CC-BY 4.0 license](#). Copyright 2023 Kumar *et al.*

Characterizing Dipole Orientation

In this section, apart from identifying promising microscopic origins, we address two questions: (Q2) why do the excitation and emission dipoles misalign? and (Q3) how do the dipoles specifically align with respect to the crystal axes? Although the ZPL characterization from the previous section has narrowed down the candidates to be

$C_B C_N C_B C_N$ and $C_N V_N$, we have not excluded other defects yet. In other words, we re-examine the C- and O-based defects to determine if the dipole properties corroborate the same defect candidates as predicted by our initial calculations. This includes 126 defects, whose raw data can be accessed from the hBN online database <https://h-bn.info> or the repository <https://doi.org/10.5281/zenodo.10288562>.

The electronic transition associated with a defect can theoretically be modeled using the Huang-Rhys framework, as depicted in Fig. 4.10(a). The ground and excited states, represented by the blue and orange curves, respectively, are key contributors to the transition. Each state encompasses vibrational modes, indicated by the dots on their corresponding curves. Transitions between any pair of vibrational modes in the ground and excited states give rise to the absorption and emission spectra, which include the ZPL and PSB. It is noteworthy that the transition dipole moment for absorption is influenced by the specific phonon mode involved, and thus depends on the wavelength of the excitation laser relative to the ZPL [207]. The excitation process corresponds to the transition from point 1 to point 2 in Fig. 4.10(a), followed by a relaxation to point 3 on ultrafast timescales (typically within a few picoseconds) via phonon scattering. From point 3, emission can occur either directly to the ground state (point 1) or through an intermediate phonon mode (point 4). We computed the transition dipole moments for both the ZPL (transition from 3 to 1) and a randomly selected phonon mode in the PSB (transition from 3 to 4). For the latter, we observed negligible differences in the relative angles (less than 1° ; see Tab. C.1 in Appendix C). Experimentally, the dipole moment averaged over the ZPL and PSB would be measured with reduced polarization visibility if there is misalignment between the two transition dipole moments. Consequently, our theoretical analysis is restricted to the transition dipole moment at the ZPL pathway (transition from point 3 to point 1).

Since these specific points originate from distinct electronic states and ionic relaxation configurations, their corresponding wave functions are then different. This observation is consistent with prior DFT calculation [135]. Figs. 4.10(b)-(d) illustrate the probability densities ($|\psi|^2$) of electron occupation for the defect $C_B C_N C_B C_N$, corresponding to points 1 through 3, respectively. The variations between points 1 and 2, as well as between points 3 and 1, are shown in Fig. 4.10(e) and (f), respectively. Given that the transition dipole moment is proportional to $\langle \psi_f | \mathbf{p} | \psi_i \rangle$ (see Eq. (3.2) in Sec. 3.1.4), where i and f denote the initial and final states of the transition, differences in wave functions can lead to variations in dipole moments. This, in turn, results in different angles between the excitation and emission polarizations, thereby addressing our research question Q2. Nonetheless, we do not entirely dismiss the possibility that the misalignment of dipoles may also be influenced by additional intermediate states, as previously reported [207].

To identify the defect type that best agrees with the experimental observations, we computed the properties of 126 native, carbon-, and oxygen-based defects across various charge states (see Appendix C and the accompanying dataset). We employed the following criteria to select the most promising defect candidates: (i) the ZPL range, (ii) the

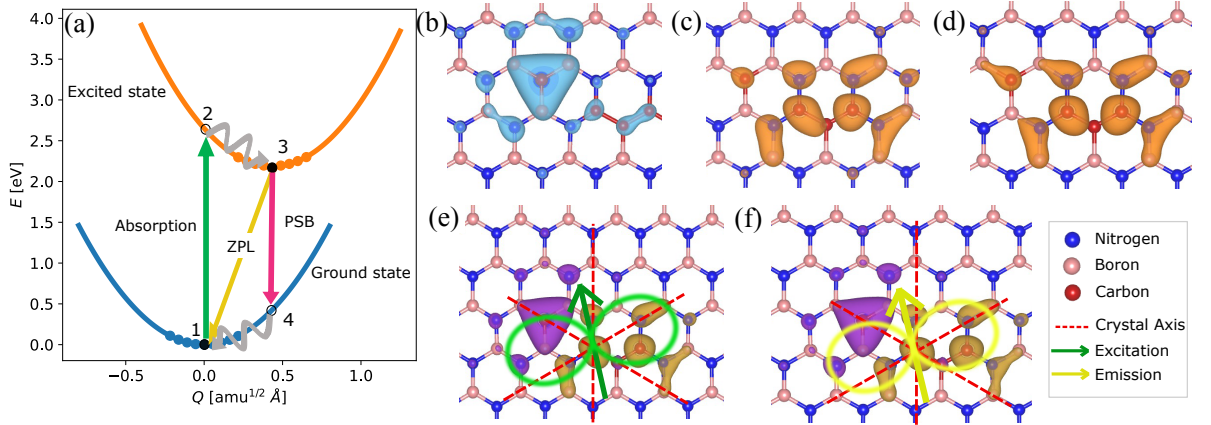


Figure 4.10: Theoretical characterization of the neutral-charged $C_B C_N C_B C_N-3$ defect without strain. (a) Potential energy surface, illustrating the full excitation and emission process. This includes absorption (green line), the zero-phonon line (ZPL, yellow line at 573 nm), and the phonon sideband (PSB, magenta line). (b)-(d) Probability density $|\psi|^2$ of electron occupations: (b) in the ground state at point 1, and (c, d) in excited states at points 2 and 3, respectively. (e) Charge difference between points 1 and 2, visualized by isosurfaces, with the green arrow indicating the excitation dipole axis, aligned with light radiation shown in green. The excitation axis is tilted 11.1° relative to the crystal axis (red dashed line). (f) Charge difference between points 1 and 3, with the yellow arrow showing the emission dipole axis, aligned with light radiation in yellow. The emission axis is tilted 12.1° relative to the crystal axis. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

orientation of the absorption polarization axis relative to the crystal axis (ranging from 3.9° to 11.6°), and (iii) the degree of linear in-plane polarization visibility. These criteria prioritize the absorption dipole, given that our experimental absorption/excitation dipole exhibits a finite angle relative to the crystal axis, whereas the experimental emission data is inconsistent and necessitates further investigation to confirm its behavior.

Oxygen and carbon were selected as impurities due to their suspected role in the 2 eV emission [173, 175] and their inherent chemical stability. Among the 126 defects analyzed, only 22 satisfy the excitation polarization range criteria; however, most of these are subsequently excluded based on polarization visibility. Many charged defects exhibit significant out-of-plane contributions. Our analysis indicates that the dipoles of charged-state defects are influenced by excessive positive or negative charges and out-of-plane structural deformations, leading to an alignment perpendicular to the crystal plane. This finding confirms that dipoles are sensitive to charge distribution and struc-

tural deformation. The remaining candidates were further narrowed down by considering the ZPL (see Appendix C), ultimately leaving the $C_B C_N C_B C_N$ defect complex as the only viable option.

The most likely defect candidates are consistent with our findings in Sec. 4.5.2, namely the neutral-charged $C_B C_N C_B C_N$ -3 and the neutral-charged $C_B C_N C_B C_N$ -5, with ZPLs at 573 nm and 562 nm, respectively. Given the current theoretical and experimental uncertainties, we cannot definitively distinguish between these cases, and it is plausible that a mixture of both defects is present in our sample. While the experimental excitation polarization yields from 3.9° to 11.6° , the calculated excitation (emission) polarization axes of $C_B C_N C_B C_N$ -3 and $C_B C_N C_B C_N$ -5 defects align at 11.1° (12.1°) and 12.3° (13.7°), respectively, relative to the nearest crystal axis, as indicated by the arrows in Figs. 4.10(e) and (f). The calculation is therefore consistent with the experiment. However, when also taking into account the emission polarization, the experiment can quantify the misalignment between both polarizations and yield $18.9(100)^\circ$ whereas the calculated misalignment yields 1.2° and 1.6° for $C_B C_N C_B C_N$ -3 and $C_B C_N C_B C_N$ -5. This indicates that the calculated misalignment does not match the experimental value. This can be attributed to many factors such as the uncertainty of the experimental emission data mentioned before and inhomogeneous strain distribution in the flake or localized charge within the lattice due to the irradiation process.

When considering the excitation polarization together with the overall properties, including ZPL and polarization visibility, the $C_B C_N C_B C_N$ defect emerges as the most favorable emitter among all the defects studied (see Appendix C). This has addressed question Q1 of the promising defect candidate and question Q3 of how the dipoles align relative to the crystal axis.

Effects of Strain on Dipole Orientation

Now we aim to address the question Q4: Are the dipoles distributed by 60° around the crystal axis corresponding to a hexagonal lattice? Thus far, our model has been unable to explain the observed symmetry breaking, specifically, why the emission axis centers are not aligned with the crystal axes and are not spaced 60° apart, as well as the large distribution in angle differences between excitation and emission. We speculate that strain could be responsible for these discrepancies.

There are two types of strain to consider: global and local. Global strain is unlikely to be significant, as it would skew the SHG pattern in Fig. 4.6(c). Hence, we suspect there could be substantial local strain around the irradiated spots of Fig. 4.6(a).

As illustrated in Fig. 4.11, we qualitatively modeled this scenario using DFT by applying biaxial strain in the range of $\pm 1\%$ to the lattice and monitoring the orientations of the dipoles. For vacancy-based defects, the shifts can exceed 4° , whereas for the $C_B C_N C_B C_N$ -3 defect, the shifts remain below 0.5° within the strain range investigated. Furthermore, we observed that local strain affects the excitation and emission dipoles differently, which could contribute to symmetry breaking and result in unequal shifts

relative to the crystal axis. Thus, we can partially address the question Q4 by attributing the observed symmetry breaking to significant local strain around the irradiated spots or other, as yet unidentified, local modifications within the crystal environment. A quantitative analysis of this phenomenon is beyond the scope of the current work and will be pursued in future studies.

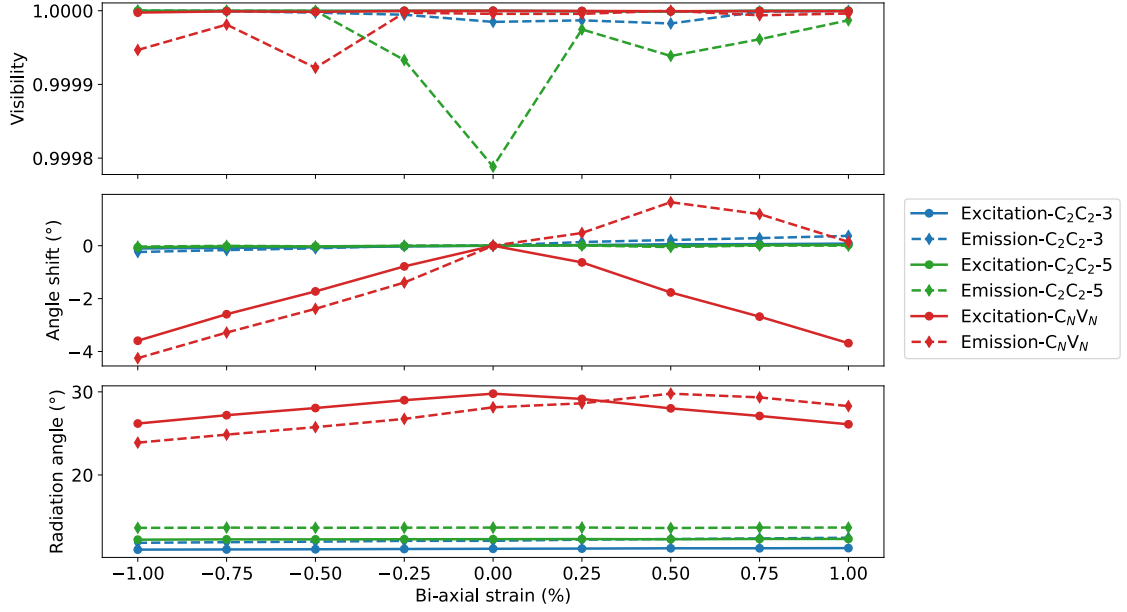


Figure 4.11: Variation of excitation and emission axes affected by bi-axial strain. The solid line represents the excitation, whereas the dotted line represents the emission. (a) The linear in-plane polarization visibility, (b) the angle of excitation/emission axes shifted from that with the unstrained condition, and (c) the excitation/emission angle measured with respect to the nearest crystal axis. Note that C_2C_2 stands for $C_B C_N C_B C_N$. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

Effects of Electric Charges on Temporal Dynamics of Polarization

Lastly, we address the question (Q5); that is, can excess electric charges of defects cause temporal variations of polarization, as shown in Fig. 4.7? To model the temporal variations observed in the experiment [61], we applied an external electric field (up to 0.7 V/Å) to simulate the redistribution of the local charge environment around the defects. We thought that this could mimic the experimentally observed temporal dynamics. It is worth noting that the electric field magnitude of about 0.7 V/Å corresponds to that from a single electron as a point charge sitting either above or below the defect by a few

angstroms (i.e., in the neighboring layer). This field strength is also similar to the one realized in an hBN experiment involving Stark tuning and was shown to have an impact on the emitters (even though no polarization was studied) [208].

The results presented in Fig. 4.12 indicate that, for all defects studied, the in-plane dipoles exhibit a significant out-of-plane contribution when subjected to a strong out-of-plane electric field. Our analysis focuses on the regime of weak electric fields, which only minimally affect the photophysical properties (i.e., induce only adiabatic changes without abrupt transitions). Within this limit, we observe a substantial reduction in visibility (exceeding 20%), accompanied by a change in the polarization axis of more than 5° . This qualitative observation confirms that the dipoles are indeed sensitive to the local charge distribution, potentially explaining the observed temporal dynamics of polarization.

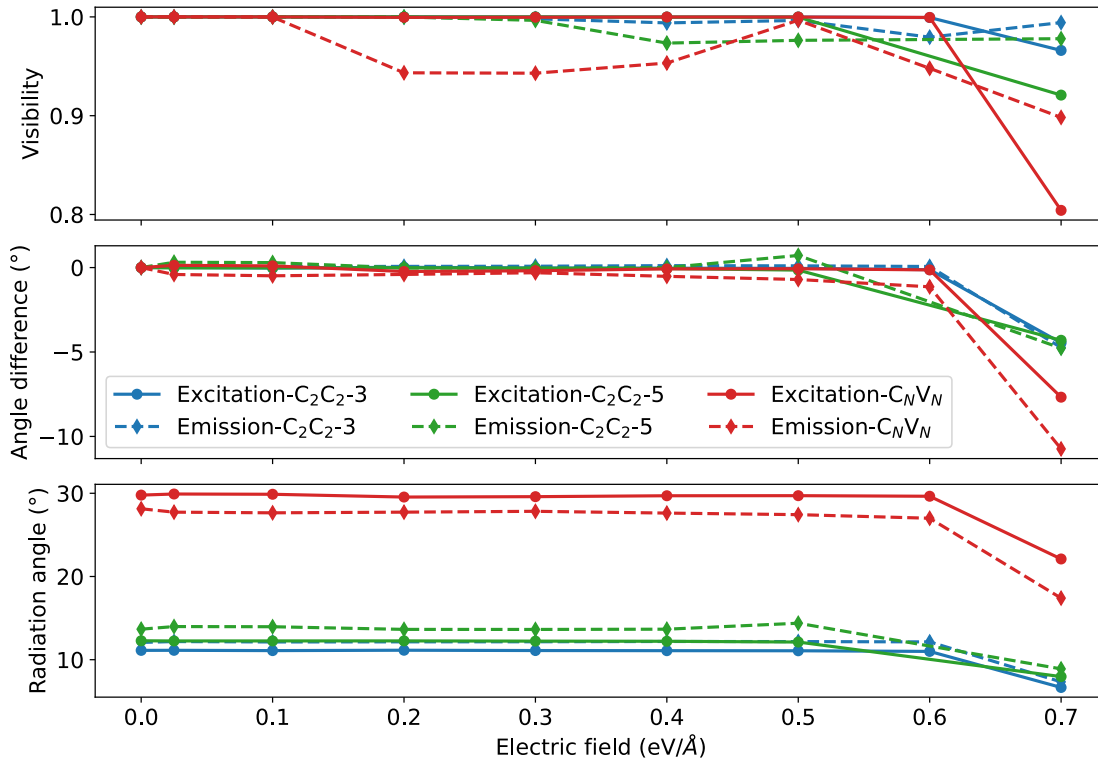


Figure 4.12: Variation of excitation and emission axes affected by an out-of-plane electric field. The solid line represents the excitation, whereas the dotted line represents the emission. (a) The linear in-plane polarization visibility, (b) the angle of excitation/emission axes shifted from that with the absence of electric field, and (c) the excitation/emission angle measured with respect to the nearest crystal axis. Note that C_2C_2 stands for $C_B C_N C_B C_N$. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

Comprehensive Photophysical Properties

Despite our extensive investigation into the properties of emitters and polarization, another defect candidate, the carbon trimer $C_B C_N C_N$, has been proposed by another DFT study [175]. To ascertain which defect is responsible for our observed yellow emission, we systematically compare our candidate, $C_B C_N C_B C_N$, with their proposed candidate, $C_B C_N C_N$.

The complete fingerprints of these defect candidates are presented in Tab. 4.3. Note that the presence of ODMR is indicated based on the stability of spin configurations without an external magnetic field. For a defect to exhibit ODMR, it must have a decay pathway via the intersystem crossing channel, where the triplet spin configuration is the preferred state and the singlet spin configuration is metastable. In the triplet configuration, sub-level states can split into $m_s = 0, \pm 1$ states due to zero-field splitting, even in the absence of an external magnetic field. This splitting is crucial for the ODMR effect. We leveraged this criterion to evaluate our candidate defects and found that the triplet state must be the most stable for this state splitting to occur. Using this method, we confirmed that the well-studied V_B^{-1} defect is likely ODMR-active, which aligns with previous studies [178]. However, further investigation of defect state splitting under an external magnetic field is necessary, and ODMR simulation will be addressed in Chapter 7.

Fig. 4.13(a) illustrates the most stable configuration of the $C_B C_N C_B C_N$ defect in its singlet state, which permits either spin-up or spin-down transitions. If one spin-down electron is excited, it will subsequently relax via the ZPL at 573 nm or through the PSB, as depicted in Fig. 4.13(c). It is important to note that when comparing the DFT-calculated spectrum with experimental data [61, 179], no temperature broadening mechanism was taken into account. For comparison, the electronic transition and spectrum of the $C_B C_N C_N$ trimer are also presented in Figs. 4.13(b) and (c). As listed in Tab. 4.3, the phonon contribution is relatively weak, with a HR factor around 1, which is consistent with the experimental range of 0.70 to 1.70 [209, 210].

For the decay channel, the radiative lifetime is estimated to be 16.94 ns in a vacuum and 20.31 ns when accounting for the Purcell effect (see Fig. C.7 in Appendix C). The non-radiative lifetime is approximately 1.17 ns, causing a quantum efficiency of around 6.47%. Experimentally, the lifetime has been measured to be approximately 4 ns [179], although the quantum efficiency has not been directly determined. Based on the emitter's brightness in comparison to other emitters with known quantum efficiency in a similar setup, we estimate the experimental quantum efficiency to be a few percent, which aligns with our simulations.

Regarding dipole orientation, our calculations indicate that the excitation and emission polarizations are 11.12° and 12.14° away from the crystal axis, respectively, as listed in Tab. 4.3 and depicted in Fig. 4.10. The calculated excitation polarization falls well within the experimental range of 3.90° to 11.57° , while the emission polarization is slightly misaligned compared to the experimental angles of 16.24° and 20.73° [61].

4.5 Thorough Comparison with Experimental Findings

Photophysical Properties	Defects					
	$C_B C_N C_N$			$C_B C_N C_N$		$C_B C_N C_B C_N$
	Ours HSE06	Ref.[174] HSE06	Ref.[175] GW	Ours HSE06	Ref.[175] GW	Ours HSE06
Transition order	1st	1st	1st	2nd	2nd	1st
Most stable config.	doublet	doublet	doublet	doublet	doublet	singlet
Spin transition	$\downarrow - \downarrow$	$\downarrow - \downarrow$	$\downarrow - \downarrow$	$\downarrow - \downarrow$	$\downarrow - \downarrow$	$\downarrow - \downarrow$
ZPL (nm)	751	765	1025	495	582	573
E_0 (eV)	1.65	1.62	1.21	2.50	2.13	2.16
ΔQ (amu ^{1/2} Å)	0.43	-	0.19	0.39	0.27	0.44
HR	0.97	-	0.95	0.85	1.35	1.00
DW	0.38	-	0.39	0.43	0.26	0.37
Excitation polarization (°)	0.05	-	-	0.49	-	11.12
Excitation In-plane visibility	1.00	-	-	1.00	-	1.00
Emission polarization (°)	1.54	-	-	18.77	-	12.14
Emission In-plane visibility	1.00	-	-	1.00	-	1.00
Γ_R (1/s)	6.38×10^7	-	1.26×10^6	2.42×10^7	1.93×10^7	5.90×10^7
τ_R (ns)	15.67	-	795.00	41.36	51.90	16.94
Γ_{NR} (1/s)	6.99×10^2	-	$\sim 1 \times 10^3$	7.47×10^5	4.37×10^8	8.53×10^8
τ_{NR} (ns)	1.43×10^6	-	$\sim 1 \times 10^6$	1.34×10^3	2.29	1.17
η (%)	~ 100.00	-	-	97.00	4.23*	6.47
ODMR	unlikely	-	-	unlikely	-	unlikely

* This quantum efficiency was calculated differently from Eq. (3.14).

Table 4.3: Complete comparison of optical fingerprints in the $C_B C_N C_N$ and $C_B C_N C_B C_N$ defects as defect candidates for 2 eV emitter in hBN. The arrow $\downarrow - \downarrow$ represents a transition from the spin-down occupied defect state to the spin-down unoccupied defect state. The table is adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

There remains significant experimental uncertainty that requires refinement for a more accurate comparison. However, the degree of polarization matches well with the experimentally observed polarized light.

We can directly compare these results for the $C_B C_N C_B C_N$ defect with those of the $C_B C_N C_N$ defect. Our calculated ZPLs are 1.65 eV and 2.50 eV for the first and second electronic transitions, respectively, which are in excellent agreement with previous HSE06 studies that reported 1.64 eV and 2.41 eV [174, 175]. For the lifetimes, we estimated 15.7 ns and 41.4 ns for the first and second transitions, respectively. The excitation (emission) polarization of this defect is found to be in-plane, yielding 0.05°

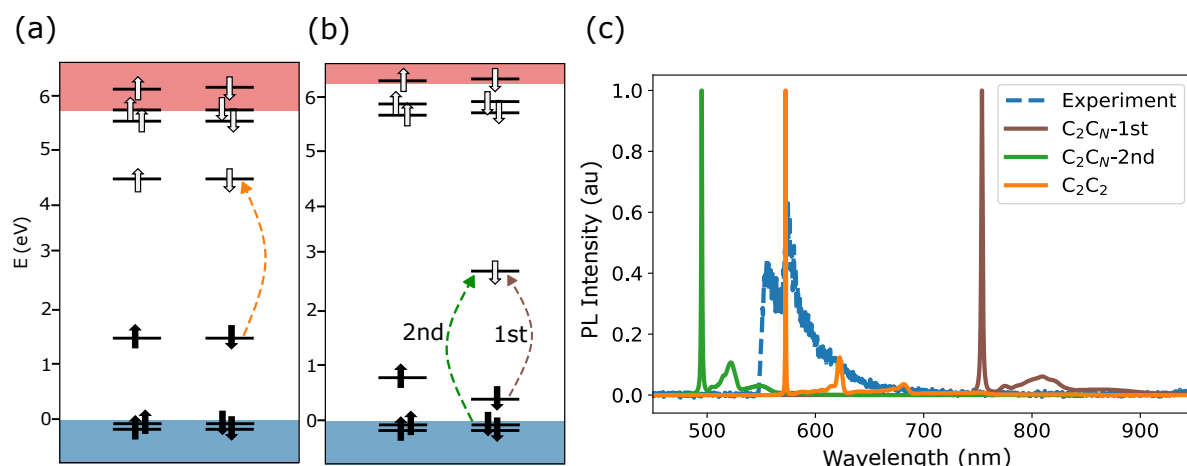


Figure 4.13: Comparison of optical properties among $C_B C_N C_B C_N$, $C_B C_N C_N$, and experiment. (a) Kohn-Sham electronic transition diagram of $C_B C_N C_B C_N$ (abbreviated as $C_2 C_2$). The orange dashed line is the electronic transition corresponding to the orange PL. The blue and pink shaded areas denote the valence and conduction bands, with a calculated band gap of 5.84 eV. (b) Kohn-Sham electronic transition diagram of $C_B C_N C_N$ (abbreviated as $C_2 C_N$) where the brown and green dashed lines are the 1st and 2nd electronic transitions corresponding to the brown and green PL. The filled and unfilled arrows represent occupied and unoccupied states, respectively. The band gap is around 6.46 eV. (c) Photoluminescence (PL) spectrum showing experimental data (blue line) and calculated transitions for $C_B C_N C_N$ (1st and 2nd transitions), and $C_B C_N C_B C_N$, respectively. Details of the convergence test are provided in Fig. C.8 of Appendix C. Some sub-figures are adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

(1.54°) and 0.49° (18.77°) for the first and second electronic transitions, respectively. This is quite consistent with the experimental data [61]; however, deviations in other photophysical properties suggest that this defect is unlikely to be responsible for our specific 2 eV emitter [61, 179]. Regarding the potential for ODMR, both defects are unlikely to exhibit this feature, as their most stable ground-state configuration is not a triplet. Further investigation, including the application of a magnetic field, is required.

4.5.3 Proposed Defect for Yellow Emitter

As elaborated in the previous section about addressing the microscopic origin of our yellow quantum emitter at 575 nm, we performed simulations to compare several experimental photophysical properties. We found that, among possible 27 defect candi-

dates, the comparison through the PL, ZPL, lifetime, HR factor, and quantum efficiency suggested the $C_B C_N C_B C_N$ defect having the most consistent properties. In addition, an independent DFT calculation was also performed to investigate the polarization behavior of 126 defects. This calculation also pointed out to the $C_B C_N C_B C_N$ defect. This consensus across several properties indicates the $C_B C_N C_B C_N$ defect as the most feasible one for the yellow emitter. In the meantime, another DFT calculation [175] pinpointed the $C_B C_N C_N$ as a candidate for the 2 eV emitter. We cross-checked it, as discussed in the previous section, and found inconsistencies between simulation and experiment for this defect. Therefore, we conclude that $C_B C_N C_B C_N$ emerges as the most likely candidate for our yellow emitter while any other defects, which were not considered in this work, can also be responsible.

Most importantly, we emphasize the importance of implementing all optical properties when identifying quantum emitters in solid-state crystals. In particular, measuring the dipole orientations can be achieved with a simple experiment and easily compared with DFT calculations. It is crucial to compare a broad range of photophysical characteristics rather than a single property. This significantly reduces the risk of defect misassignments.

4.5.4 Promising Defects for Quantum Communication

By applying the same methodology used for defect identification, we can characterize the photophysical fingerprints of novel defects and evaluate their potential for quantum technologies. Previously, this analysis has been conducted using only the ZPL energy [90]. However, even when the wavelength is suitable, factors such as an out-of-plane oriented dipole or an excessively long excited-state lifetime may limit the defect's applicability in, for example, quantum communication.

In our study, we investigate the defects Al_N and $P_N V_B$. The former is predicted to be useful for coupling with NV centers in diamond [90], while the latter is considered promising for free-space daylight quantum communication [66]. In such a scheme, a quantum light source is required at one of the Fraunhofer lines in the solar spectrum. By narrowly filtering around this line in a free-space receiver, solar background noise can be eliminated, enabling the transmission of quantum information under ambient conditions in scenarios such as roof-to-roof or space-to-ground communication.

Their stability was initially assessed, as illustrated in Fig. C.9 in Appendix C. Under both nitrogen-rich and nitrogen-poor conditions, the neutral charge state of both defects is thermodynamically stable. Regarding their electronic properties, detailed in Tab. 4.4, both defects exhibit emission wavelengths that are compatible with the NV center (which has a ZPL at 637 nm and a very broad PSB) or the hydrogen- α Fraunhofer line (656 nm), which may require fine-tuning through strain [90].

Fig. 4.14 illustrates the photophysical properties of Al_N . The most stable configuration is the singlet state, as shown in Fig. 4.14(a). However, a triplet configuration can also arise due to full electron occupation, as depicted in Fig. 4.14(b) when constrained

Photophysical Properties	Defects	
	Al _N	P _N V _B
Transition order	1st	1st
Most stable configuration	Singlet	Doublet
Spin transition	↑ - ↑	↓ - ↓
ZPL (nm)	682	673
ΔQ (amu ^{1/2} Å)	0.83	0.70
HR	2.94	1.87
DW	0.05	0.15
Excitation polarization (°)	9.66	5.02
Excitation In-plane visibility	0.61	1.00
Emission polarization (°)	5.43	16.85
Emission In-plane visibility	0.99	1.00
E ₀ (eV)	1.82	1.81
μ_{e-h}^2 (Debye ²)	2.57×10^4	9.46×10^4
Γ_R (1/s)	4.74×10^2	1.70×10^6
τ_R (ns)	2.11×10^6	5.89×10^5
ODMR	unlikely	unlikely

Table 4.4: Complete photophysical properties of defects in hBN for quantum technologies. The table is adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

to a triplet state. This suggests the presence of both triplet and singlet configurations, which may allow for a decay pathway between them via the intersystem crossing mechanism. Given that the singlet configuration is energetically more favorable than the triplet, ODMR may not be feasible for this defect. Consequently, this defect is likely unsuitable for quantum sensing (magnetometry). Focusing on the singlet configuration, the ZPL is observed at 682 nm, potentially facilitating coupling between Al_N and a strong phonon mode of the NV center without requiring frequency conversion. Regarding the PSB, as shown in Figs. 4.14(b) and 4.14(c), it is evident that the PSB of Al_N is weaker than that of the NV center, indicating low phonon coupling, which is also corroborated by an HR factor of approximately 2.94. The estimated lifetime is on the order of milliseconds, which may be suitable for quantum memory but less ideal for quantum communication. Additionally, we examined the dipole orientation, as depicted in Figs. 4.14(e)-(f). The excitation polarization exhibits a significant out-of-plane component, resulting in a visibility of only 61% and aligning at 9.66° from the nearest crystal axis. Although this may be mitigated by using higher excitation laser power, the emission is fully polarized in-plane, providing near-ideal polarization visibility in reflection, with an angle of 5.43° away from the crystal axis.

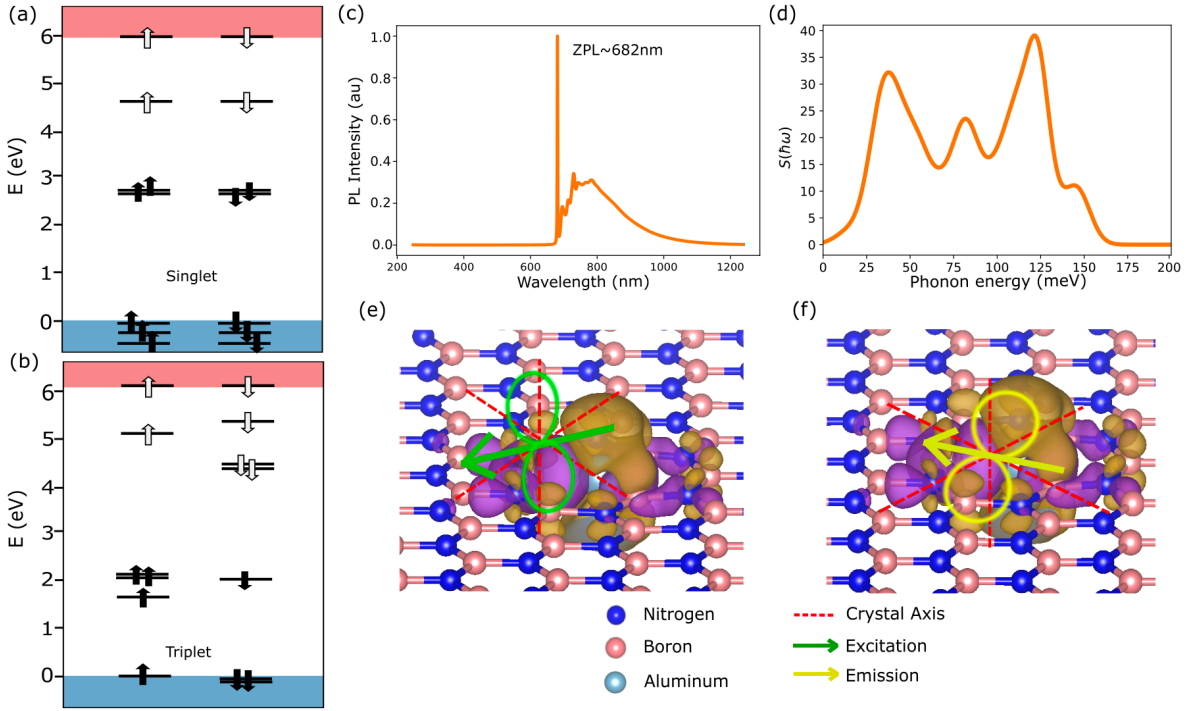


Figure 4.14: Photophysical properties of the Al_N defect. (a) Single-particle electronic transition for a singlet configuration, showing a band gap of 6.02 eV. (b) Single-particle electronic transition for a triplet configuration, with a band gap of 6.16 eV. Filled and unfilled arrows represent occupied and unoccupied states, respectively, with the blue and red shaded areas indicating the valence and conduction bands. (c) Simulated photoluminescence spectrum. Details of the convergence test are provided in Fig. C.8 in Appendix C. (d) Spectral function of the phonon energy distribution. (e) Excitation dipole orientation (green arrow) and polarization pattern. (f) Emission dipole orientation (yellow arrow) and polarization pattern. Some sub-figures are adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

Regarding the $\text{P}_\text{N}\text{V}_\text{B}$ defect, its electronic structure, depicted in Fig. 4.15(a), favors a doublet-spin configuration with a ZPL at 673 nm. The triplet and singlet configurations, having partial electron occupation and higher total energy than the doublet, are less favorable. This suggests the likely absence of an intersystem-crossing feature, in contrast to the NV center; however, the emission wavelength remains close to both the NV center and the hydrogen- α Fraunhofer line. The phonon coupling is characterized by a relatively weak HR factor of 1.87, indicating strong coupling into the ZPL (see Figs. 4.15(b)-(c)). Additionally, Tab. 4.4 reports a lifetime for this defect on the order

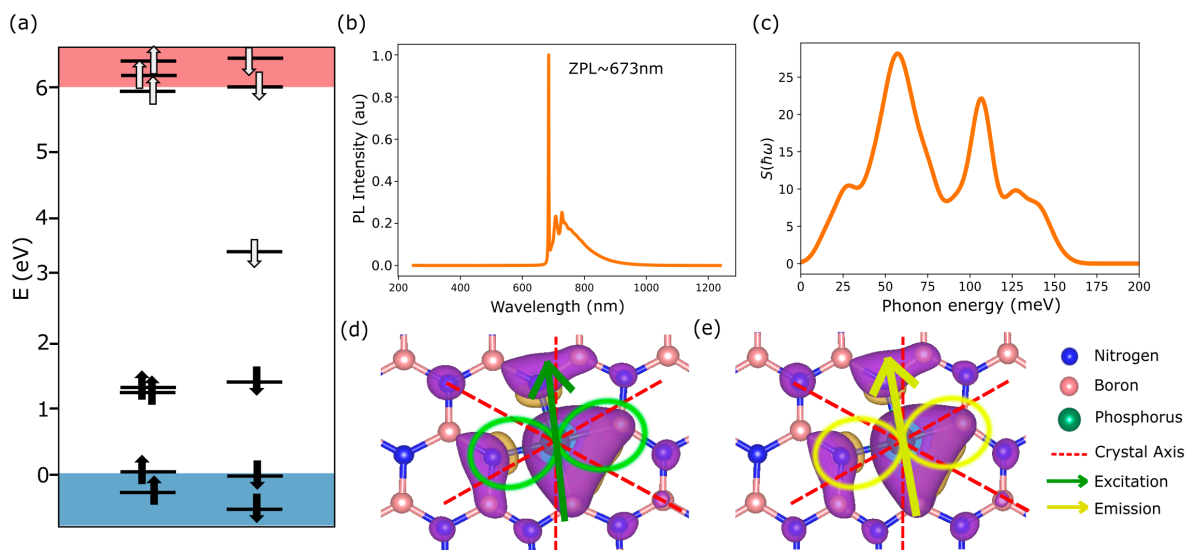


Figure 4.15: Photophysical properties of the $P_N V_B$ defect. (a) Single-particle electronic transition, with filled and unfilled arrows representing occupied and unoccupied states. The blue and red shaded areas denote the valence and conduction bands, respectively, with a calculated band gap of 6.02 eV. (b) Calculated photoluminescence spectrum. Convergence testing details are shown in Fig. C.8 in Appendix C. (c) Spectral function of the phonon energy distribution. (d) Excitation dipole orientation (green arrow) and polarization pattern. (e) Emission dipole orientation (yellow arrow) and polarization pattern. Some sub-figures are adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

of microseconds, which is less suitable for communication applications. Finally, the excitation and emission polarizations are oriented in-plane, with angles of 5.02° and 16.85° from the crystal axis, respectively. This high polarization visibility facilitates coupling in a typical reflection geometry.

4.6 Conclusion

This chapter has presented a comprehensive investigation of hBN color centers as potential quantum emitters, with two major findings highlighted: the wavelength distribution emitted by hBN color centers and the comprehensive properties of yellow emitters that align with experimental observations. Firstly, we have demonstrated that hBN quantum emitters can span the entire wavelength spectrum, from UV to NIR, thereby offering a wide array of hBN fluorescent defects. Simple criteria based on elec-

tronic structures were proposed to identify high-quality defect candidates. The results indicate that most hBN color centers possess the desired characteristics, such as isolated two-level state systems and a stable wide-band gap. Although the emission wavelength may not always precisely match the target wavelengths for quantum technologies, we have shown that strain-induced mechanisms can effectively tune the ZPL.

Secondly, extensive calculations of photophysical properties have been performed to identify plausible microscopic origins and elucidate the behavior of temporal polarization dynamics observed in experiments. This was done through the analysis of an emitter associated with the experimentally observed PL peak at 575 nm, specifically the yellow emitter. For defect identification, our study employed two independent approaches: one focusing on emitter properties and the other on polarization properties. Both approaches consistently identified the $C_B C_N C_B C_N$ defect as the most promising candidate. We also emphasized that defect identification should be based on a complete set of properties rather than a single attribute, thereby minimizing the risk of misassignment. Regarding the temporal polarization dynamics, the results suggest that additional environmental charges may induce polarization variations.

Finally, leveraging our ability to calculate comprehensive properties, we have proposed two novel hBN defects for quantum communication applications. This chapter thus not only maps the distribution of hBN emission wavelengths, but also lays the foundation for the microscopic assignment that is compatible with experimental results.

Chapter 5

Raman-based Quantum Memory from hBN Color Centers

In this chapter, we investigate the applications of hBN color centers for quantum memories. As introduced in Chapter 1 and Sec. 3.2.1 of Chapter 3, quantum memory is a fundamental component for the implementation of quantum repeaters, which are critical for advancing large-scale quantum technologies such as quantum communication [9, 66, 143, 144], networked quantum computing [145, 211], and quantum-enhanced sensing [212]. Solid-state quantum memories, including nitrogen-vacancy centers in diamond [69, 70, 71, 213, 214], transition metal defects in silicon carbide [215], and carbon centers in silicon [216], have shown promise in addressing these challenges.

These systems generally require two critical properties: a Λ -shaped electronic structure and a robust storage state. The former can be obtained from the Λ structure with the transition either between triplet and singlet states via intersystem crossing or between ground and excited states of the sub-states $m_s = 0, -1$, and 1 in the triplet configuration. The latter can employ either the electron spin or the nuclear spin for a storage state, depending on the quantum memory types. However, these systems also face challenges, such as unwanted phonon transitions in NV centers caused by thermal noise [74] and the need for pure quantum states in the ground-state hyperfine manifold of SiC [215]. Despite substantial recent advancements, such as detuning the control laser to avoid the phonon sideband (PSB) [74] and developing novel nuclear spin preparation protocols for SiC [215], further development and research are ongoing and active.

In this chapter, we focus on off-resonance Raman-based quantum memory. While this protocol has been theoretically demonstrated with NV centers [149] and SiV centers in diamond [148], it has not yet been realized with hBN color centers. With a variety of hBN defects, we can select ones having unique and advantageous properties, such as low Fresnel reflection [56], relatively low phonon coupling [57], the Λ structure, and the ability to integrate with other quantum-network components [90, 136]. These attributes may help mitigate some of the challenges present in bulk systems [69, 70, 71, 213, 214, 215].

Among solid-state quantum memories, the well-known NV center has been proposed; however, its integration with photonic devices faces limitations due to its zero-phonon line (ZPL) at 637 nm. Consequently, NV center-based quantum memories require wave-

length conversion to shift from their ZPL to the C-band wavelength [77]. This conversion introduces additional noise and losses to the communication system and complicates integration with photonic devices. Recently, SiC quantum memory has been shown to overcome this potential drawback of NV centers, thanks to its optical transition at the telecom C-band [215, 216].

With this motivation, this work aims to investigate the feasibility of hBN optical transitions. One of our criteria for an ideal quantum memory is having a ZPL that aligns with the telecommunication wavelength. This strategy is also applicable to matching the ZPL of the quantum memory with the Fraunhofer line, where the solar background is suppressed, allowing quantum information to be transmitted under ambient conditions in roof-to-roof or space-to-ground scenarios.

A theoretical model has been proposed in the chapter by assuming that hBN color centers are embedded in a cavity with two pulses for operation: signal and control. As such, given the limited exploration of hBN for quantum memory applications to date, this chapter aims to address three research goals.

Goal 1: the feasibility and performance of hBN defects as quantum memory are assessed by evaluating efficiency, quality factor required by a cavity, bandwidth, and lifetime using a simple dynamical quantum memory model. While the current model excludes the decay terms leading to the ideal efficiency, we aim to quantify the value of the required quality factor of a cavity based on the control condition in which the ideal efficiency can be reached. This, therefore, can be considered as the upper limit and preliminarily indicates the feasibility of hBN color centers for being a quantum memory.

Goal 2: electronic transitions of 257 triplet and 211 singlet configurations are characterized and classified. Following the control conditions to achieve the desired efficiency, we map those conditions to the electronic transitions of hBN defects, leading to the different required quality factors for a cavity. Then, the bandwidth and lifetime will also be estimated.

Goal 3: the compatibility between hBN defects as a quantum memory and other quantum components has been matched.

As a consequence, this chapter provides a comprehensive overview pointing out the importance of hBN electronic transition, estimating the quality factor and bandwidth for future experiments, and feasibility of coupling with other quantum systems.

The results from this chapter have been published in Refs. [146, 217].

5.1 Modelling Raman-based Quantum Memory

This section summarizes the computational techniques covering the material-free quantum memory model until mapping the model to actual hBN physical systems. It is important to note that the numerical method from Sec. 5.1.1 to Sec. 5.1.3 was developed in the Bachelor thesis of Takla Nateeboun.

5.1.1 Numerical Simulations

The hBN quantum memory is modeled under the assumption that electronic transitions occur within a Λ -type three-level system, comprising a ground state $|g\rangle$, an excited state $|e\rangle$, and a metastable state $|s\rangle$. The key parameters utilized in this study are outlined below. The Hamiltonian describing these transitions is expressed as

$$H = \hbar \left(\Omega(t) \hat{\sigma}_{se} \otimes \hat{1} + g_c \hat{\sigma}_{ge} \otimes \hat{a} + \text{H.c.} \right) + \Delta \hat{\sigma}_{ee} \otimes \hat{1} + \delta \hat{\sigma}_{ss} \otimes \hat{1}. \quad (5.1)$$

In this model, an incoming photon transition between $|g\rangle$ and $|e\rangle$ is coupled by a signal field with the coupling constant g_c . A control pulse, governing the transition between $|e\rangle$ and $|s\rangle$, is modeled using a sigmoid function with a characteristic time T , as exemplified in Eq. (5.2).

$$\Omega(t) = \frac{\Omega_0}{1 + \exp \frac{t}{T}}. \quad (5.2)$$

Here, Ω_0 represents the peak Rabi frequency. The transitions are expressed using the atomic operators $\hat{\sigma}_{ij} = |i\rangle \langle j|$. The parameters Δ and δ denote the one-photon detuning from the $|g\rangle$ to $|e\rangle$ transition and the two-photon detuning from the $|g\rangle$ to $|s\rangle$ transition, respectively. In our current model, both detunings are neglected for simplicity. It is worth noting that other functions can also be utilized.

To map between the initial atomic state and a photon, the stimulated Raman adiabatic passage (STIRAP) process is employed [218]. This technique leverages the evolution of the dark state $|\Phi_0\rangle$ to modulate the wavefunction $|\Psi\rangle$ via the mixing angle θ [218, 219], as explained in Sec. 3.2.1. During the adiabatic process, $|\Psi\rangle$ must evolve sufficiently slowly to remain in $|\Phi_0\rangle$. The $|\Phi_0\rangle$ state can be expressed as

$$|\Phi_0\rangle = \cos \theta |g, 1\rangle + \sin \theta |s, 0\rangle \quad (5.3)$$

$$\theta = \arctan \frac{g_c}{\Omega(t)}, \quad (5.4)$$

where $|\Phi_0\rangle$ is written in the form of a total wavefunction for a composite system, i.e. $|\Psi\rangle = |\text{atomic state}\rangle \otimes |\text{photon number state}\rangle$; that is, $|g, 1\rangle$ represents the ground state with one photon present, whilst $|s, 0\rangle$ represents the metastable state with no photons present. In this process, the incoming photon (signal pulse) couples $|g\rangle$ to $|e\rangle$ states, initiating the storage process. At the same time, a strong control pulse is applied to couple $|s\rangle$ to $|e\rangle$ states. The interplay between the signal pulse and the control pulse modifies the mixing angle θ , as expressed in Eq. (5.4). This results in the coherent transfer of the atomic population from $|g, 1\rangle$ to $|s, 0\rangle$, achieving the storage.

Additionally, the quantum memory is assumed to be situated within a cavity of volume V . Consequently, g_c between an incoming photon and the signal field can be calculated using the expression [147]

$$g_c = \langle e | \hat{\mathbf{d}}_{ge} \cdot \epsilon | g \rangle \sqrt{\frac{\omega_1}{2\hbar\epsilon_0 V}}. \quad (5.5)$$

We assume that the cavity volume V scales as $V = n\lambda^3$, where n is a constant. In our model, $n = 1.76$ is used in our calculations, based on experimental data from an hBN defect coupled to a microcavity [220]. The term $\hat{\mathbf{d}}_{ge}$ represents the transition dipole moment computed from DFT calculations for the transition between $|g\rangle$ and $|e\rangle$, and ϵ is the polarization unit vector of the signal field.

5.1.2 Quantum Memory Performance

The evolution of a quantum memory is modeled by the Lindblad master equation, which incorporates population decay rates and is expressed as follows:

$$\frac{d}{dt}\rho = -i[H, \rho] + \sum_{i,j} C_{ij}\rho C_{ij}^\dagger - \frac{1}{2}\{C_{ij}^\dagger C_{ij}, \rho\}, \quad (5.6)$$

where $C_{ij} = \sqrt{\gamma_{ij}}|i\rangle\langle j|$ represents a jump operator between states i and j . In our analysis, these states include the ground, excited, and meta-stable states, denoted by $i, j \in \{g, e, s\}$. The parameter γ_{ij} corresponds to the decay rate between these channels. Given the critical role of the $|s\rangle$ state as a storage state, the writing efficiency was calculated by determining the probability of transition from $|g\rangle$ to $|s\rangle$, utilizing the QuTiP package [221, 222]. The $|s\rangle$ state is chosen as the storage state due to the low probability of transition between $|s\rangle$ and $|g\rangle$.

In the absence of decay processes, the writing efficiency is equal to the reading efficiency owing to the reversible nature of the transition pathways. Nonetheless, a transition between $|s\rangle$ and $|g\rangle$, while theoretically possible through another intersystem crossing, is typically dipole-forbidden. The relevance of this transition relies on the required storage duration; specifically, the lifetime of the $|s\rangle$ state must exceed the storage time to prevent the loss of stored quantum information through relaxation to the ground state.

5.1.3 Mapping Materials Properties into Quantum Memory Performance

To evaluate the performance of a quantum memory based on the properties of the material, the quality factor of a cavity and the bandwidth corresponding to each defect were computed. To do so, we computed the dark-state population $d(t)$ among $|g\rangle$, $|e\rangle$, and $|s\rangle$, influenced by the decay rate of the cavity using the following equation

$$\kappa(t) = k \cos^2 \theta(t), \quad (5.7)$$

where k is a non-zero constant representing the loss of photons in the cavity. The equation governing the decay of the dark-state population under the adiabatic process is given by

$$\frac{d}{dt}d(t) = -\kappa(t)d(t) = -k \cos^2 \theta(t)d(t). \quad (5.8)$$

Given the control field $\Omega(t)$ defined by Eq. (5.2), the mixing angle θ can be expressed as:

$$\theta = \arctan \left(\frac{g_c}{\omega_0} \left(1 + \exp \left\{ \frac{t}{T} \right\} \right) \right). \quad (5.9)$$

The analytical solution to Eq. (5.8) is

$$\begin{aligned} d(t) = c_1 \exp & \left(\frac{k\Omega_0^2 \left(T \log \left(\left(e^{t/T} + 1 \right)^2 + \Omega_0^2 \right) - 2t \right)}{2(\Omega_0^2 + 1)} \right) \\ & \times \exp \left(\frac{2k\Omega_0 T \tan^{-1} \left(\frac{e^{t/T} + 1}{\Omega_0} \right)}{2(\Omega_0^2 + 1)} \right), \end{aligned} \quad (5.10)$$

where c_1 is a constant determined by the initial conditions. We set the initial dark-state population $d(t_0) = d_0 = 0.999$ at a specific time t_0 , implying that a photon enters the cavity when 99.9% of the dark-state population is in the $|g\rangle$ state. This condition is trivially satisfied for an appropriate quantum emitter system at room temperature, where the defect states are localized at the mid-gap region. The initial time t_0 is given by

$$t_0 = T \log \left(\frac{p|\Omega_0|}{\sqrt{p(1-p)}} - 1 \right), \quad (5.11)$$

where p is the probability of the dark state overlapping with the metastable state.

The next step is to determine the decay rate that meets the required writing efficiency. Once the appropriate decay rate is found, the quality factor Q for each specific defect can be calculated as

$$Q = \frac{\omega}{2\kappa}, \quad (5.12)$$

where ω is the resonance frequency of the $|g\rangle$ to $|e\rangle$ transition, corresponding to the ZPL.

Finally, the bandwidth Δ for each defect is calculated to determine the operational range of the memory under the desired writing efficiency threshold. This is achieved by computing the half-width at half maximum (σ_Δ) of the writing efficiency affected by one-photon detuning, yielding:

$$\Delta = g_c \sigma_\Delta. \quad (5.13)$$

For further details on the derivation of this model, we refer to Ref. [146].

5.1.4 DFT Computational Details

All DFT calculations incorporating spin polarization in this study were conducted using VASP [183, 184]. A plane wave basis set was employed to manage the periodic

structures of the $7 \times 7 \times 1$ supercell. The pseudopotentials were treated using the projector augmented wave (PAW) method to account for the interactions between the nucleus and valence electrons [185, 186].

While hBN has a large band gap (~ 6 eV) and the conventional PBE functional typically underestimates it, we circumvent this issue by employing the HSE06 functional instead, as it has been benchmarked well with experimental results [110, 177]. It should be acknowledged that every DFT methodology possesses inherent limitations in accuracy, influenced by the defect environment and interactions. Specifically, the HSE06 functional exhibits an uncertainty ranging from 0.3 to 0.8 eV, depending on the electronic states of the defects [223]. Furthermore, intrinsic crystal strain can affect defect properties, particularly in cases where defects are introduced via ion implantation, resulting in significant residual strain. As a consequence, for a precise microscopic assignment to identify defects and their photophysical properties, it may be beneficial to compare outcomes obtained from various DFT methods, such as periodic models and molecular cluster models. Cross-referencing these results with different properties is also advisable [136, 223]. However, given that our investigation contains a total of 468 electronic structures, the computational demands of employing multiple DFT techniques are considerable. Therefore, our study is confined to using the HSE06 functional exclusively, while still offering a comprehensive fingerprint of all defects for benchmarking purposes in future experimental work.

To account for spin multiplicity, we relaxed each structure while simultaneously constraining the total spin of all defects using NUPDOWN settings of 0, 1, and 2 in VASP, corresponding to singlet ($S = 0$), doublet ($S = 1/2$), and triplet ($S = 1$) spin configurations. Defects that exhibit full electron occupancy in both singlet and triplet configurations meet our defect screening criteria and are subsequently examined in their excited-state configurations under the Δ SCF scheme [187]. For neutral-charge defects that show full electron occupancy in the doublet configuration, we apply singly positive and negative charges, as depicted in Fig. 5.1. Since optical transitions require two-level defect states with conserved spin polarization, and can occur via both spin-up and spin-down pathways, we further investigate the ZPL, transition dipole moment (μ), and lifetime for both spin-up and spin-down transitions, provided that spin-conserved two-level defect states are present. Note that the calculations for transition dipole moment, radiative lifetime, and radiative transition rate are described in Secs. 3.1.4 and 3.1.6.

5.1.5 Criteria for Quantum Memory Performance

Typically, fidelity, memory efficiency, and storage time are the primary parameters used to evaluate the performance of a quantum memory system. However, these parameters alone do not fully address the necessary electronic structures and compatibility with other systems. Therefore, this work introduces additional criteria to ensure a comprehensive assessment of all factors essential for optimal performance, as detailed below.

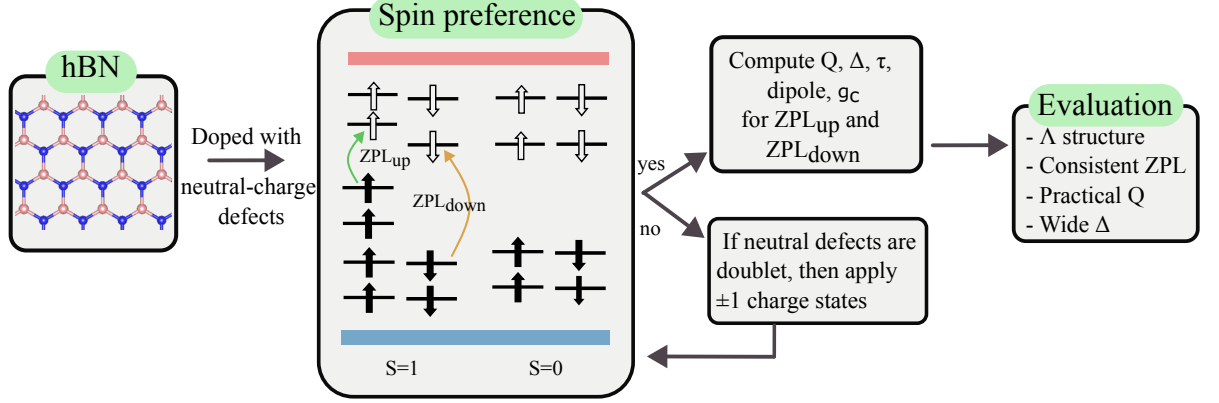


Figure 5.1: Flowchart illustrating the collection process for the DFT database. Occupied (unoccupied) defect states with spin-up and spin-down polarization are denoted by filled (unfilled) up and down arrows. The parameters Q , Δ , τ , and g_c correspond to the quality factor, bandwidth, lifetime, and coupling constant, respectively. The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

- i) Possession of Λ Structure: A suitable quantum memory defect must exhibit the Λ structure, incorporating both triplet and singlet configurations. The triplet configuration facilitates transitions between $|g\rangle$ and $|e\rangle$, crucial for the signal pulse, while the singlet configuration enables the $|s\rangle$ state, crucial for the control pulse. The transition between triplet and singlet states occurs via the intersystem-crossing channel.
- ii) Matching ZPL with Applications: Ideally, defects should emit photons at wavelengths that are compatible with other quantum systems. This is important because quantum memory in NV centers often faces challenges in long-distance quantum communication due to the need for wavelength conversion for compatibility with photonic devices [77]. By aligning the ZPL of hBN defects with other systems, we can mitigate this issue. Defects with non-matching ZPLs remain valuable, as their compatibility can be adjusted or coupled with systems not discussed in this study.
- iii) Feasible Quality Factor for Cavities: The quality factor of a cavity, determined by the optical frequency ω of the signal field, the coupling constant g_c , and the cavity decay rate κ (as per Eq. (5.12)), must be practical. While high-quality factors are desirable, physical implementations are typically limited to around 10^3 for dielectric cavities [220] and up to 10^7 for photonic crystal cavities [224]. Thus, we aim to identify defects that require cavities with a quality factor below 10^7 .
- iv) Broad Acceptance Bandwidth: A broad acceptance bandwidth eases the require-

ments on the linewidth of the quantum state to be stored, simplifying the mode-matching process between the quantum state and the memory.

It is important to note that, in this context, fidelity is presumed to be one due to the assumption of a non-decaying and non-dephasing quantum memory model.

5.2 Condition for Writing Efficiency

In this section, we investigate the conditions required of the control pulse to achieve the desired writing and reading efficiencies. Considering the Hamiltonian without decay and dephasing, as shown in Eq. (5.1), there are only two adjustable parameters in the control pulse described by Eq. (5.2), namely the strength (Ω_0) and the characteristic time (T). According to Ref. [146], the writing efficiency has been computed, as depicted in Fig. 5.2, indicating that an efficiency greater than 95% can be achieved with $T > 2/g$ and $\Omega_0 > 10$. This 95% writing efficiency can be justified under the assumption that there is no loss during the transition, which implies that the reading efficiency would also be equal to the writing efficiency. Additionally, it is assumed that initially, 99.9% of the dark state population is in $|g\rangle$. This state preparation is practically feasible. Consequently, the writing efficiency is likely to be high under these conditions.

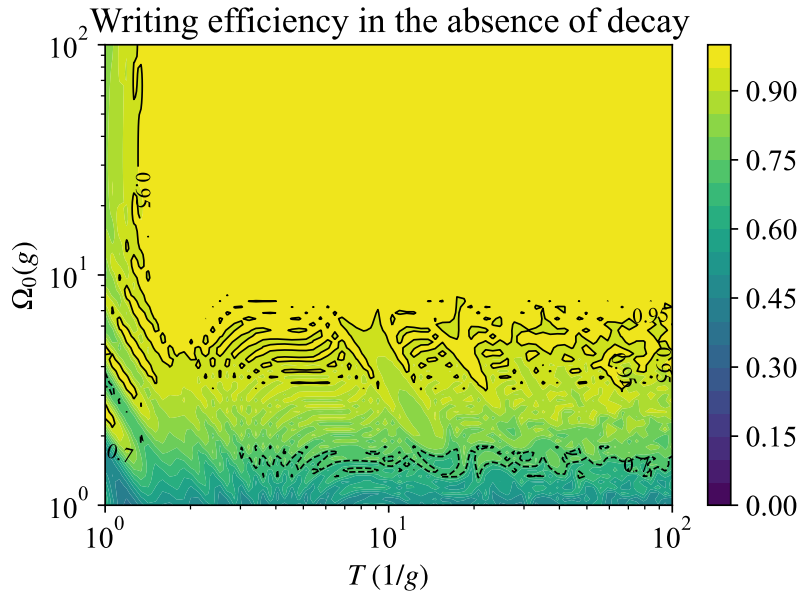


Figure 5.2: Diagram representing the values of writing efficiency influenced by characteristic time (T) and control-pulse intensity (Ω_0). The figure is adapted from Ref. [146] available under a [CC-BY 4.0 license](#). Copyright 2024 Nateeboon *et al.*

Then, assuming that the hBN defects are embedded in a cavity, the cavity decay rate should then be investigated, as illustrated in Fig. 5.3(a) based on the criterion that the maximum decay rate should ensure that the dark-state population remains greater than 50% until the writing process loses the photon at a characteristic time $T > 2$. Under this condition, the quantum memory can achieve a 95% writing efficiency, surpassing the no-cloning limit, which is crucial for quantum networks [225, 226].

Fig. 5.3(a) shows that the maximum permissible decay rate is $0.06g_c$. Although lower decay rates also meet the specified condition, they would necessitate an even higher quality factor, which is impractical for a typical cavity (according to the relation in Eq. (5.12)). Consequently, we fix the decay rate at $0.06g_c$ for all calculations. By substituting this decay rate, the required quality factor for the cavity and the bandwidth can be estimated from Eqs. (5.12) and (5.13), respectively. As demonstrated in Fig. 5.3(b), the bandwidth is calculated to be $6.20g_c$. The exact value of the quality factor and bandwidth will be subsequently examined based on the properties of each individual defect.

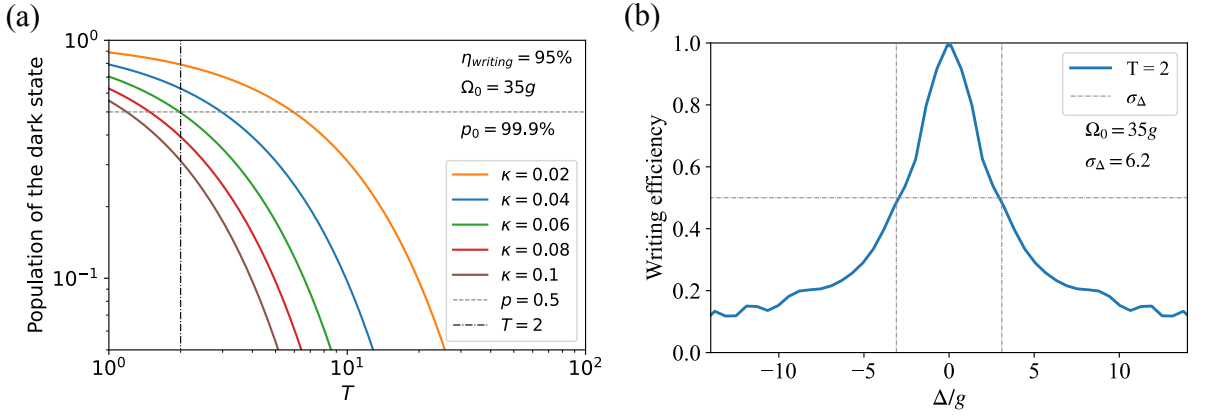


Figure 5.3: Optimizing the cavity decay rate and the bandwidth from the specific control pulse. (a) Variation of the decay rate of a cavity where the intensity of the control pulse is fixed to satisfy 95% writing efficiency and the initial dark state population is located at $|g\rangle$ with 99.9%. The desired decay rate should maintain the dark-state population to be greater than 0.5 (the dashed horizontal line) for characteristic time (T) longer than 2. In this figure, the red, blue, and orange curves satisfy the criterion. All parameters are scaled with the coupling constant g_c . (b) Determining the bandwidth by considering the decrease in writing efficiency influenced by one-photon detuning. The dashed horizontal line indicates the writing efficiency at 50%, while the dashed vertical line under the blue curve indicates the desired bandwidth (Δ). The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

5.3 Evaluating Quantum Memory Performances

In this section, we investigate the quality factor and bandwidth among 257 triplet-spin transitions of 211 defects in hBN under 95% writing efficiency. To establish a correlation between quantum memory performance and the material's properties, the coupling constant is computed based on the specific characteristics of each defect, including the ZPL, transition dipole moment, and radiative transition rate.

From the DFT calculation, we observed that for neutral-charge defects preferring a doublet spin multiplicity, the addition or removal of an electron can rearrange the occupation, converting the doublet configuration into triplet or singlet configurations, respectively. Consequently, the simulation was compiled such that if a neutral-charge defect cannot naturally adopt triplet or singlet spin configurations, an electron is added or removed. This approach allows us to manipulate the defects to support the Λ structure by ensuring they possess triplet and singlet configurations suitable for quantum memory applications. This manipulation is also feasible experimentally, as demonstrated by previous charge-state manipulation mechanisms [194]. However, the charge preference based on defect formation energy is beyond the scope of this dissertation.

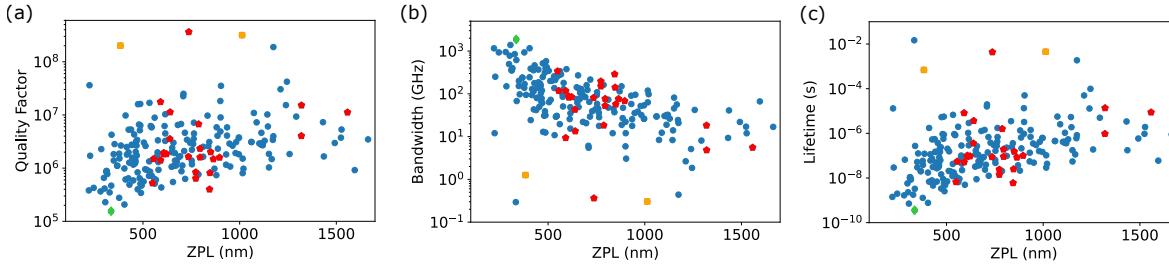


Figure 5.4: Evaluation of hBN-based quantum memory using 257 optical triplet-spin transitions, showing (a) quality factor Q , (b) bandwidth Δ , and (c) lifetime τ . The green diamond indicates the defect with the lowest quality factor and highest bandwidth. Red stars represent defects compatible with other quantum systems (as listed in Tab. 5.1), while orange squares, corresponding to $\text{In}_\text{N}\text{V}_\text{B}^+$ and S_B^+ , denote defects with the highest quality factor and lifetime. The remaining blue dots represent all other studied defects. The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

To achieve 95% writing efficiency, Fig. 5.4(a) demonstrates that most hBN defects require the quality factor around $10^5 - 10^8$ with random ZPL emission. The minimum required quality factor is at 1.55×10^5 by the As_B defect; however, its ZPL at 335 nm is out of the range of interest for quantum technology applications. We then use the stated criteria in Sec. 5.1.5 to address the last research question by narrowing down the defects with ZPLs matching those of other physical systems. The result is listed

in Tab. 5.1, together with examples of potential applications. Some hBN defects have ZPLs consistent with other single photon sources. Meanwhile, ZPLs of some hBN defects are matched with those for quantum memories or wavelengths used for quantum computing, and quantum communication. This suggests the potential comparable integration between hBN-based quantum memory and other components without a need for wavelength conversion. We observed that all defects in Tab. 5.1 except for $\text{Al}_\text{B}\text{V}_\text{N}^{+1}$ and $\text{In}_\text{B}\text{V}_\text{N}^{+1}$ require a quality factor reachable by a photonic crystal cavity (no more than 10^7) [224]. It should be noted that $\text{In}_\text{B}\text{V}_\text{N}^{+1}$ is ruled out due to the very low radiative transition, which suggests that the transition from $|g\rangle$ to $|e\rangle$ in this defect is unlikely, such that this defect has effectively no practical Λ structure.

Table 5.1: Properties of 25 selected hBN defects that are compatible with the emission wavelengths of other quantum systems (within ± 5 nm). Quality factor and bandwidth are provided under conditions ensuring 95% writing efficiency. The naming convention of $\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{C}_\text{N}$ -number is visualized in Appendix B. Note that QE, FL, QM, QCP, and QC in this table stand for quantum emitter, Fraunhofer line, quantum memory, quantum computing, and quantum communication, respectively. The table is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

Quantum application	Target λ (nm)	Other quantum systems	Compatible hBN defects	Triplet transition	ZPL (nm)	τ (ns)	Q	Δ (GHz)
QE [227]	552	PbV^- (diamond)	$\text{Se}_\text{B}\text{V}_\text{B}$	down	549.1	6.7	5.2×10^5	338.9
			$\text{Ge}_\text{N}\text{V}_\text{N}$	up	555.1	54.7	1.5×10^6	117.9
FL [66]	589 590	Na-D2 Na-D1	$\text{O}_\text{N}\text{O}_\text{B}\text{V}_\text{B}^{-1}$	up	590.8	8.2×10^3	1.8×10^7	9.4
			$\text{Sb}_\text{B}\text{V}_\text{B}$	down	591.1	51.7	1.4×10^6	117.6
QE [228]	602	GeV^- (diamond)	$\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{V}_\text{B}$	down	606.7	90.3	1.8×10^6	87.8
QM [229]	606	$\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$	$\text{Ge}_\text{B}\text{N}_\text{B}\text{V}_\text{N}$	up	607.7	101.7	1.9×10^6	82.7
QE [230]	620	SnV^- (diamond)	$\text{Si}_\text{N}\text{V}_\text{N}$	up	621.6	95.0	1.9×10^5	84.6
QE [231]	637	NV^- (diamond)	Sb_B	up	638.7	359.6	3.6×10^6	42.9
QM [214]			$\text{C}_\text{B}\text{V}_\text{N}\text{V}_\text{B}^{-1}$	up	640.3	3.6×10^3	1.1×10^7	13.4
QCP [232]	729	Ca^+	Ga_N	down	735.1	87.8	1.6×10^6	80.9
QE [197]	738	SiV^- (diamond)	$\text{Al}_\text{B}\text{V}_\text{N}^{+1}$	up	737.0	4.4×10^6	3.6×10^8	0.4
QM [233]			$\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{V}_\text{B}$	up	773.0	14.1	6.4×10^5	196.6
QM [234]	780	Rb-D2	$\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{C}_\text{N}-3$	down	773.0	24.1	8.4×10^5	150.4
			$\text{P}_\text{B}\text{V}_\text{B}^{+1}$	down	787.8	1.6×10^3	6.7×10^6	18.4
QM [235]	793	$\text{Tm}^{3+}:\text{Y}_2\text{SiO}_5$	$\text{C}_\text{N}\text{V}_\text{N}$	up	794.9	192.0	2.3×10^6	52.6
QM [234]	795	Rb-D1	$\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{C}_\text{N}-2$	up	795.2	90.3	1.6×10^6	76.7
			$\text{Al}_\text{N}\text{Al}_\text{N}$	up	844.3	6.0	4.0×10^5	288.5
QC [236]	850	Telecom-1	$\text{P}_\text{B}\text{N}_\text{B}\text{V}_\text{N}^{-1}$	down	846.6	25.0	8.1×10^5	141.3
QM [237]	852	Cs-D2	$\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{V}_\text{N}\text{V}_\text{B}^{-1}$	up	850.0	152.6	2.0×10^6	57.1
FL [66]	854	Ca-II						
QM [215]	862	V_Si^- (silicon carbide)	$\text{As}_\text{N}\text{V}_\text{N}^{+1}$	up	864.1	83.9	1.5×10^6	76.3
QM [237]	894	Cs-D1	$\text{In}_\text{B}\text{V}_\text{N}^{+1}$	up	894.4	6.2×10^9	1.3×10^{10}	0.0
			$\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{C}_\text{N}-1$	up	896.0	100.8	1.6×10^6	68.4
QC [238]	1330	Telecom O-band	$\text{C}_\text{B}\text{C}_\text{N}\text{V}_\text{N}^{-1}$	up	1319.8	1.4×10^4	1.5×10^7	4.8
			$\text{Ga}_\text{N}\text{N}_\text{B}\text{V}_\text{N}^{-1}$	up	1319.1	957.9	4.0×10^6	18.3
QC [239]	1550	Telecom C-band	$\text{P}_\text{B}\text{V}_\text{B}^{-1}$	up	1557.8	8.8×10^3	1.1×10^7	5.6

Furthermore, we compare the performance with the bandwidth as shown in Fig. 5.4(b). The result indicates that the quality factor has an inverse relationship with the bandwidth; specifically, a lower quality factor results in a higher bandwidth. However, for all defects listed in Tab. 5.1, with the exception of those with unachievable quality factors, their bandwidths range from 10^1 to 10^3 GHz. This bandwidth range is attainable for hBN at room temperature with a cavity [220].

Another essential parameter is the lifetime (τ) for each defect, as depicted in Fig. 5.4(c). We found that defects with unusually high lifetimes (represented by the orange squares) require quality factors that are unachievable with common cavities and also exhibit narrow bandwidths. This is attributed to a small transition dipole moment between the $|g\rangle$ and $|e\rangle$ states, resulting in a low transition rate, as detailed in Sec. 5.4. When comparing the lifetimes of other defects, it is apparent that the lifetime likely has a direct correlation with the quality factor, but an inverse correlation with the bandwidth. For the defects listed in Tab. 5.1, their lifetimes are typically in the range of 10^{-1} to 10^{-2} microseconds. This is significantly longer than the commonly found lifetimes of hBN quantum emitter defects, which are on the order of a few nanoseconds.

5.4 Identifying Electronic Transitions for Quantum Memory

Electronic transitions are identified as displayed in Fig. 5.5 for some defects and in Appendix D for the rest of defects in Tab. 5.1. We analyzed both triplet and singlet configurations to ensure their existence. Since transitions in triplet states can occur via both spin-up and spin-down pathways, provided the spin-conserved transition remains valid, we divided the ZPL calculations into two decay paths: spin-up and spin-down. While the two-level defect states should exist, the occupied defect state should be localized far away from the valence band greater than 1.0 eV. Consequently, for some triplet-state defects, ZPL energies are reported separately for spin-up and spin-down transitions.

Fig. 5.5(a) illustrates that As_B can theoretically exist in both triplet and singlet states. However, for the triplet configuration, only the spin-up transition exists, resulting in a ZPL at 335 nm. This occurs because an occupied defect state for spin-down is absent, making it challenging to excite a single electron directly from the valence band. This ZPL at 335 nm is relatively low, rendering it impractical for experimental implementation. For the singlet configuration, the electronic structure has been validated to be possible.

Similarly, Fig. 5.5(b) displays the electronic transition of $\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{V}_\text{B}$. Its triplet-spin electronic states offer two transition pathways: spin-up and spin-down. The calculated ZPLs are 486 nm and 607 nm for spin-up and spin-down, respectively (see the Supplementary File for additional properties). This suggests that only the spin-down transition pathway provides a consistent ZPL with other systems. While the spin-up and

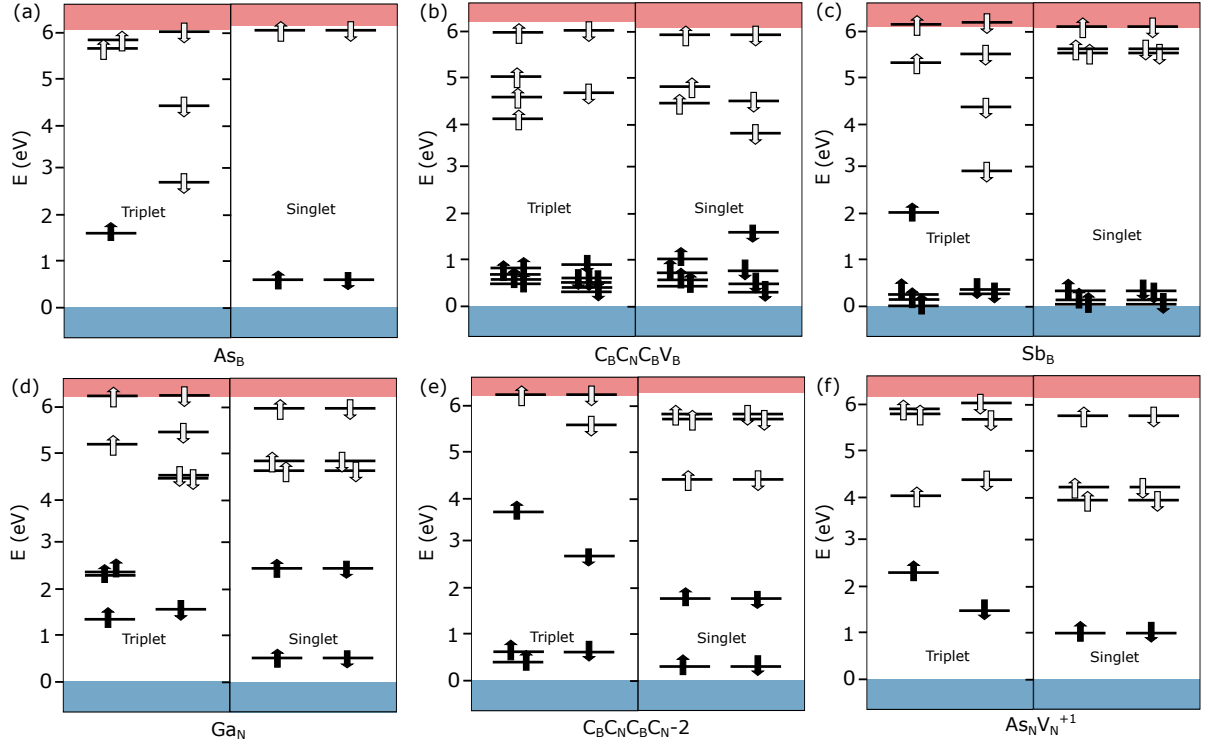


Figure 5.5: Kohn-Sham electronic transition for some selected triplet and singlet spin configurations where the spin-up and spin-down occupied (unoccupied) defect states are represented by the up and down filled (unfilled) arrows, respectively. (a) As_B , (b) $\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{V}_\text{B}$, (c) Sb_B , (d) Ga_N , (e) $\text{C}_\text{B}\text{C}_\text{N}\text{C}_\text{B}\text{C}_\text{N}-2$, and (f) $\text{As}_\text{N}\text{V}_\text{N}^{+1}$. All other electronic transitions are visualized in the database <https://h-bn.info>. The figure is adapted from Ref. [217] available under a CC-BY 4.0 license. Copyright 2024 Cholsuk *et al.*

spin-down states of its singlet configuration do not align at the same energy level, which differs from As_B , the singlet configuration remains possible. This defect thus satisfies the Λ structure criterion.

Regarding Sb_B , as indicated in Tab. 5.1, only the spin-up transition has a ZPL consistent with coupling systems, and its singlet configuration is theoretically feasible. Therefore, this defect is also a promising candidate. For the remaining defects illustrated in Fig. 5.5, all possess both triplet and singlet configurations with ZPLs consistent with other systems and are well-localized in the mid-gap region. However, the electronic structures of all defects are different, indicating that the quality factor and bandwidth are independent of the electronic structure characteristics. Thus, each defect requires a separate quantum memory performance evaluation.

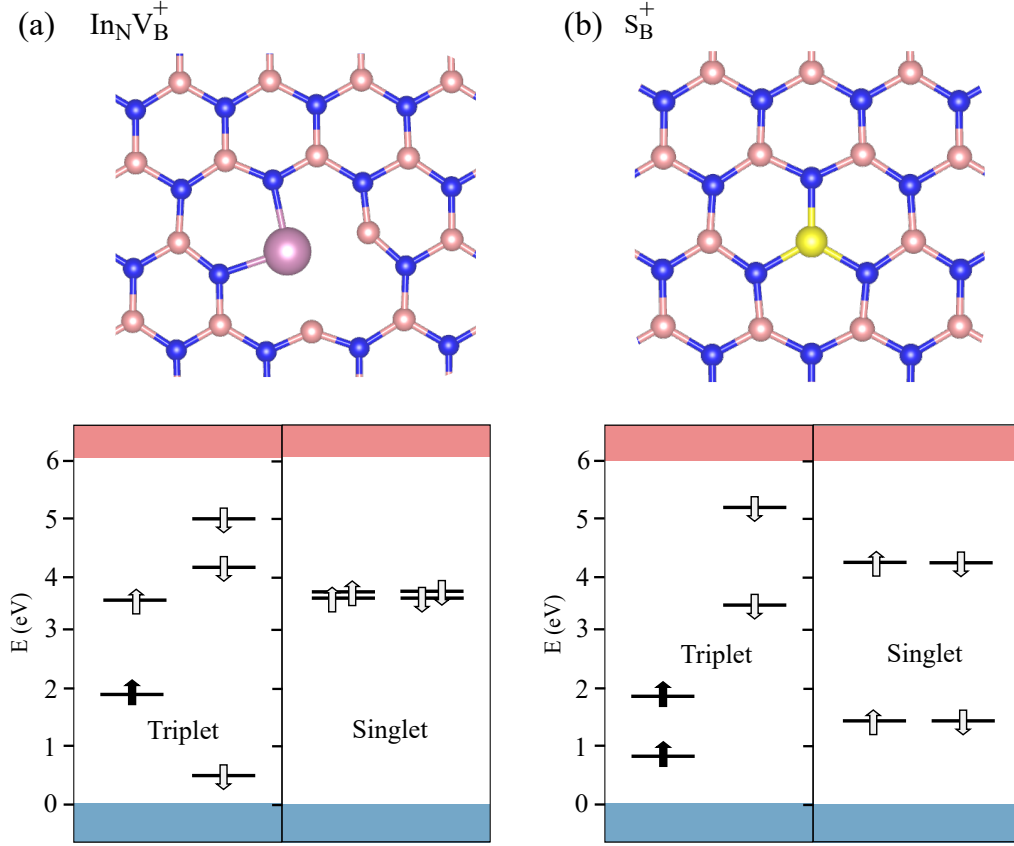


Figure 5.6: Lattice structures (top) and Kohn-Sham electronic transitions (down) for (a) $\text{In}_\text{N}\text{V}_\text{B}^+$ and (b) S_B^+ . In the lattice structure, the nitrogen, boron, indium, and sulfur atoms are depicted by the blue, pink, orange, and yellow circles, respectively. The spin-up and spin-down occupied (unoccupied) defect states are represented by the up and down filled (unfilled) arrows. The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

Turning to consider the defects inheriting an unusually long lifetime: $\text{In}_\text{N}\text{V}_\text{B}^+$ and S_B^+ . Fig. 5.6 illustrates that the electronic transition remains the same pattern as Fig. 5.5 and those in Appendix D, i.e., well-localized defect states, formable triplet and singlet configurations, and the wide bandgap maintained. This implies that the out-of-range lifetime cannot be determined solely by the electronic transition. Having considered the inverse of the lifetime, which is the transition rate, we found that the transition dipole moment plays a critical role in this. For $\text{In}_\text{N}\text{V}_\text{B}^+$ and S_B^+ , their atypically long lifetime results from the small transition dipole moment. Therefore, these defects can be ruled out from being the promising candidates for quantum memory.

5.5 Conclusion

In this chapter, we have investigated the potential implementation of quantum memory using various hBN defects and developed a model to evaluate quantum memory performance, establishing the relationship between hBN defect properties and the effectiveness of the quantum memory. DFT calculations were performed to explore numerous defects, characterizing their spin multiplicity as well as ground and excited state properties. The results indicate that the lifetime of defects directly correlates with the quality factor and inversely correlates with the bandwidth, suggesting that the radiative transition decay rate is a crucial parameter for quantum memory performance (both quality factor and bandwidth). Additionally, fine-tuning performance might be more challenging than identifying optimal defect choices. Among the 257 triplet-spin transitions analyzed, 25 defects matched the ZPL of other quantum systems within ± 5 nm variation. Moreover, most hBN defects require quality factors of a cavity reachable by the experiment in the range of 10^5 to 10^7 (for photonic crystal cavities) to achieve 95% writing efficiency with broad bandwidth, indicating their potential as candidates for quantum memory.

Furthermore, all simulations in this chapter can later be used in the online database, which benefits other quantum technologies, such as ODMR, due to the available ISC channels between triplet and singlet configurations. The details of the ODMR and the database will be emphasized in Chapters 7 and 8, respectively.

Finally, we have identified hBN defects that support the Λ structure, qualifying them for coupling with other mechanisms, such as nuclear spins. This scenario will be further investigated in detail in Chapter 6. Our work provides a promising pathway for developing relatively simple quantum memories based on room-temperature solid-state photonics. This represents an important milestone, given the role of quantum memories in space applications [143]. The hBN quantum emitter system has already demonstrated compatibility with space applications [59]. Additionally, our model can be easily applied to other color centers in solid-state crystals. We expect that the techniques described in this chapter will facilitate the evaluation of the largely unexplored potential of color centers in materials beyond diamond for quantum memory applications.

Chapter 6

Exploiting hBN Nuclear Spins for Quantum Memory

In this chapter, we extend the application of hBN color centers to nuclear-spin quantum memory. Unlike the Raman-based type as investigated in Chapter 5, nuclear spin quantum memory exploits the nuclear spin as a storage state, resulting in longer storage times due to the relatively longer coherence time than electron spins [240]. However, controlling electron and nuclear spins is challenging and remains an active area of research. This is due to several factors. (i) Although nuclear spins offer long coherence time, they can cause significant decoherence to electron spins, thereby limiting storage time [116, 127, 128]. (ii) While electron and nuclear spins are inherently coupled, achieving coherent control and manipulation of individual nuclear spins is difficult. (iii) The coupling strength in some quantum systems is weak, resulting in prolonged information transfer durations and consequently higher fidelity loss due to decoherence [75].

To overcome these challenges, several strategies have been proposed to improve the performance of quantum memory based on the NV center in a diamond [68, 69, 75, 240]. For this system, it inherits a long-lived spin triplet in its electronic ground state. This allows for electronic sub-spin states ($m_s = 0, \pm 1$) to be initialized, manipulated, and measured, as elaborated by the nuclear spin control mechanism in Sec. 3.2.2 of Chapter 3. Coherent control can be further maintained using pulse sequences like the Hahn echo and dynamical decoupling techniques, which mitigate dephasing by averaging out the effects of fluctuating magnetic fields through the application of multiple π pulses [76]. While most of the procedures remain similar, some additional techniques have also been introduced to improve performance. For example, the qubit system between $|m_s, m_I = \uparrow\rangle$ and $|m_s, m_I = \downarrow\rangle$ where m_s is an electron spin state whilst m_I is a nuclear spin state, i.e. $\uparrow$ for a spin up and $\downarrow$ for a spin down, is purified by a cycle of (i) initializing the electron spin into the $m_s = 0$ states by a laser pulse, (ii) swapping the polarization to the nuclear spin by the microwave and RF pulses, and (iii) reinitializing the electron spin with a subsequent short laser pulse without significantly depolarizing the nuclear spin. This purification process can increase the initial state population from 50% to 80%, substantially enhancing the fidelity of the read-write process [75]. Additionally, using the isotopically pure diamond (99.99% spinless ^{12}C) minimizes the perturbation

of the NV center by ^{13}C nuclear spins, allowing for long electronic spin coherence times [240]. While most studies have employed the ^{13}C nuclear spin [75, 240], the ^{14}N nuclear spin has also been proposed [214]. The coherent storage in the ^{14}N nuclear spin can be achieved via the Landau–Zener transitions, which involve sweeping the magnetic field through a level-anti crossing. Nonetheless, the coherence time is shorter than that of the ^{13}C spin [214]. Recent advancements have applied NV centers to quantum memory for quantum networks [68, 69, 70, 71, 72]. A significantly reduced ^{13}C concentration to 0.01% minimizes the perturbation of the NV center by other ^{13}C environment spins, leading to longer coherence times.

In comparison to hBN color centers, advancements in quantum memory are relatively limited, primarily due to the rich presence of non-zero nuclear spins in hBN, which causes significant decoherence of electron spin qubits, thereby restricting both spin relaxation time (T_1) and spin coherence time (T_2). To tackle this issue, many experiments have been recently conducted on T_1 and T_2 enhancement as well as on the coherent control of nuclear spins, especially in a negative boron vacancy V_{B}^{-1} defect [79, 80, 81, 150]. For this defect, its electronic state was identified to act as the triplet state split by the zero field of 3.5 GHz. This was first observed from the Rabi oscillation [80], which is subsequently characterized by the weak and strong magnetic fields [82]. They revealed that the former is driven by a single electron spin system while the latter is driven by a multi-spin system with the additional coupling from three ^{14}N nuclei [82]. Later, due to the contribution of the first nearest neighbors, seven and four hyperfine peaks have been observed in the ODMR spectra for ^{14}N and ^{15}N , respectively [79, 241]. The T_1 time at room temperature has been reported in the range of 15 - 18 μs , independent of the magnetic field and isotopes [79, 80, 81]. At low temperature, T_1 is increased up to 2.5 ms [80]. For T_2 , it depends on isotope types and yields 82.12 ns for natural isotopes [82], 46 ns for h^{11}BN , and 62 ns for h^{10}BN [83]. While most prior works investigated in ^{14}N , a very recent study revealed that $\text{h}^{10}\text{B}^{15}\text{N}$ is expected to be an optimal isotope in the sense of longest T_1 and T_2 [79]. This is likely because of the narrowest linewidth in the electron spin resonance (ESR) spectrum of $\text{h}^{10}\text{B}^{15}\text{N}$. In other words, the narrow linewidth means less decoherence from environmental spins. Note that electron spin impurities in the environment are found to contribute as another significant factor causing decoherence, thereby limiting T_2 . This was experimentally observed in the reduction of T_1 due to the cross relaxation [83].

In terms of coherent control, hBN has been performed in ^{14}N and ^{15}N nuclear spins by making use of ground-state level anti-crossing (GSLAC) and excited-state level-anti crossing (ESLAC) [79, 150, 151] based on MW and RF pulses [82, 242]. While both nuclear spins seem controllable, ^{15}N can be controlled similarly to ^{13}C thanks to the same nuclear spin, as very recently demonstrated in Ref. [79]. This suggests that ^{15}N is likely capable of performing storage/retrieval processes similarly to ^{13}C in the NV center in a diamond. Nonetheless, this realization remains unfulfilled owing to the limited T_1 and T_2 . Therefore, prolonging T_1 and T_2 times in hBN is vital for its qualification in quantum memory application.

So far, it is apparent that considerable experimental progress has been made; however, the theoretical understanding is still in its early stages. In particular, in the T_1 calculation, no prior simulations have been conducted before. As a consequence, this chapter is dedicated to theoretically investigating coherent control as well as the T_1 and T_2 times for hBN defects. First, coherent control is demonstrated by revealing GSLAC and ESLAC. Second, T_2 enhancement is shown via isotopic purification. Last, a theoretical understanding of the mechanisms affecting T_1 is provided. Although all studies in this chapter are exemplified through the V_B^{-1} defect, the methodologies can be applied to any other defects hosted by hBN.

6.1 Modelling Nuclear-Electron Spin Coupling

6.1.1 Spin Hamiltonian

Following the details of spin Hamiltonian elaborated in Sec. 2.3.3, the system contains electron spins acting as central spins and nuclear spins acting as bath spins (environment). To describe this system, the governing Hamiltonian H_{total} is expressed as

$$H_{total} = H_S + H_B + H_{SB}, \quad (6.1)$$

where H_S accounts for the central spin and comprises two terms: the Zeeman splitting for central spins due to a magnetic field ($\vec{B}$); and the zero-field splitting ($\vec{D}$) for central spins $m_s = 0$ and ± 1 , as given below,

$$\begin{aligned} H_S &= \gamma_e \vec{B} \cdot \vec{S} + \vec{S} \cdot \vec{D} \cdot \vec{S}, \\ &= \mu_B \vec{B} \cdot g \vec{S} + D \left(S_z^2 - \frac{S(S+1)}{3} \right) + E(S_x^2 - S_y^2). \end{aligned} \quad (6.2)$$

Here, γ_e is the gyromagnetic ratio for an electron; μ_B is Bohr magneton; g is the gyromagnetic ratio, $\vec{S}$ is the total spin of the central spin; D and E are zero-field splitting terms. For the bath spins, H_B consists of two terms: the Zeeman interaction of the nuclei and nuclear-spin dipole-dipole interaction, as provided below.

$$H_B = -\vec{B} \cdot \sum_i \gamma_i \vec{I}_i + H_{nn}, \quad (6.3)$$

where

$$H_{nn} = \frac{\mu_B}{4\pi} \sum_{i>j} \gamma_i^n \gamma_j^n \frac{\vec{I}_i \cdot \vec{I}_j - 3(\vec{I}_i \cdot \hat{r}_{ij})(\vec{I}_j \cdot \hat{r}_{ij})}{r_{ij}^3}. \quad (6.4)$$

The last term in the total Hamiltonian is H_{SB} representing the interaction between electron and nuclear spins through the hyperfine (HF) interaction. It can be explicitly

written as

$$\begin{aligned}
 H_{SB} &= \vec{S} \cdot \sum_i \vec{A}_i \cdot \vec{I}_i, \\
 &= \sum_{j=1}^3 \left(A_{zz}^j S_z I_z^j + A_{xx}^j S_x I_x^j + A_{yy}^j S_y I_y^j + A_{xy}^j S_x I_y^j + A_{yx}^j S_y I_x^j \right), \\
 &= \sum_{j=1}^3 \left[A_{zz}^j S_z I_z^j + \frac{1}{4} A_{xx}^j (S_+ + S_-) (I_+^j + I_-^j) - \frac{1}{4i} A_{yy}^j (S_+ - S_-) (I_+^j - I_-^j) \right. \\
 &\quad \left. + \frac{1}{4i} A_{xy}^j (S_+ + S_-) (I_+^j - I_-^j) + \frac{1}{4i} A_{yx}^j (S_+ - S_-) (I_+^j + I_-^j) \right], \quad (6.5)
 \end{aligned}$$

where $\vec{A}$ is the hyperfine-interaction tensor; and $\vec{I}$ is the nuclear-spin operator. A_{xy} is assumed to be equal to A_{yx} for hBN defects. As a consequence, we can obtain the eigenenergies and eigenstates. Combining Eqs. (6.2), (6.3), and (6.5), we can diagonalize the Hamiltonian and obtain eigenenergies and eigenstates, as will be explained in Sec. 6.2

6.1.2 Details of Spin Coherence Time T_2 Simulation

To compute the spin coherence time T_2 , the cluster correlation expansion (CCE) scheme, as detailed in Sec. 2.3.4, was utilized to solve the total Hamiltonian described in Eq. (6.2) by using the open-source PyCCE Python package [129]. The CCE method was expanded up to the second order (CCE-2) in this work, as it was verified to adequately capture the interactions in two-dimensional materials, which will be elaborated in more detail in Sec. 6.3.

For this calculation, a Hahn-echo pulse sequence was employed to measure the coherence. The simulation was conducted within the framework of the conventional CCE method. Additionally, a magnetic field of 5.0 T was applied perpendicular to the monolayer. Given that the actual system is infinitely periodic, the CCE method addresses this by defining specific simulation regions: one for the spin bath (environmental spins) radius (R) and another for the cutoff radius for the pairwise distance between two nuclear spins (r), as shown in Fig. 6.1. In this dissertation, the nuclear bath is represented by all nuclear spins located within a 50 Å radius from the central spin. This chosen bath radius ensures that the T_2 value is converged, which will be further discussed in Sec. 6.3. Meanwhile, the maximum distance between two nuclear spins (dipole radius) was set to 15 Å. This configuration allows the CCE method to accurately account for the relevant interactions influencing the central spin's coherence.

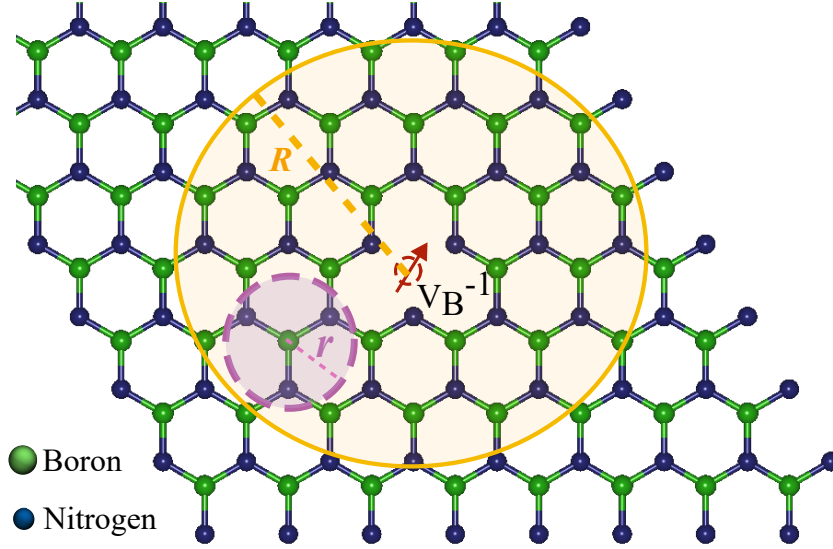


Figure 6.1: Schematics of cluster correlation expansion (CCE) for calculating T_2 in V_B^{-1} hosted by hBN. The orange zone, denoted by R , is a bath radius, while the purple zone, denoted by r , is a dipole radius. In this simulation, $R = 50 \text{ \AA}$ and $r = 15 \text{ \AA}$.

6.1.3 Details of Spin Relaxation Time T_1 Simulation

To calculate the spin relaxation time T_1 , the simulation in this section is based on the methodology developed by our collaborator, Dr. Viktor Ivády [243] and under the condition that the coupling of inter-spins is weaker than that of intra-spins. A brief summary of this approach is as follows.

Considering the aforementioned many-body spin system containing a central spin surrounded by several environmental spins (bath spins), the governing Hamiltonian can be expressed as

$$H_{total} = H_S + \sum_{i=1}^N H_B + \sum_{i \neq j}^N H_{SB}, \quad (6.6)$$

where H_S accounts for the electron spin (the central spin); H_B represents the Hamiltonian of bath spins (nuclear spins (N) in the environment); H_{SB} is the Hamiltonian representing the interaction between electron and nuclear spins through the hyperfine (HF) interaction. The dimension of the given total Hamiltonian depends on the dimension of the Hilbert space of electron and nuclear spins. This implies that the computational demand increases exponentially with the number of nuclear spins, limiting the capability of the exact solution. To resolve this issue, the system is divided into clusters by using the cluster expansion scheme. Note that the cluster expansion is different from CCE.

Then, the cluster Hamiltonian H_{C_k} can be written as

$$H_{C_k} = H_S + \sum_{i \neq 0, i \in C_k} H_{B_i} + \sum_{i \neq j, i, j \in C_k} H_{S,B} + \beta_{C_k}, \quad (6.7)$$

where β_{C_k} is an effective intra-spin-bath field acting only on the central spin for each cluster. This term takes into account energy shifts due to spins outside the cluster. To simulate the dynamics of the system and allow for the spin flip flops induced by environmental spins affecting the diagonal elements of the central spin density matrix, an extended Lindbladian ($\mathcal{L}_{C_k}$) is introduced into the Master equation as denoted below

$$\frac{d\rho_{C_k}}{dt} = -\frac{i}{\hbar}[H_{C_k}, \rho_{C_k}] + \mathcal{L}_{C_k}(\{\dot{b}_{C_k,mn}\}, \rho_{C_k}), \quad (6.8)$$

where $\dot{b}_{C_k,mn}$ determines spin flip-flop rates of the central spin induced by environmental spins. Eq. (6.8) is solved with numerical simulation based on the finite difference method. We refer to Ref. [243] for derivation in further detail.

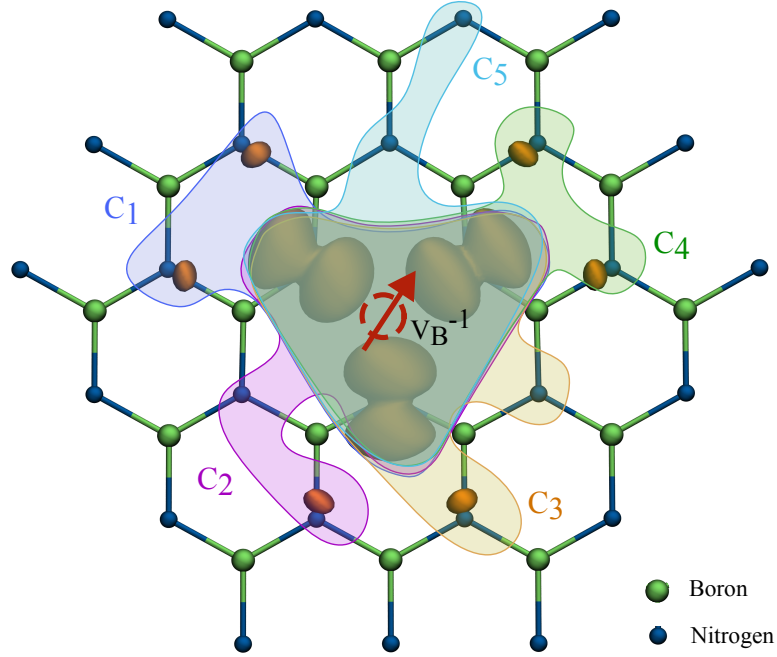


Figure 6.2: Clustering spin systems in V_B^{-1} for computing T_1 based on the cluster expansion scheme. The brown isosurface around nitrogen atoms visualizes the spin density. Each shaded area represents a six-spin cluster, including an electron spin, three nitrogen nuclei in the central spin, and two nitrogen nuclei from the bath. In this simulation, 28 clusters are taken into account. Each cluster has the same four-spin central spin and two different environmental spins. Boron nuclei are neglected.

In our simulation, V_B^{-1} in hBN is chosen. As depicted in Fig. 6.2, the first nearest neighboring nitrogens from the vacancy possess strong spin densities, indicating strong hyperfine interactions reported at around 47 MHz and 66 MHz for ^{14}N and ^{15}N , respectively [178]. Meanwhile, the second neighbors possess much weaker spin densities, suggesting comparatively weak hyperfine interactions. Beyond the second neighbors in V_B^{-1} , their hyperfine interaction reduces rapidly with distance. This characteristic implies that the electron spin from V_B^{-1} dominantly couples with the first neighboring nitrogens. Thus, in our simulation, we define the central spin as one electron spin and three nearest neighboring nitrogens to capture such a strong interaction. Then, we take into account decoherence and spin-spin relaxation from the two environmental nitrogen spins. Therefore, each cluster system contains six spins consisting of a triplet electron spin of V_B^{-1} , three first-nearest ^{15}N nuclear spin neighbors, and two ^{15}N nuclear spins from the bath, as visualized in Fig. 6.2. This implies that each cluster is different in terms of two different bath spins. In this dissertation, 28 clusters are considered and correlated through the extended Lindbladian. Note that boron nuclear spins can be negligible due to their weak hyperfine interactions; hence, they have weak decoherence effects. While the electron spin of V_B^{-1} has the total spin of 1, we neglect $m_s = 1$ for simplicity. This reduces its Hilbert space to contain only $m_s = 0$ and -1 . Then, the dimension of the total Hilbert space is equal to 2^6 for each cluster.

The simulation is divided into two case studies: (1) the closed system, where each cluster is completely isolated, and (2) the open system, where electron spins and nuclear spins in every cluster are synchronized through Eq. (6.8). Note that synchronization means the diagonal elements of the reduced density matrix of the central spin system are the same throughout the simulation. In both case studies, the polarization of an electron spin is initialized at 70% polarized in $m_s = 0$, corresponding to experimental findings [244, 245]. For the nuclear spins, they all are set to be initially depolarized. The magnetic field is set to 90 Gauss, corresponding to the experimental value [79].

6.1.4 DFT Calculation Details

Spin-polarized DFT has been utilized in this chapter to calculate the zero-field splitting (ZFS) and hyperfine tensors using VASP [183, 184]. In the simulation, the supercell size of $9 \times 9 \times 1$ and the vacuum layer of 20 Å are applied as these are sufficiently large to have near zero hyperfine at the distant nuclei from the defect. In order to compute these two properties, geometry optimization is initially conducted with the convergence threshold of 10^{-4} eV for the total energy and $0.01 \text{ eV} \cdot \text{Å}^{-1}$ for the forces. Only the atoms are allowed to move. The plane-wave basis set is expanded up to the energy cutoff at 500 eV. The single Γ -point scheme was applied to reduce computational demand, and HSE with the adjusted mixing parameter (α) at 0.32 was implemented in this chapter to calculate the hyperfine tensor. This value was selected for its better agreement with experimental results compared to HSE06, as discussed in Sec. 6.2.2, likely due to this functional's improved accuracy in describing spin density, similar to

findings in the NV center [246].

For the hyperfine tensor calculation, the self-consistent field (SCF) calculation was performed. The nuclear gyromagnetic ratios of 13.663 MHz and -4.316 MHz for ^{11}B and ^{15}N were set. For the ZFS calculation, the spin decontamination method suggested by Ref. [142] was incorporated in our calculation with the details elaborated in Sec. 3.1.8.

6.2 Nuclear-Electron Coupling

To investigate the coupling between nuclear and electron spins, we exemplified through V_{B}^{-1} in hBN. Its hyperfine structure is first revealed to understand the feasible coupled states. After that, the coupling points between the two eigenstates are identified.

6.2.1 Hyperfine Splitting

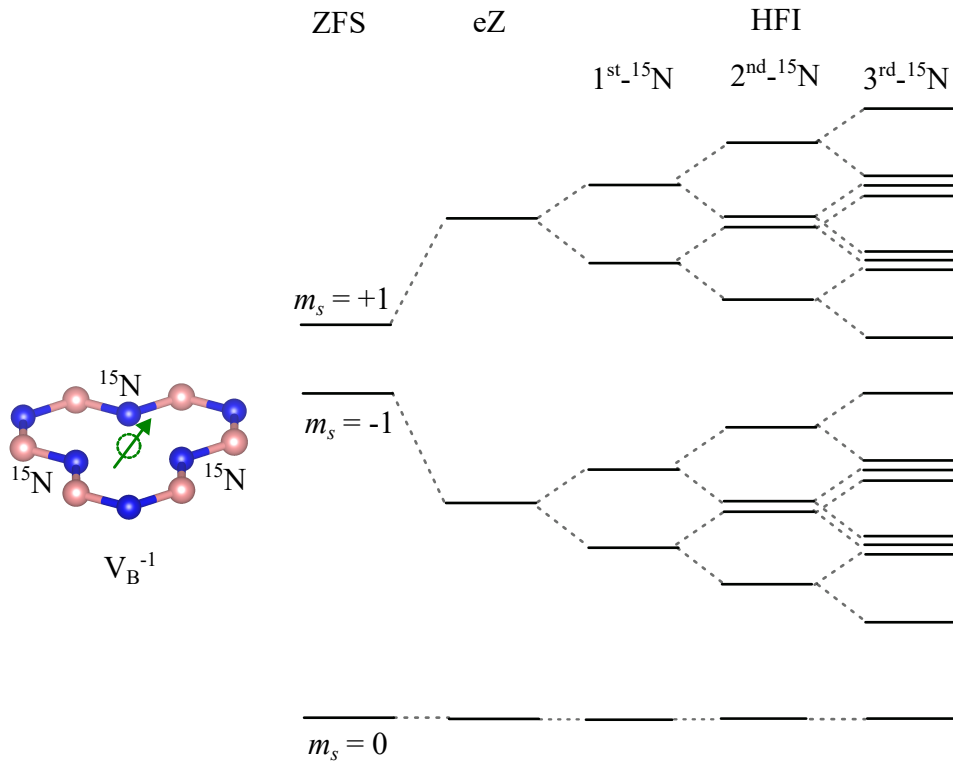


Figure 6.3: Hyperfine splitting of V_{B}^{-1} with the first neighbors including three nitrogen (^{15}N) nuclei. Note that the $m_s = \pm 1$ states are degenerate for the case of ZFS. However, in this figure, these levels are shown as separated for clarity.

As depicted in Fig. 6.3, the V_{B}^{-1} defect is surrounded by three nitrogen nuclei, which are the first nearest neighbors. The electron spin associated with this defect can

be described as a triplet state ($S = 1$), with eigenstates $m_s = 0, -1$, and $+1$. Even without an external magnetic field, there is an intrinsic energy separation between the $m_s = 0$ and $m_s = \pm 1$ states due to ZFS. Upon application of an external magnetic field, additional energy splitting occurs as a result of the electron Zeeman effect (eZ). Although not shown in Fig. 6.3, the nuclear Zeeman effect also contributes to this splitting. Our investigations reveal that the hyperfine coupling strength is particularly strong for the first nearest neighbors, indicating a high likelihood of interaction between the electron spin of V_B^{-1} and the three surrounding nitrogen nuclei. The nitrogen isotopes can be either ^{14}N or ^{15}N . However, the ^{15}N isotope is found to be optimal in terms of T_2 and broadening which will be demonstrated in further detail in Chapter 7. Consequently, we focus on ^{15}N , which possesses a nuclear spin of $1/2$. The electron spin couples with the first nuclear spin, leading to two eigenstates: $|m_s, m_I = +1/2\rangle$ and $|m_s, m_I = -1/2\rangle$, corresponding to the nuclear spin up and down, respectively. Subsequently, these coupled states interact with the next nuclear spin, resulting in nine states with three degeneracies. The interaction with the last nuclear spin further splits $m_s = \pm 1$ state into four sub-levels, determined by the hyperfine coupling constant A_{zz} . This results in a total of 24 coupled eigenstates for all m_s values.

We conclude that the electron and nuclear spins in the V_B^{-1} defect are consistently coupled via hyperfine interactions, particularly with the first three nearest nitrogen nuclei. The subsequent section explores methods to coherently control this coupling, which remains a significant challenge.

6.2.2 Level Anticrossing

This section investigates the mechanism of coherent control between electron and nuclear spins. By considering the spin Hamiltonian in Eq. (6.1), our DFT calculation yields ZFS of 3.47 GHz and 2.01 GHz for ground and excited states, respectively. This agrees well with the experimental values at 3.47 GHz and 2.10 GHz [80, 150, 247]. Meanwhile, the hyperfine coupling is also consistent with other calculations, as summarized in Tab. 6.1. It is worth noting that only the A_{zz} component is compared since this component is parallel to the applied magnetic field, giving rise to the dominant splitting of the electron spin states. In contrast, other components exist with small contribution.

By substituting these parameters and diagonalizing the Hamiltonian in Eq. (6.1), the eigenenergies as a function of the external magnetic field can be obtained, as illustrated in Fig. 6.4. At zero magnetic field, the eigenstates $m_s = 0$ and $m_s = \pm 1$ are split for both ground and excited states. This splitting is influenced by zero-field splitting, which is 3.4 GHz for the ground state and 2.1 GHz for the excited state. When a non-zero magnetic field is applied, all eigenstates split further due to the Zeeman interaction, causing $|m_s = \pm 1, m_I\rangle$ states to separate.

It is important to highlight that, regardless of the magnetic field, each $|m_s\rangle$ state consists of eight states coupled with the three nuclear spins due to hyperfine interactions, as explained in Fig. 6.3. As shown in the insets of Fig. 6.4, these states are further

separated by the hyperfine interaction strengths of approximately 47 MHz and 66 MHz for ^{14}N and ^{15}N , respectively, as explained in the previous section.

At magnetic fields of approximately 1250 G and 750 G, the eigenenergies of eigenstates $|m_s = 0, m_I\rangle$ and $|m_s = -1, m_I\rangle$ become nearly degenerate. These points allow for the mixing of the wavefunctions of electron and nuclear spin states, leading to a spin flip-flop mechanism. In other words, such a spin flip-flop process gives rise to changes in the diagonal terms of the spin reduced density matrices; hence, altering the T_1 time, as experimentally observed [83]. In experiments, these magnetic field strengths, referred to as GSLAC and ESLAC, have been used to coherently control the nuclear spin [79, 151].

Table 6.1: Calculated values for hyperfine coupling and ZFS of V_B^{-1} in hBN.

Calculation	ZFS (GHz)	Site	Hyperfine A_{zz} of ^{14}N (MHz)
This work (Ground states with HSE($\alpha = 0.32$))	3.471	N1	47.960
		N2	47.935
		N3	47.937
This work (Ground states with HSE($\alpha = 0.25$))	3.086	N1	45.902
		N2	45.881
		N3	45.885
Ref. [150] (Ground states)	3.450	N1	47.555
		N2	47.555
		N3	47.555
Ref. [150] (Experiment)	3.45	N	47
This work (Excited states with HSE($\alpha = 0.32$))	2.010	N1	39.076
		N2	39.066
		N3	37.550
This work (Excited states with HSE($\alpha = 0.25$))	1.847	N1	37.558
		N2	37.902
		N3	37.902
Ref. [150] (Excited states)	2.100	N1	39.283
		N2	36.403
		N3	36.403
Ref. [247] (Experiment)	2.10	N	39

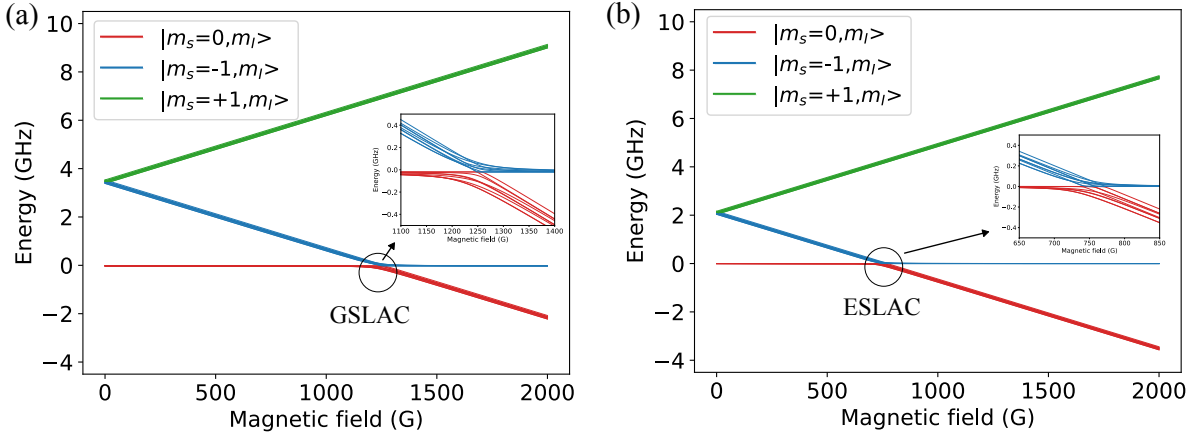


Figure 6.4: Level crossing of electron-spin magnetic sublevels in V_B^{-1} at (a) the ground state and (b) the excited state. The insets depict GSLAC in (a) and ESLAC in (b).

6.3 Calculating Spin Coherence Time T_2 in hBN

In this section, the T_2 time is investigated. To ensure accuracy, the convergence test is performed for all initial setting parameters. Then, the T_2 time with different isotope compositions is computed to find the optimal case.

6.3.1 Convergence Verification

This section presents the computation of T_2 . To ensure computational accuracy, an initial convergence test was conducted. As demonstrated in Fig. 6.5, three critical parameters were verified: the CCE order, R , and r .

Fig. 6.5(a) illustrates that the CCE-1 fails to capture the system's decoherence, as the coherence function remains unchanged. Although coherence might decay at later times (beyond 0.1 ms), this behavior contradicts the results obtained from higher CCE orders. Theoretically, this is plausible because CCE-1 only accounts for interactions between the central spin and individual bath spins, excluding interactions among the bath spins themselves (nuclear-nuclear interactions). Consequently, this significantly underestimates the decoherence contributions from the nuclear spins to the central spin. In contrast, both CCE-2 and CCE-3 expansions show the onset of coherence decay around 0.010 ms, with similar behaviors thereafter. This observation suggests that CCE-2 is likely sufficient to capture all relevant decoherence effects. This can be attributed to the fact that CCE-2 includes interactions between the central spin and individual bath spins, as well as interactions between pairs of bath spins. While CCE-3 additionally incorporates interactions among triplets of nuclear bath spins, the marginal differences

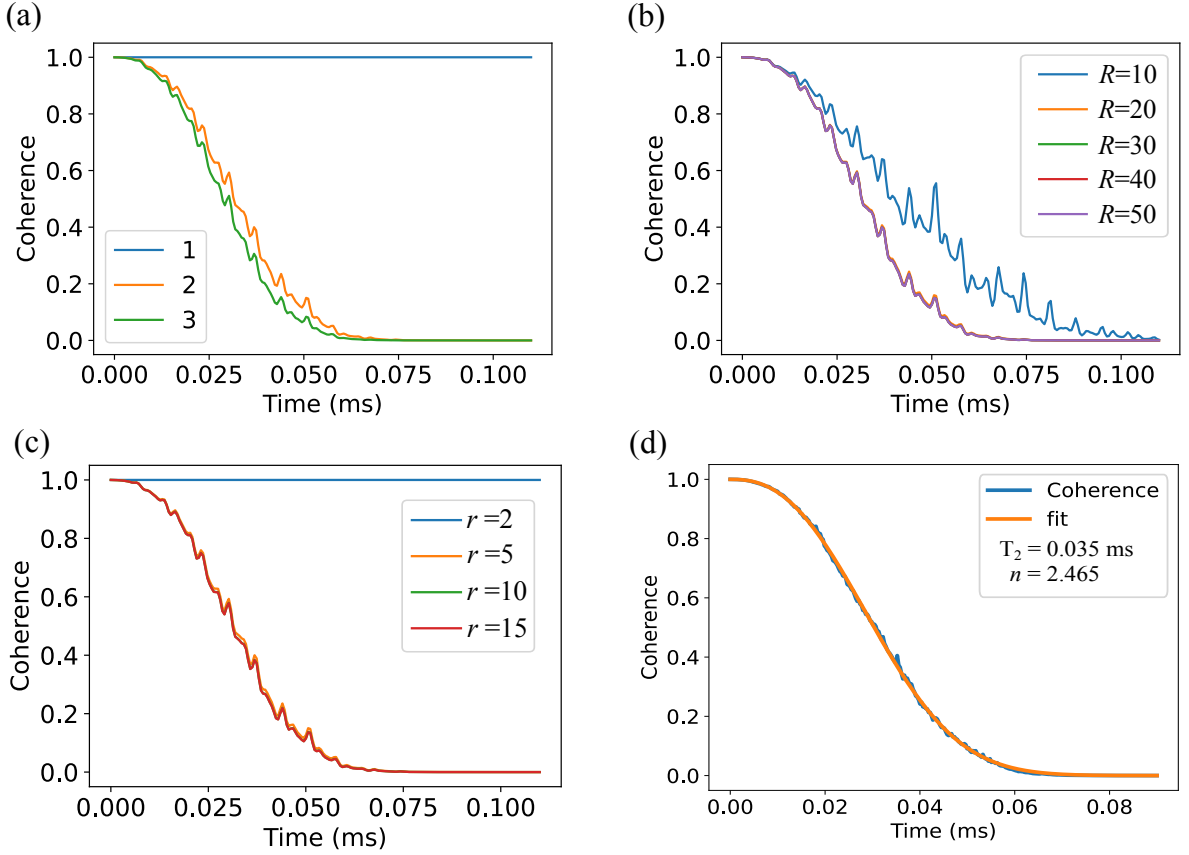


Figure 6.5: Convergence tests of parameters for coherence function. (a) Variation of CCE order. (b) Variation of nuclear spin bath radius (R) in angstrom unit where the dipole radius (r) is fixed at 5 Å. (c) Variation of dipole radius (r) in angstrom unit where the bath radius (R) is fixed at 10 Å.

in coherence decay indicate that these contributions are minor. Based on these findings, this work employs CCE-2 for all subsequent calculations, as it balances computational efficiency with the necessary accuracy in capturing decoherence phenomena.

To limit the number of bath spins included in the simulation to a manageable number while accurately capturing the interactions that contribute to the decoherence of the central spin, we determined the maximum distance from the central spin within which the bath spins (e.g., nuclear spins in the environment) are included. As shown in Fig. 6.5(b), R greater than 20 Å appears to be sufficiently large to capture bath-spin interactions. Nevertheless, in this study, we apply $R = 30$ Å.

The final parameter is r radius. Fig. 6.5(c) varies the distance between two bath spins for their mutual interaction to be included in the simulation. It indicates that r greater than 5 Å is adequate to include the relevant pairwise interactions contributing

to the central spin without incorporating all possible pairs. Consequently, this study employs $r = 10 \text{ \AA}$ for all calculations.

By applying the converged setting, in this work, we selected the hBN monolayer instead of bulk structures as it was discovered earlier that the monolayer offers longer spin coherence time than bulk counterparts [100]. This can be justified by the reduced nuclear spin density in low-dimensional layers. By fitting the coherence function using a stretched exponential model, $\exp\{-(t/T_2)^n\}$, as depicted in Fig. 6.5(d), we determined T_2 to be 0.035 ms. This result is in excellent agreement with other prior works [100, 248].

Nonetheless, when comparing T_2 with other solid-state systems, it is evident that T_2 of the NV center in diamond is approximately 2 ms [69], and T_2 of SiC ranges up to several ms [249]. In contrast, T_2 of hBN is substantially shorter. Given that the optical interface of hBN outperforms these two systems, the prolongation of T_2 is worthwhile, and it is investigated in Sec. 6.3.2.

6.3.2 Enhancing Spin Coherence Time T_2 via Isotropic Purification

Fig. 6.6 illustrates the T_2 time for each isotope combination and suggests that hBN samples containing ^{10}B isotopes (e.g. $^{10}\text{B}^{14}\text{N}$ and $^{10}\text{B}^{15}\text{N}$) demonstrate substantially longer T_2 times compared to those containing ^{11}B . The nuclear spin of ^{10}B is $I_{10\text{B}} = 3$, whereas ^{11}B has a nuclear spin of $I_{11\text{B}} = 3/2$. The lower spin quantum number of ^{11}B leads to a significantly less nuclear magnetic moment interaction, which results in less decoherence. Therefore, the shorter T_2 in samples with ^{11}B can be attributed to the greater extent of nuclear spin interactions.

Interestingly, the nitrogen isotopes (^{14}N with $I_{14\text{N}} = 1$ and ^{15}N with $I_{15\text{N}} = 1/2$) do not appear to significantly impact T_2 . Both ^{14}N and ^{15}N containing samples show similar T_2 times, indicating that the difference in their nuclear spins is not as impactful on decoherence as that of the boron isotopes. This could be due to the relatively small nuclear spins of both nitrogen isotopes, which may not introduce substantial decoherence effects.

In addition to isotropic purification, we have investigated the T_2 of hBN with V_{B}^{-1} defect. The T_2 of all isotope combinations in V_{B}^{-1} defect remains unchanged from Fig. 6.6. This can be justified by the fact that the T_2 is considered from the magnetic fluctuation of thousands of nuclear spins. A point defect located at the host material is then not an influential factor in altering T_2 . This behavior was also observed from other simulations [100, 248]. As a consequence, T_2 for every defect is expected to be the same.

These findings suggest that the primary source of spin decoherence in hBN is the boron isotope composition. The substantially improved T_2 in samples with ^{10}B highlights the potential of isotopic purification to enhance the spin coherence properties of hBN. By reducing or eliminating ^{11}B in favor of ^{10}B , it is possible to significantly extend T_2 , making hBN more suitable for quantum applications.

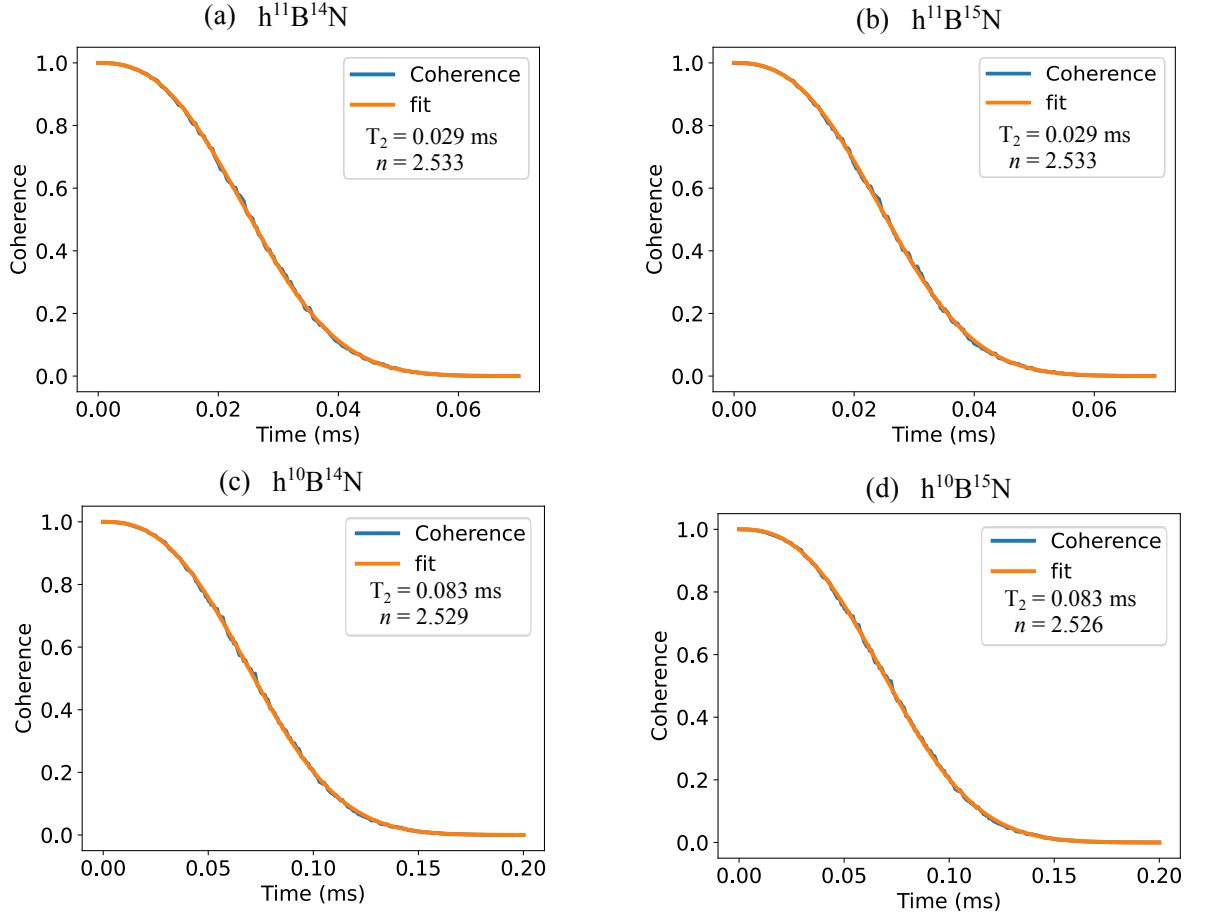


Figure 6.6: Spin coherence time T_2 of pristine hBN with different composition of isotopes. Note the coherence time of hBN with V_B^{-1} defect exhibits the same behavior.

6.4 Revealing Spin Relaxation Mechanisms T_1 in hBN

Turning to consider T_1 mechanism, two case studies, as introduced in Sec. 6.1.3, have to be analyzed to accurately capture the decoherence and spin relaxation effects. The details are following. It should be noted that this analysis has been conducted with our collaborator; Dr. Viktor Ivády.

6.4.1 Closed Quantum System Dynamics for V_B^{-1}

The closed quantum system is initially analyzed to determine an appropriate timestep for all the subsequent calculations. Since the simulation is concerned with the dynamics of electron spin population, it is crucial to capture the oscillation of spin polarization

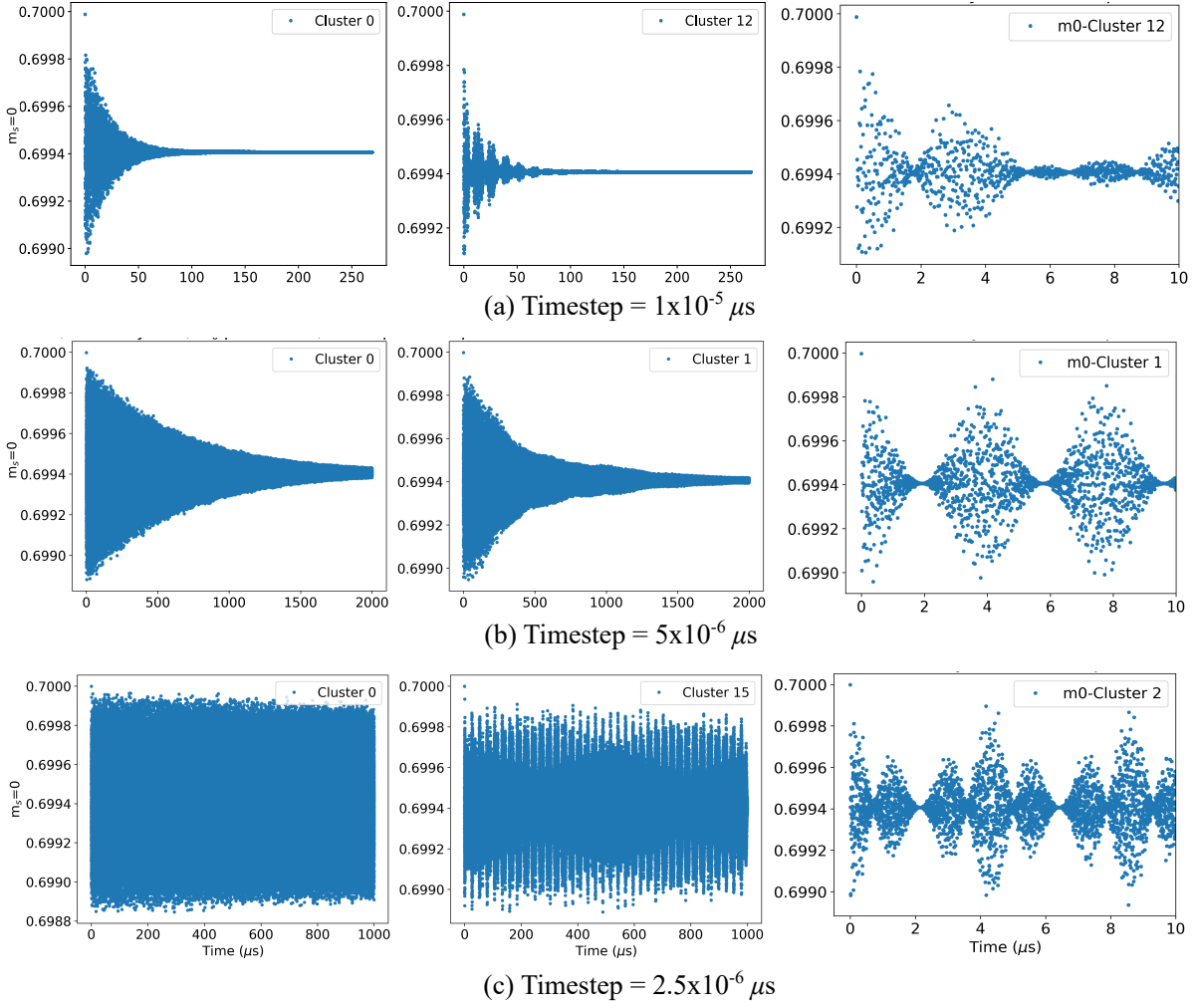


Figure 6.7: Dynamics of electron spin's polarization population in $m_s = 0$ state of V_B^{-1} in a closed quantum system dynamics with $B = 90$ G. The first and second columns represent the population from two randomly chosen clusters out of 28 clusters to verify the behavior patterns (for actual analysis, the behavior of all 28 clusters are compared; however, only two of them are chosen in this figure for visualization), whilst the last column captures the first $10\text{-}\mu s$ evolution time to analyze the behavior in detail. Timesteps are varied by (a) $1 \times 10^{-5} \mu s$, (b) $5 \times 10^{-6} \mu s$, and (c) $2.5 \times 10^{-6} \mu s$. Note that the last timestep case has reached the maximum runtime allowed in our supercomputer, which is 20 days.

transfer between $|m_s = 0, m_I = -1/2\rangle$ and $|m_s = -1, m_I = +1/2\rangle$. As illustrated in Fig. 6.4(a), the gap between $|m_s = 0, m_I\rangle$ and $|m_s = -1, m_I\rangle$ at 90 G is around 3.3

GHz. This means that the timestep less than the order of 10^{-10} s is required to accurately resolve these oscillations. This dissertation therefore divides the timesteps into three cases: 1×10^{-5} μ s, 5×10^{-6} μ s, and 2.5×10^{-6} μ s. We hypothesized that the coherent oscillation should not die out if the appropriate timestep is applied, given that there is no decoherence effect.

Fig. 6.7 illustrates the polarization of an electron spin $m_s = 0$ in the closed system. It shows that the coherent oscillation starts decaying at around 30 μ s and 250 μ s for the cases of timesteps at 1×10^{-5} μ s and 5×10^{-6} μ s. Compared to the timestep of 2.5×10^{-6} μ s, the population is maintained until 1000 μ s. We note that the evolution time of 1000 μ s for this finest timestep case took the maximum allowed runtime in our supercomputer, which is 20 days. Therefore, the calculation is forced to terminate at this evolution time. However, from the trend, we believe that the population still remains constant after that. From this comparison, it suggests that the timestep of 2.5×10^{-6} μ s is the most appropriate one, which can likely capture the oscillation. The major reason why the coarser timesteps fail can be observed from the zoom-in version of the population, which illustrates the envelope of the oscillation. The result indicates that the coarse timestep cannot capture all envelopes or even have some artificial oscillations due to numerical artifacts. This behavior fails to resolve the system's dynamics accurately. Consequently, the rest of the calculations in this dissertation employ the timestep of 2.5×10^{-6} μ s to ensure the accuracy of the simulation.

6.4.2 Open Quantum System Dynamics for V_B^{-1}

In this model, the initial polarization of the electron spin is set to 70% of the $m_s = 0$ state while all nuclear spins are fully depolarized. Fig. 6.8 depicts the changes in a population of polarization among electron spin, three first-nearest nuclear spins, and the sum of two bath spins. The results suggest that the electron spin gradually transfers its polarization to all nuclei including its neighbors and the ones in the bath, as can be seen from the increasing of their nuclear spin polarization. Later, while the electron spin keeps losing its polarization until becoming depolarized, all neighboring nuclei also turn to become depolarized again. In contrast, after the two-bath spins obtain the polarization transfer from the electron spin, they start losing their polarizations. Finally, all spin populations will converge towards a value of 0.5, indicating that the spins are depolarizing and approaching thermal equilibrium. The zoom-in version of polarization transfer at one nitrogen nuclear spin is also plotted in Fig. 6.8(f) to verify that this timestep can capture the envelope of the oscillation, as proved in the closed system simulation.

Now, turning to quantify the T_1 time, the envelope of the electron spin population decay is fitted with an exponential function of the form $a \times \exp\{(-t/T_1)^n\} + y_0$, as demonstrated in Fig. 6.9. The reason behind the selection of this fitting function can be explained by the relaxometry techniques, which measure the exponential decay of a state. Fig. 6.9 suggests that the simulated polarization has not reached the equilibrium point

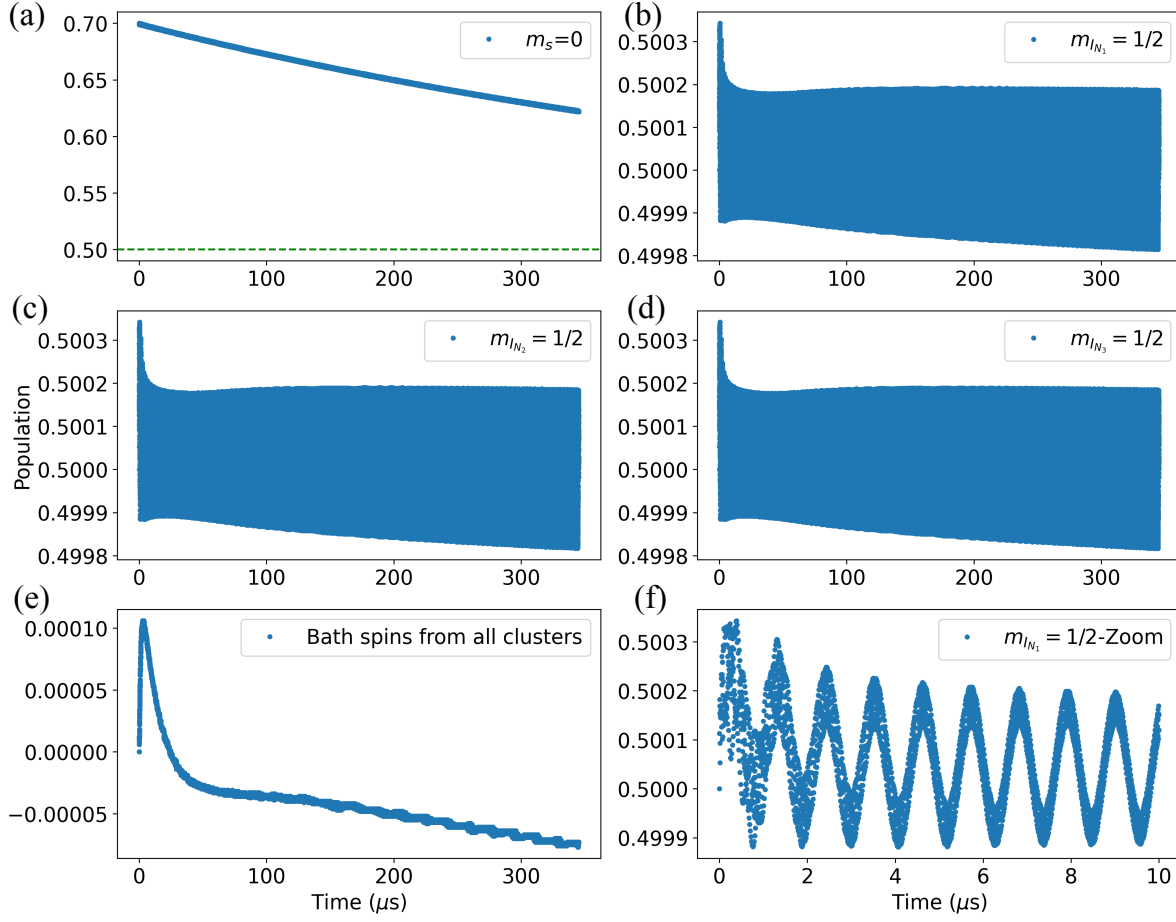


Figure 6.8: Polarization dynamics at $B = 90$ G in an open quantum system dynamics among 28 clusters, each containing six spins. (a) Population of polarization of an electron spin of V_B^{-1} in $m_s = 0$ state of the first cluster. (b)-(d) Population of spin-up polarization of the three first nearest nitrogen nuclear spins of the first cluster, namely N_1 , N_2 , and N_3 . (e) Summation of all 28-cluster populations of spin-up polarization of two nitrogen nuclear spins from the bath. The value is shifted by 0.5 for simplicity in analyzing the spin-bath contribution. (f) Population of spin-up polarization of the N_1 first nearest nitrogen nuclear spin at the first 10 μ s evolution time.

as the simulation has reached the limitation of allowed runtime in our supercomputer, which is 20 days. We anticipated that the simulation could take up to 80 days to reach the equilibrium point. To resolve this limitation, we simulated the polarization dynamics until it reached the maximum of 20 running days. Then we fitted the curve and extrapolated the rest of the behavior. This is still valid given that the polarization will, in

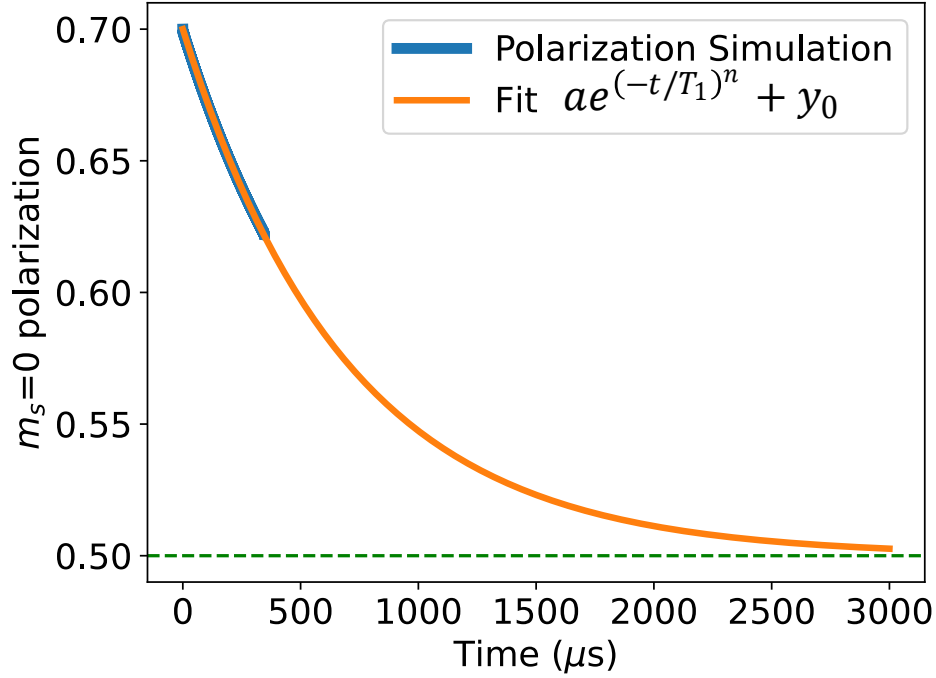


Figure 6.9: Polarization dynamics at $B = 90$ G of an electron spin of V_B^{-1} in $m_s = 0$ state of the first cluster. The blue curve represents the simulated data run for 20 days, while the orange curve is obtained from an extrapolation with the indicated exponential function. The green horizontal line indicates the thermal equilibrium point. The fitted parameters yield $T_1 = 694.77 \mu s$, $n = 1$, $a = 0.2$, and $y_0 = 0.5$.

principle, reach the equilibrium point at the polarization equal to 0.5. Furthermore, we have cross-checked with the polarization behavior at $B = 800$ G and found the behavior equilibrium pattern. Note that the polarization can be simulated farther in the large B field due to the narrower gap between $|m_s = 0, m_I\rangle$ and $|m_s = -1, m_I\rangle$, as shown in Fig 6.4(a). As a result, the fitted value of T_1 at $B = 90$ G yields $694.77 \mu s$, which is quite consistent with the experimental value of 1 ms reported at low temperature [79]. For the small discrepancy, we hypothesize that this might arise from the absence of some cluster-cluster correlations. Thus, this leaves an open research question.

In conclusion, despite the observed small inconsistency, this study has shed light on theoretically understanding the decoherence mechanisms in V_B^{-1} . The model has been expanded to the hBN color centers, in addition to its established use in NV centers [243] and SiC systems [249]. Hence, this developed model can be applied to other defects in hBN.

6.5 Conclusion

This chapter has extensively explored the potential of utilizing nuclear spins in hBN as a quantum memory. We exhibited the coupling between electron and nuclear spins in hBN and found that the nuclear spins in V_B^{-1} can be coherently controlled, in particular, ^{15}N showing promise due to offering a similar control mechanism as ^{13}C in NV centers as quantum memory. Despite strong decoherence in hBN due to its intrinsic nuclear isotopes, we employed isotopic purification to identify the dominant decoherence factors and enhanced T_2 time. Our results indicate that $h^{10}\text{BN}$ offers the longest T_2 . Furthermore, with V_B^{-1} defect dopants, the T_2 remains unaltered due to defect's minimal influence. Therefore, considering the coherent control, $h^{10}\text{B}^{15}\text{N}$ emerges as the most promising candidate for quantum memory.

The latter part of this chapter was dedicated to exploring the T_1 time, as this is directly related to the storage time of the quantum memory. We employed the cluster expansion model to investigate the decoherence mechanisms in V_B^{-1} and found that the strong decoherence originates primarily from nuclear spins. Although the model is effective for NV centers and SiC, it presents slight inconsistency for V_B^{-1} in hBN due to the stronger decoherence. This, therefore, becomes an ongoing work that needs to optimize the model to accurately capture the T_1 time.

In summary, this chapter has investigated and highlighted the crucial role of isotopic composition in determining T_2 . It has also laid the foundation for a theoretical investigation of T_1 . Broadly speaking, the implications of these results are still far-reaching for the quantum memory based on nuclear spins like that in NV centers and SiC, given the short T_1 and T_2 times observed. Future research could further refine isotopic purification techniques and explore additional methods, such as dimensional reduction, dynamical decoupling, and strain engineering, to optimize both T_1 and T_2 times of hBN to make it suitable for quantum memory applications in the sense of meeting long storage time requirement.

Chapter 7

Characterizing EPR and ODMR spectra of hBN Color Centers

In addition to the aforementioned quantum applications in quantum communication and quantum memory in Chapters 4 - 6, quantum sensing represents another critical area where single photons can contribute significant advancements. In solid-state quantum systems, nitrogen-vacancy (NV) centers in diamonds have been extensively utilized due to their remarkable properties [154, 157, 158, 159, 160, 161, 162, 250, 251]. NV centers are well-known optically addressable point defects that possess triplet and singlet spin configurations, enabling spin-selective decay pathways. This can be observed in ODMR measurements. That is, the energy level difference between the $m_s = -1$ and $m_s = +1$ sublevels is separated by $2\gamma_e B_z$ where B_z is the magnitude of the axial magnetic field. By continuously polarizing the spin states with a 532 nm laser and sweeping the microwave frequencies, the resonant frequencies $\omega_{\pm} = D_{gs} \pm \gamma_e B_z$ can be obtained. This can thus be utilized as a magnetic sensor manifested in the Zeeman interaction of the spin sublevels.

This unique spin-selective property of NV centers enables the precise detection of magnetic and electric fields [157, 158, 159, 160], as well as strain [161] and temperature [162], with high spatial resolution and sensitivity. Nevertheless, NV centers are inherently bulk systems, and they have dangling bonds at the surface, which poses significant challenges for applications requiring near-surface sensitivity [252, 253]. This is because the unpaired electron spins from the surface dangling bonds lead to the magnetic noise and hence the decoherence [254, 255]. To overcome this limitation, wide-bandgap van der Waals semiconductors such as hBN offer a promising alternative. The hBN can be exfoliated into thin layers while its surface can host optically addressable point defects. The distance between the sensor and the targeted system can then be reduced, making it highly suitable for various sensing applications where surface-level interactions are critical [81, 245, 256, 257]. In recent years, extensive studies have attempted to address the spin qubits in hBN, which exhibit triplet states and, in turn, feature ODMR properties similar to those of NV centers. A notable defect that has been theoretically and experimentally confirmed to meet the desired spin properties is the negatively charged boron vacancy (V_B^{-1}) [178, 245, 257].

The identification of this defect was accomplished by comparing the EPR spectrum between simulations and experiments [241]. This method is particularly robust because it reflects the true characteristics resulting from the interaction between the electron and neighboring nuclear spins, known as the hyperfine interaction. The Fermi contact term in the hyperfine interaction is associated with the overlap of the spin density with the nuclei, and its strength also depends on the gyromagnetic constant of the specific nuclei [155]. Consequently, the EPR spectrum is essentially unique to the defect structure and provides direct insights into the types of nuclei involved in the defect. Additionally, this method is based on ground-state properties, simplifying the plane-wave DFT simulations compared to those involving optical signals, which require excited-state simulations. Moreover, the strength of the hyperfine interaction is generally less sensitive to environmental variations compared to optical signals, making it a reliable approach for defect identification and characterization.

Given the robustness of the EPR strategy, it has been successfully employed for identifying various defects such as $\text{O}_\text{N}\text{V}_\text{B}$ [155], $\text{C}_\text{N}\text{V}_\text{B}$ [156], and carbon tetramer [132]. Nevertheless, our hBN database [258], which will be discussed in details in Chapter 8, reveals that there are 158 defects featuring triplet states. This indicates that the EPR spectra of many hBN defects remain largely uncharacterized. Thus, this chapter aims to fill this gap by characterizing the EPR spectra of selected point defects. To that end, we investigate the impact of ZFS on the EPR characteristics. Subsequently, we aim to reveal the EPR spectra of specific point defects, which can later be used for precise identification.

Another key aspect addressed in this chapter is the linewidth of the ODMR spectrum. Technically, ODMR characteristics are based on point defect qubits that possess high-spin ground and optically excited states, featuring spin-dependent optical emission. While EPR spectra are obtained by fixing the microwave frequency and varying the external magnetic field, ODMR spectra are achieved by varying the microwave frequency while keeping the magnetic field constant. Experimentally, it has been observed that the V_B^{-1} defect is less sensitive compared to the NV center, primarily due to a lower photon emission rate and the noisy environment created by boron and nitrogen isotopes [45, 46]. To address this, we simulate the ODMR by varying the isotope types. This approach provides justification for the observed sensitivity differences.

7.1 Simulation Details for EPR and ODMR Spectra

To model EPR and ODMR spectra, DFT calculations are first performed to compute the hyperfine tensors and ZFS from the optimized geometry with the same setting as that in Chapter 6 via VASP [183, 184]. Then, the group symmetry of each defect structure is analyzed via QuantumATK [180]. These outputs are then input into the MATLAB toolbox EASYS PIN package [259]. The gyromagnetic ratio and the nuclear Zeeman interaction are considered, while the Quadrupole interaction is assumed to be small and

negligible. The natural abundance is defined with the same proportion as that in the DFT calculations. All EPR spectra are simulated at the X band region around 9.4 GHz, while all ODMR spectra are simulated at the magnetic field strength of 10 mT. The room temperature is set in the simulation. The Hamiltonian for simulating the EPR and ODMR is given by the spin Hamiltonian written in Eq. (2.67).

7.2 Characterizing EPR Spectra

In this section, we characterize the EPR spectra of some point defects in hBN. We start by investigating the influence of ZFS on the EPR shape, as the calculated ZFS from DFT can be inconsistent with the experiment despite the implementation of spin decontamination, as elaborated in Sec. 3.1.8. Then, some point defects in hBN are chosen to study the impact of defects on the EPR characteristics.

7.2.1 Effect of Zero-Field Splitting on EPR

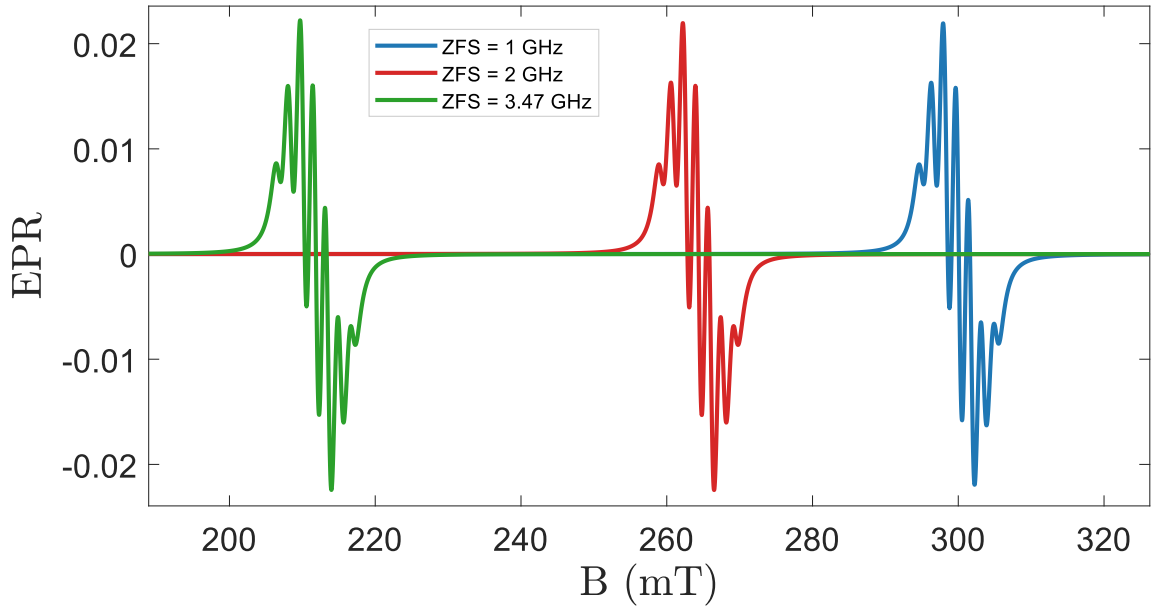


Figure 7.1: EPR spectra of V_B^{-1} in $h^{11}B^{14}N$ with the transition from $m_s = -1$ to $m_s = 0$ with the fixed microwave frequency at X band (9.4 GHz). Each curve is simulated with different ZFS values. Only the first-nearest nuclear spins from V_B^{-1} are taken into account in the spin Hamiltonian.

Fig. 7.1 depicts the EPR spectra across different ZFS values: 1 GHz and 2 GHz are random numbers, whereas 3.47 GHz is calculated from our DFT consistent with the

experimental ZFS. While the overall characteristics remain unchanged, a shift in the spectrum has been observed. We computed the mean square errors (MSE) comparing point-by-point for each spectrum and found that each curve is distinct in the order of 10^{-8} , implying no difference among these curves. The position of each curve varies due to the ZFS value, where the curve of the low ZFS appears at a high magnetic field region from Fig. 7.1. This can be explained by the fact that the ZFS represents the gap between $m_s = 0$ and $m_s = -1$ states (or between $m_s = 0$ and $m_s = 1$ states). As a result, the low ZFS would require a stronger magnetic field to split the two states with the Zeeman interaction. Then, considering the number of peaks in EPR, there comprise of multiple peaks, corresponding to $2nI + 1$ peaks where n is the number of the considered nuclear spins (in this case, $n = 3$ for the first-nearest neighbors with the hyperfine A_{zz} equal to 47 MHz while I is the nuclear spin, in this case, I of ^{14}N is 1, so there appear seven peaks in each spectrum). We can then deduce that EPR characteristics are independent of ZFS values. In other words, in spite of possible errors in the calculated ZFS, the simulated EPR can still reliably be compared with the experimental spectrum for defect identification purposes, as will be further discussed in Sec. 7.2.2.

7.2.2 Defect Identification from EPR Spectrum

As mentioned in the introduction that an EPR spectrum has been used to identify V_{B}^{-1} defect in hBN, this section aims to characterize EPR spectra for identifying other point defects as well, such as Se_{N} , Al_{N} , P_{B} , P_{N} , Ga_{N} , and As_{N} . These defects have been verified to act as triplet states similar to V_{B}^{-1} , and their photophysical properties have been revealed in our online database: <https://h-bn.info>, that will be discussed in Chapter 8. It should be noted that all EPR simulations consider up to the first-nearest nuclei as the second neighbors hardly contribute to the spectral profile, as observed in V_{B}^{-1} , $\text{O}_{\text{N}}\text{V}_{\text{B}}^{-1}$ [155], $\text{C}_{\text{N}}\text{V}_{\text{B}}^{-}$ and $\text{C}_{\text{B}}\text{V}_{\text{N}}^{+}$ defects [156].

Fig. 7.2(a) depicts the EPR spectrum of Se_{N} defect, which displays 11 peaks. These peaks correspond to the hyperfine tensor of Se itself and its first nearest neighbors. Specifically, the hyperfine coupling constants are $A_{zz,\text{Se}} = 54.44$ MHz and $A_{zz,\text{B}}$ (for the first nearest neighbors) are 21.34 MHz, 33.31 MHz, and 28.64 MHz, respectively. According to the relation $2nI + 1$, where $I_{75\text{Se}} = \frac{1}{2}$ and $I_{11\text{B}} = \frac{3}{2}$, this results in 11 peaks. Next, Fig. 7.2(b) illustrates the EPR spectrum of Al_{N} defect. While 15 peaks are observed from the simulation, the calculated number of peaks yields 14, based on $2nI + 1$ where $I_{27\text{Al}} = 5/2$ and $I_{11\text{B}} = 3/2$. We speculate that this one additional peak is due to feasible interaction from the second neighbors. This is because the hyperfine coupling of the first neighbors are still high ($A_{zz,\text{Al}} = -91.68$ MHz, $A_{zz,\text{B}} = 113.57$ MHz, 114.69 MHz, and 116.88 MHz). As such, the second neighbor should likely be taken into account. However, this is beyond the scope of this work. It is worth noting that the negative sign of A_{zz} affects only the level of the coupled states in Sec. 6.2.1 while the EPR spectrum remains unchanged. Fig. 7.2(c) displays the EPR spectrum of P_{B} . The calculated hyperfine constants yield $A_{zz,\text{P}} = 1051.34$ MHz and $A_{zz,\text{N}} = 18.73$ MHz, 36.58

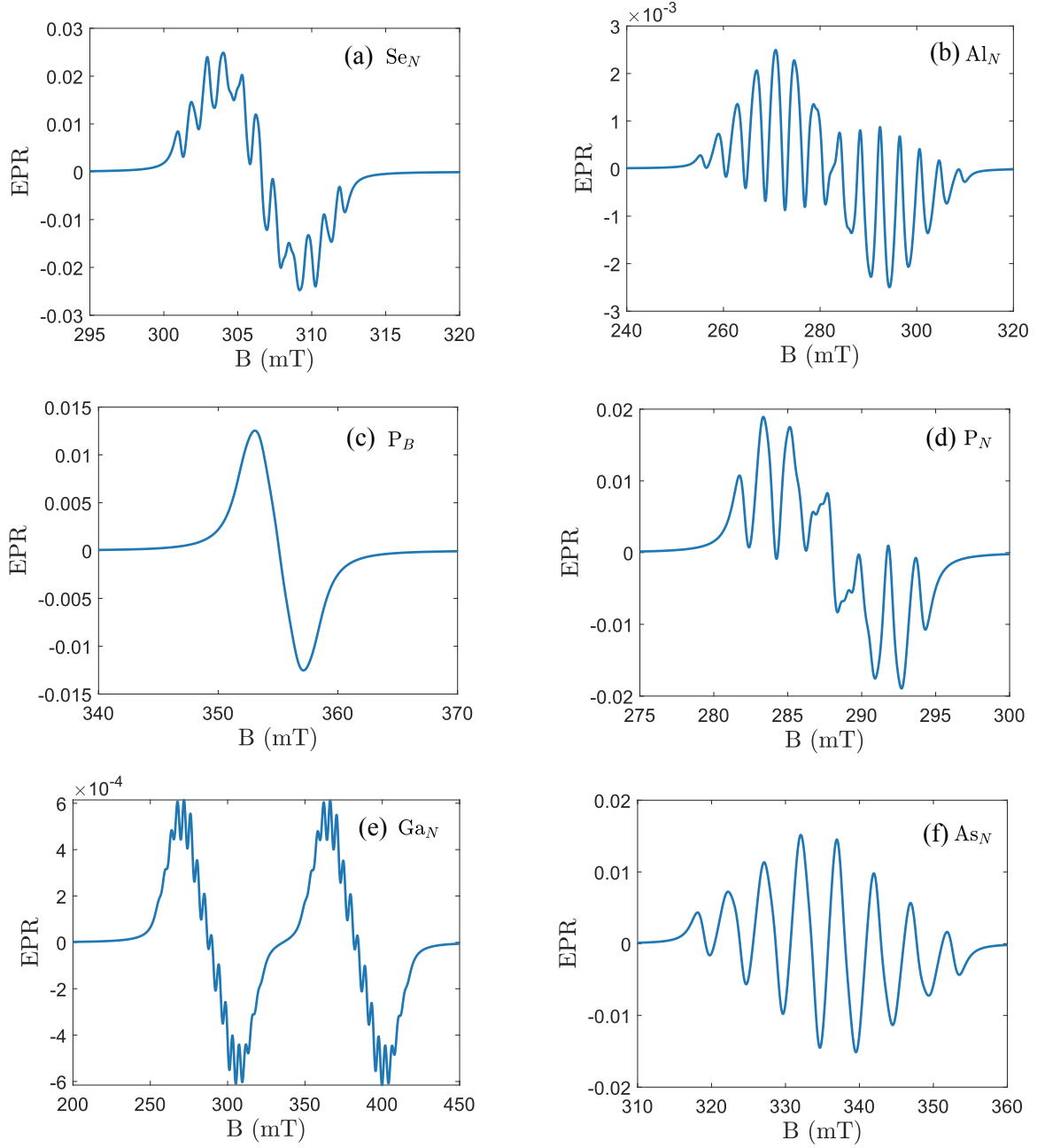


Figure 7.2: EPR spectra of point defects at X band with the transition from $m_s = -1$ to $m_s = 0$ with the fixed microwave frequency at X band.

MHz, and 18.11 MHz. This exceptionally significant difference of the hyperfine coupling between P and N causes two peaks observed in the EPR simulation, in good agreement with $2nI + 1$ where $I_{31P} = 1/2$. For P_N , on the other hand, the hyperfine coupling is

$A_{zz,P} = -53.09$ MHz and $A_{zz,B} = 1.24$ MHz, 54.07 MHz, and 38.82 MHz. This pinpoints that one B atom exhibits weak hyperfine coupling, potentially influencing the number of hyperfine peaks. As a result, from $2nI + 1$ with $n_B = 2$ for $I_{11B} = 3/2$ and $n_B = 1$ for $I_{31P} = 1/2$, it yields eight peaks, corresponding to that of the simulated EPR, as shown in Fig. 7.2(d). Then, Fig. 7.2(e) exhibits the EPR spectrum of Ga_N . Unlike other defects, it shows two peak patterns between 250–320 mT and 350–420 mT, representing transitions of from $m_s = -1$ to $m_s = 0$ and from $m_s = +1$ to $m_s = 0$, respectively. It should be noted that all other defects also exhibit the second EPR spectrum for the transition from $m_s = +1$ to $m_s = 0$; nonetheless, they are not shown in this result.

Turning back to Ga_N , the gap between these two EPR patterns is affected by the ZFS. We found that its ZFS is 1.32 GHz, which is in the typical order of hBN defects and then can be ruled out as a reason for this behavior. Then, its hyperfine couplings have been computed and resulted in $A_{zz,\text{Ga}} = -260.23$ MHz and $A_{zz,B} = 110.55$ MHz, 111.33 MHz, and 114.42 MHz. No exceptionally high magnitude of the hyperfine values has been observed; thus, the justification of the two EPR spectra being close to each other is likely due to the broadening of each spectrum. That is, the broadening of each spectrum is expanded up to 100 mT interval. This becomes a unique characteristic of Ga_N defect. Then, the number of peaks in the EPR simulation is 13 peaks, consistent with the calculation of $2nI + 1$ where $I_{69\text{Ga}} = 1/2$. Lastly, the EPR of As_N has been characterized as shown in Fig. 7.2(f). The computed hyperfine couplings yield $A_{zz,\text{As}} = 142.17$ MHz and $A_{zz,B} = 137.54$ MHz, 6.71 MHz, and 6.63 MHz. This suggests that two boron nuclei seem to have weak interaction with the defect; thus, this can be neglected from the hyperfine peaks. Hence, the calculated number of peaks from $2nI + 1$ yields seven peaks from $n_B = 1$ for $I_{75\text{As}} = 3/2$ and $n_B = 1$ for $I_{11B} = 3/2$. Nevertheless, the EPR simulation shows eight peaks, indicating that interactions with second-neighbor nuclei may need to be considered, which is beyond the scope of this work.

Comparing these defects, their EPR signals are uniquely different despite the same types of the first nearest nuclei. This implies that this property can be used for microscopic origin assignment by comparing it with experimental signals.

7.3 Effects of Isotopes on Broadening in ODMR

While the EPR signal is advantageous in identifying the microscopic origin, ODMR serves as another crucial tool that not only facilitates defect identification, but also provides valuable information about the linewidth of the signal.

Fig. 7.3 illustrates the ODMR spectra of V_B^{-1} with different nitrogen isotopes. The simulation reveals five dips for ^{14}N and seven dips for ^{15}N , corresponding to the distinct hyperfine states of each isotope. A detailed analysis of these hyperfine splittings is presented in Sec. 6.2.1. Both isotopes exhibit two distinct spectra associated with the transitions from $m_s = 0$ to $m_s = -1$ and from $m_s = 0$ to $m_s = +1$. When considering the broadening of the spectra, it becomes apparent that different isotopes contribute to the

broadening differently. Narrow broadening means low spin crowding, which is desirable for achieving higher sensitivity.

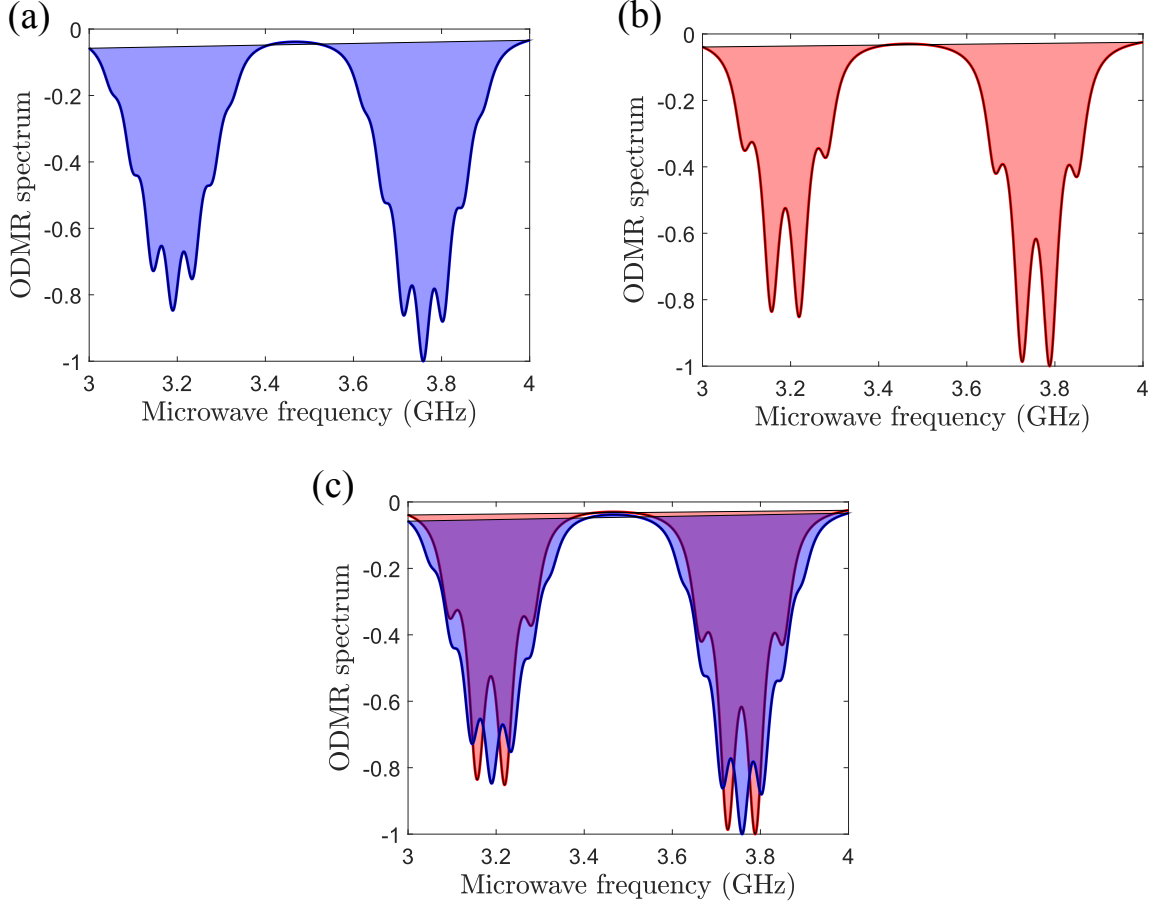


Figure 7.3: Simulated ODMR spectra of V_B^{-1} in hBN with three different nearest-neighbor nitrogen isotopes where (a) ^{14}N , (b) ^{15}N , and (c) overlay of both nitrogen isotopes. The external magnetic field is applied at 10 mT.

As depicted in Fig. 7.3, the spectrum associated with ^{14}N is broader compared to that of ^{15}N , indicating a higher degree of decoherence. This observation can be explained by examining the nuclear spin properties, including the nuclear spin quantum number (I) and the gyromagnetic ratio (γ). The isotope ^{14}N has a nuclear spin quantum number I equal to 1 and a gyromagnetic ratio γ of 3.077 MHz/T, whereas ^{15}N has a nuclear spin quantum number I equal to 1/2 and a gyromagnetic ratio γ of -4.316 MHz/T.

As a consequence, the broader linewidth observed for ^{14}N is likely attributed to its higher nuclear spin quantum number, which leads to increased spectral crowding and stronger nuclear-spin decoherence. In contrast, ^{15}N , with its lower nuclear spin quantum number, exhibits less spectral crowding, thereby suppressing decoherence and enhancing

sensitivity. Therefore, ^{15}N isotopes are preferred for applications requiring high precision and sensitivity in quantum sensing.

7.4 Conclusion

This chapter has explored the utilization of two key properties in quantum sensing applications to assign microscopic origins, namely EPR and ODMR.

For EPR, it has been established that the uncertainty arising from ZFS values is independent of the EPR characteristics. Consequently, this chapter has presented a detailed characterization of the EPR spectra for six novel triplet defects in hBN. The findings have demonstrated distinct differences in the EPR spectra, even among defects with identical neighboring nuclei. This differentiation underscores the robustness of EPR in accurately assigning specific defects based on their unique spectral signatures. The ability to distinguish defects with the same surrounding nuclear environment reinforces the efficacy of EPR as a powerful tool for defect identification.

Furthermore, the ODMR analysis has provided additional insights. The results indicated that hB^{15}N exhibits less spectral broadening compared to the other isotopic compositions. This reduced broadening is attributed to the weaker nuclear spin quantum number of ^{15}N , which mitigates hyperfine interactions and, in turn, enhances the sensitivity of the measurements. The increased sensitivity in hB^{15}N makes it a particularly attractive candidate for high-precision quantum sensing applications, where minimizing spectral broadening is crucial for achieving accurate and reliable measurements.

In summary, the combined use of EPR and ODMR techniques has proven effective in assigning microscopic origins to defects in hBN, providing a comprehensive approach to characterizing and differentiating spin qubits. The insights gained from these analyses highlight the potential of these methods in identifying defects and, meanwhile, suggesting defect candidates for quantum sensing.

Chapter 8

Online Database for Comprehensive Properties of hBN Color Centers

The potential applications of hBN color centers span across various domains, including quantum emitters, quantum communication, quantum memory, and quantum sensing, each distributed across different defect types, as elaborated in previous chapters. This diversity underscores the necessity for distinct properties tailored to each application. One critical property is the localization of defects within hBN, where some defects are localized at shallow levels and others at deep levels. While DFT offers reasonable predictions for defect localization, attributing specific microscopic origins remains a challenge due to the abundance of possible defects and the similar properties exhibited by different defects. This complexity arises from the intrinsic wide band gap of hBN, which accommodates numerous defects [90, 177, 204]. Furthermore, experimental observations reveal that many emitters around 2 eV, commonly referred to as 2 eV emitters, may not share the same atomic origin and can vary in other photophysical properties [140, 173, 175, 179]. Therefore, accurate defect identification necessitates a comprehensive dataset integrating all potential defects and advanced theoretical approaches to precisely capture the electronic properties [136].

In recent years, numerous databases have been developed to systematically collect the properties of a wide range of defects in 2D materials. These databases include both machine learning (ML)-based resources [260, 261, 262] and DFT-based repositories [263, 264, 265, 266, 267, 268, 269, 270]. ML-based databases can handle extensive datasets efficiently, yet the identification of promising candidates often requires subsequent DFT calculations for validation. In general, a machine-learning database is sufficient for screening and predicting promising new defects that one could fabricate; on the other hand, for defect identification from a fabricated sample, one needs the most accurate simulation specifically for that sample. This can be offered by DFT calculations, in particular, the DFT-based databases. So far, the accessible databases contain structural, electronic, and energetic properties [263, 264, 265, 266, 267], Raman spectra [271], and photophysical properties of point defects [268, 269, 270]. However, some databases contain both TMD- and hBN-based quantum emitters and use the same functional for all materials [266, 268, 270]. This results in an overall comprehensive database

but not all functionals might be equally good for all materials. In contrast, specialized databases focusing exclusively on hBN defects exist [268, 270], but these often lack the complete optical fingerprint of many hBN defects.

In this chapter, we develop a searchable online database specific to fluorescent defects in hBN based on DFT using the HSE06 functional [111], which predicts properties in good agreement with experimental results [110, 136, 173]. It should be noted that while this dissertation generated the raw data, the website implementation was originally developed by Ashkan Zand. Chapter 4 has demonstrated that identifying color centers in hBN should not rely on a single property due to the diverse localization characteristics of defects, which can lead to misassignment. Consequently, this chapter compiles a comprehensive hBN database encompassing various properties, including electronic structure, ZPL, excitation and emission dipole orientations, lifetime, radiative transition rate, and spin multiplicity for 158 defects. These defects include vacancies, substitutional defects, antisites, and defect complexes (combinations of these). Certain defect structures are illustrated in Fig. 8.1.

Considering the defects in hBN, they can be further classified according to the total spin of the system, which includes singlet, doublet, and triplet states. The triplet and singlet states are particularly noteworthy as their electronic structures can be applied not only as single-photon sources but also for quantum sensing [85, 241, 257, 272] and quantum memory applications [146, 217], as elaborated in Chapters 5, 6, and 7. For quantum sensing, a recent example is the negatively charged boron vacancy, whose intrinsic triplet state allows for the splitting at $m_s = 0$ and ± 1 , facilitating ODMR measurements [85, 257, 272]. Additionally, relaxation can occur through non-radiative transitions via the intersystem-crossing pathway, necessitating the understanding of the singlet electronic structure. For a quantum memory, the triplet configuration supports the Λ structure for writing and retrieving processes, as recently proposed for implementation in hBN in Chapter 5 and Refs. [146, 217]. Consequently, in this database, in addition to collecting the properties of a neutral-charge defect that behaves in a doublet state, this defect type will also be charged with singly positive and negative charges to ensure the existence of the triplet state.

Therefore, our comprehensive database of color centers in hBN serves as a valuable resource. Complemented by the browsing website interface at <https://h-bn.info>, users can search for potential defect candidates that exhibit specific properties. Furthermore, the inclusion of optimized lattice structures facilitates further theoretical investigations.

The results from this chapter have been published in Ref. [258].

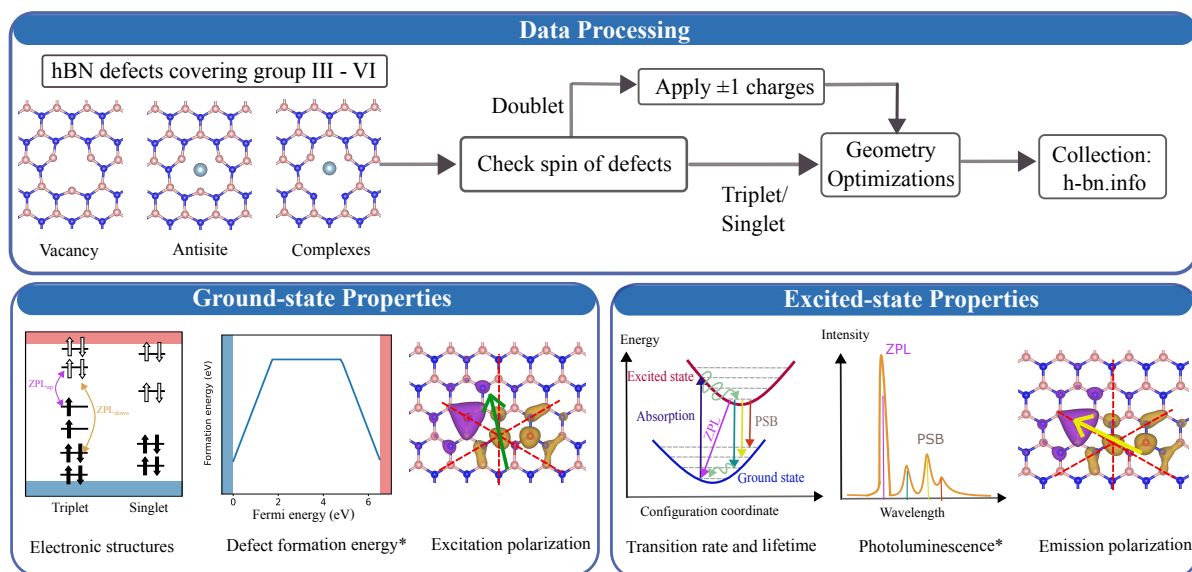


Figure 8.1: Process diagram illustrating the DFT database acquisition. The process begins with DFT calculations to investigate hBN defects, followed by the extraction of ground and excited photophysical properties for over 257 triplet transitions. The * symbol marks properties that are planned for the next updates and are currently only available for a limited set of defects. The database can be accessed openly at <https://h-bn.info>. The figure is adapted from Ref. [258] available under a CC-BY 4.0 license. Copyright 2024 Cholsuk *et al.*

8.1 DFT Calculation Details

Calculations were performed using VASP [183, 184] with the PAW method for the pseudopotentials [185, 186] to investigate all hBN structures. While all DFT settings remain unchanged from those benchmarked with experiments in Chapters 4 and 5, it is worth noting that the ground-state configuration is obtained by default Gaussian smearing with a sigma of 0.05 and the excited-state one is obtained from the so-called Δ SCF method [187]. With this constraint method, both spin-up and spin-down transitions were considered. The hBN monolayer was treated by adding the vacuum layer with 15 Å separated from the neighboring repeated cell to exclude layer-layer interaction. As most experiments are conducted on bulk structures, this difference may cause the inconsistency between simulation and experiment results in the aspect of ionization energies, charge stabilities, and charge transition level [131, 256, 273, 274]. However, the ZPL energy from a defect-defect transition is altered only slightly [275, 276]. Quantitatively, in some defects, the redshift of ZPL by 0.3 eV from monolayers can be expected [277].

8.2 Database Acquisition

Fig. 8.1 illustrates the workflow for compiling the defect database. Initially, 158 impurities from groups III-VI and their complexes were introduced into the hBN monolayer. The total spin states of these defects were determined based on their spin multiplicity, classifying them into singlet, doublet, and triplet states.

Table 8.1: Types of spin multiplicity in neutral-charge hBN color centers. Note that C_2 represents $C_B C_N$. $C_2 C_2$ -number refers to various lattice configurations, all of which are depicted in Appendix B and included in the database. The table is adapted from Ref. [258] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

hBN color centers						
Triplet/singlet				Doublet		
Al_N	$C_B C_N C_N C_N$	$O_B V_B$	$Se_B V_B$	$Al_B N_B V_N$	C_N	S_B
$Al_N Al_B$	$C_B N_B V_N$	$O_B V_N$	Se_N	$Al_B Se_N$	$Ga_B N_B V_N$	$Sb_B N_B V_N$
$Al_N Al_N$	$C_B O_B$	$O_N C_B$	$Se_N V_B$	$Al_B S_N$	$Ga_B V_N$	$Sb_B V_N$
$Al_N As_B$	$C_B O_N$	$O_N Ge_B$	$Se_N V_N$	$Al_B V_N$	$Ga_N N_B V_N$	$Sb_N N_B V_N$
$Al_N Ga_B$	$C_B Se_N$	$O_N N_B V_N$	Si_B	$Al_N N_B V_N$	$Ga_N V_B$	$Sb_N V_B$
$Al_N P_B$	$C_B V_B$	$O_N O_B$	$Si_B V_B$	$Al_N Se_N$	$Ga_N V_N$	$Sb_N V_N$
$Al_N Sb_B$	$C_B V_N$	$O_N S_B$	Si_N	$Al_N S_N$	Ge_B	$Sb_V N V_B$
As_B	$C_N C_B C_B C_B$	$O_N Se_B$	$Si_N N_B V_N$	$Al_N V_B$	$In_B N_B V_N$	$Se-V_N V_B$
As_N	$C_N N_B V_N$	$O_N Se_N$	$Si_N Si_B$	$Al_N V_N$	$In_B V_B$	$Si-V_N V_B$
$C-V_N V_B$	$C_N O_N$	$O_N S_N$	$Si_N V_B$	$As_B V_B$	$In_B V_N$	$Si_B V_N$
$C_2 C_2-1$	$C_N V_B$	$O_N V_B$	$Si_N V_N$	$As_B V_N$	$In_N N_B V_N$	$Si_N V_N$
$C_2 C_2-2$	$C_N V_N$	$O_N V_N$	S_N	$As_N N_B V_N$	$In_N V_B$	$S_N-V_N V_B$
$C_2 C_2-3$	Ga_N	P_B	Sn_B	$As_N V_B$	$In_N V_N$	$Sn_B V_N$
$C_2 C_2-3$	$Ge-V_N V_B$	$P_B P_N$	$Sn_B V_B$	$As_N V_N$	$N_B V_N$	V_B
$C_2 C_2-4$	$Ge_B N_B V_N$	P_N	Sn_N	$As_V N V_B$	O_B	V_N
$C_2 C_2-5$	$Ge_B V_B$	$P_N As_B$	$S_N N_B V_N$	$C_2 C_2 V_B$	O_N	
$C_2 C_B V_B$	$Ge_B V_N$	$S-V_N V_B$	$Sn_N V_B$	$C_2 C_B V_N V_B$	$O_N O_B V_B$	
$C_2 C_B V_N$	$Ge_N N_B V_N$	Sb_B	$Sn_N V_N$	$C_2 C_N$	$O_N O_B V_N$	
$C_2 C_N V_B$	$Ge_N V_B$	Sb_N	$S_N S_N$	$C_2 C_N V_N V_B$	$P_B N_B V_N$	
$C_2 C_N V_N$	$Ge_N V_N$	$S_B N_B V_N$	$S_N V_B$	$C_2 V_B$	$P_B V_B$	
$C_2 V_B V_B$	In_N	$S_B V_B$	V_N	$C_2 V_N$	$P_B V_N$	
$C_2 V_N V_B$	$O_B N_B V_N$	$S_B V_N$	$V_N V_B N_B$	C_B	$P_N N_B V_N$	
$C_2 V_N V_N$	$O_B Se_N$	Se_B	$V_N V_N$	$C_B C_N C_B$	$P_N V_B$	
$C_B C_N$	$O_B S_N$	$Se_B N_B V_N$		$C_B V_N V_B$	$P_N V_N$	

As summarized in Tab. 8.1, we identified that 95 out of the 158 defects exhibit triplet or singlet states in their neutral charge state, while the remaining defects favor the

doublet state. For the defects preferring the doublet state, we introduced ± 1 charges to ensure that each defect could possess both triplet and singlet configurations. The structures of these defects were then optimized for both the total spin states. For the excited states, electrons were manually occupied using the Δ SCF method. By considering electronic transitions separately, such as transitions from spin-up to spin-up or from spin-down to spin-down, we generated 257 triplet electronic structures for ground states, 257 triplet electronic structures for excited states, and 211 singlet electronic structures for ground states. It is important to note that, currently, only triplet states have been considered for their excited states, with plans to include other spin configurations in future updates to the database. The properties of these defects can now be extracted following the methodologies described in Chapters 3, 4, and 5, and have been analyzed in those previous chapters. This chapter, therefore, focuses on presenting the data in a more simplified and accessible format.

8.3 Database Screening of hBN Color Centers

Among a large number of defects, they can be classified by three properties as follows.

8.3.1 Distribution of Zero Phonon Line

After individually charging the doublet defects and considering the ZPL for each feasible transition pathway, 257 triplet electronic transitions are characterized, as depicted in Fig. 8.2. We found that most defects exhibit ZPLs within the visible range, particularly between 400 nm and 600 nm. This can be explained by the localization within a two-level system. Specifically, given that the pristine bandgap of hBN is approximately 6 eV, the occupied and unoccupied defect states are predominantly localized in the deep-lying regions around 1-2 eV and 4-5 eV, respectively. Consequently, the transition energy between these defect states typically falls within the range of 2 to 3 eV, corresponding to ZPLs around 400-600 nm.

Considering the relationship between ZPLs and the periodic table, no correlation is observed, as indicated by the unpredictable trends across different groups. This observation is reasonable since the periodic table primarily affects the number of defect states rather than their specific energy locations. This finding aligns with the previously revealed transition energy distribution as demonstrated in Chapter 4. Therefore, it can be concluded that ZPLs cannot be simply estimated based on periodic table trends and require actual calculations for accurate determination.

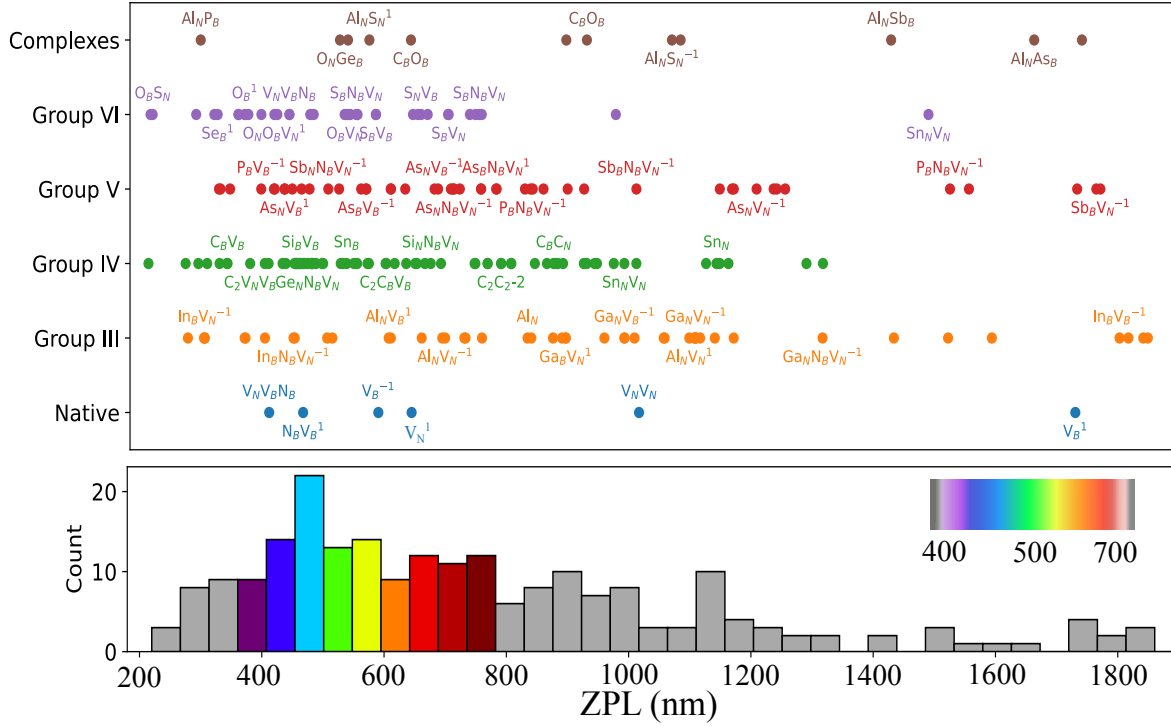


Figure 8.2: ZPL distribution categorized by elements in the periodic table, accompanied by a histogram. Annotations next to certain data points indicate specific defects, with the full list available in the database. The figure is adapted from Ref. [258] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

8.3.2 Distribution of Lifetime

Turning to consider the radiative lifetime, this essentially corresponds to ZPL pathways, as the lifetime reflects the transition rate between two defect states. Fig. 8.3 presents the lifetime values categorized by each periodic group. We found that the lifetimes predominantly range from 1 ns to 30 μs , which is consistent with typical experimental findings [179, 208, 241]. Comparing the distribution of ZPLs with that of radiative lifetimes, no correlation is observed. This is in agreement with other theoretical analyses, which found that the lifetime is related to the exciton energy rather than the ZPL values [278]. Furthermore, no relationship is found between the lifetime and the periodic table. This is reasonable because the transition rate, as shown in Eq. (3.2), is derived from the optimized wavefunctions between ground and excited states, both of which strongly depend on the type of defects.

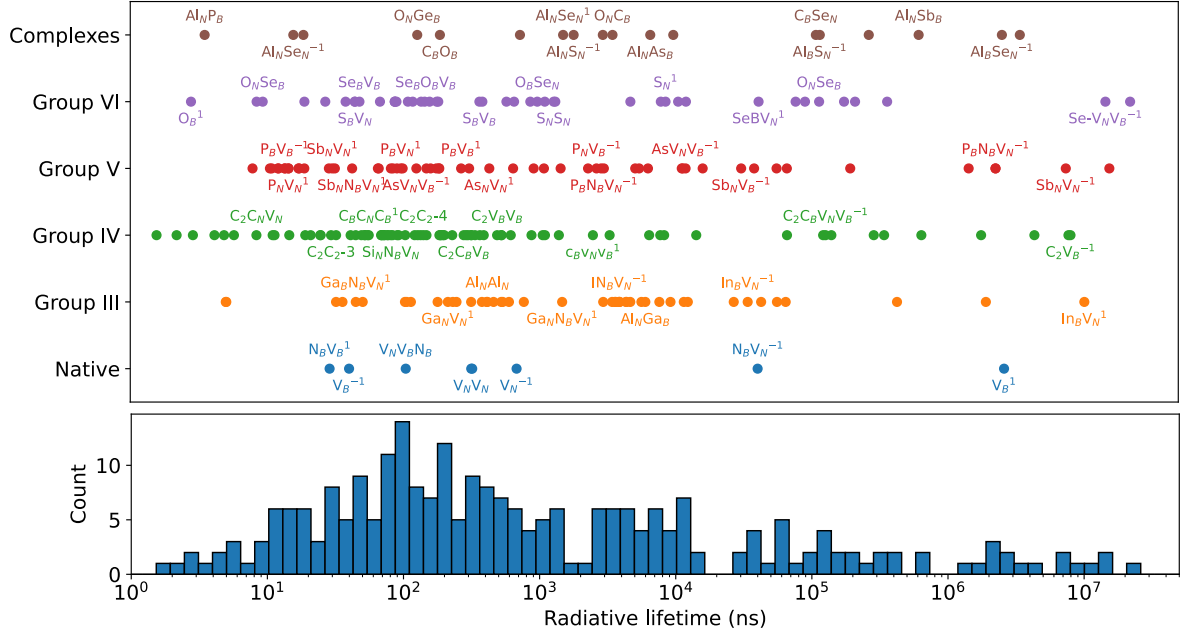


Figure 8.3: Radiative lifetime distribution categorized by elements in the periodic table, along with a corresponding histogram. Annotations next to select data points highlight specific defects, with the complete list available in the database. The figure is adapted from Ref. [258] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

8.3.3 Distribution of Polarization Misalignment

Lastly, as the excitation polarization is not necessarily aligned with the emission one, this leads to some misalignment, which can be experimentally measured and theoretically estimated. Fig. 8.4 suggests that for the majority of defects, both polarizations are parallel to each other, resulting in small misalignment. Regarding group distribution, since polarization relates to the transition dipole moment, it is plausible that there is no significant relationship between the periodic groups. In addition to the parallel polarizations, most are oriented in an in-plane direction, as indicated by the linear in-plane polarization visibility. This implies that most hBN defects exhibit polarized light. It is important to note that the in-plane *excitation* polarization can also lead to the out-of-plane *emission* polarization. Accurately approximating this behavior necessitates considering the linear in-plane polarization visibility. This phenomenon can be attributed to differences in wavefunctions, which are optimized differently for each polarization type. This phenomenon has also been observed in recent experimental work [61], as outlined in Chapter 4.

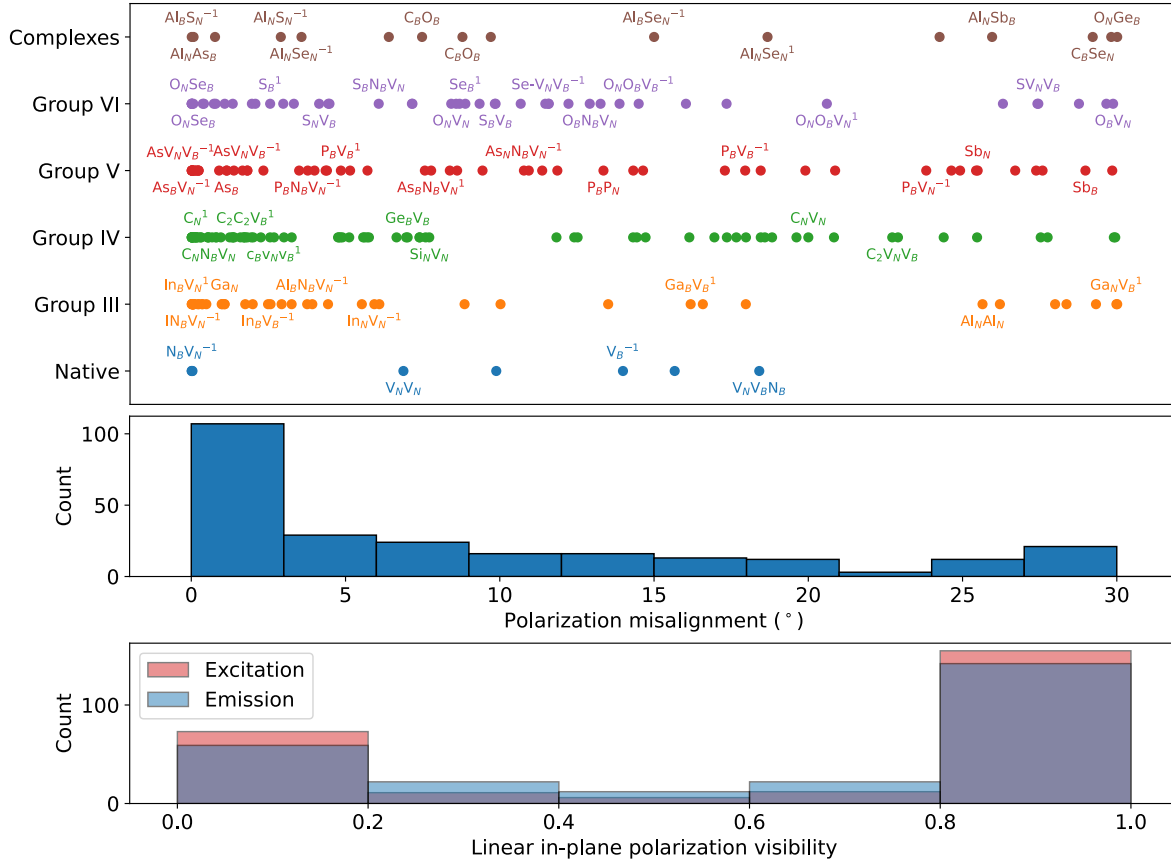


Figure 8.4: Polarization misalignment distribution categorized by elements in the periodic table, presented alongside histograms. Polarization misalignment is calculated as the difference in angles between excitation and emission polarizations, with both angles detailed in the database. Annotations next to certain data points indicate specific defects, with the full list accessible in the database. The figure is adapted from Ref. [258] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

8.4 Identification Procedure for Searching in h-bn.info Database

The database offers multiple options for the practical exploration of defect properties. For effective defect identification, it is crucial to recognize the limitations of DFT to ensure promising defects are not inadvertently overlooked. The step-by-step procedure is described below.

One key experimental observation is the ZPL, the most prominent peak in the pho-

toluminescence spectrum. This property is directly accessible in the database; however, it is recommended to provide a range rather than a specific value. This entails conducting a search within a range of ± 0.4 eV from the observed ZPL. The finite accuracy of DFT and residual strain from the experiment justify this range, rendering it incompatible with the unstrained defects documented in the database.

While the ZPL range serves as a reliable indicator, additional insights can be obtained from the fabrication technique as well. For instance, if a defect is fabricated using ion implantation, we can infer certain defects based on the ions employed. Conversely, defects formed through the use of a scanning electron microscope are likely to be carbon-related defects.

Potential defect candidates can be further narrowed down by considering other photophysical properties, such as lifetime and polarization orientation. This approach enhances the accuracy of defect identification, as demonstrated earlier [217]. The database will be frequently updated with new defects and new defect properties. Additionally, users can request specific data (defects or properties), which will be prioritized for the next update. All data, including crystallographic data, can be downloaded in various formats.

8.5 Conclusion

This chapter has provided information about a database developed from DFT methodology benchmarked against experimental data to reveal ground and excited photophysical properties for triplet color centers in hBN. The database includes over 257 triplets and 211 singlets, allowing us to determine that their properties are uncorrelated with the periodic table. The property distribution suggests dominant ranges of ZPL, lifetimes, and polarizations, which are consistent with experimental findings.

Considering quantum applications, all studied defects in this database exhibit triplet electronic structures, which are theoretically suitable for ODMR and the Λ structure for quantum memory. However, the former still requires ZFS calculations and ODMR simulations for all defects, as demonstrated in Chapter 7 for certain point defects, while the latter has been incorporated into this database through the performance metrics developed in Chapter 5. Consequently, this database can be employed to identify promising defects suitable for quantum applications.

To facilitate access to the comprehensive properties, the website was developed to feature the interface where users are allowed to browse defect candidates with specific inherited properties. Furthermore, the website also contains optimized lattice structures that can be directly used for further DFT calculations. This database will be applicable not only for future experiments but also for theoretical assignments of microscopic origins.

Notable future additions to this database include defect formation energy, which is required for analyzing the thermodynamic favorability of charged defects. While we

acknowledge this necessity, the primary focus of this database is to present the properties of hBN triplet defects under the assumption of their experimental viability. The addition of defect formation energy is scheduled for the upcoming update. Other important parameters to be included are excited properties, such as vertical excitation energy, photoluminescence, and non-radiative transitions, which are also planned for the next database update. Finally, considering the variability of the hBN refractive index across different experiments, we plan to feature this refractive index as an open parameter to allow users to obtain the corresponding transition rates and lifetimes based on the specified refractive index.

Chapter 9

Summary and Outlook

This dissertation presents a comprehensive theoretical investigation of color centers and spin qubits hosted by low-dimensional hexagonal boron nitride (hBN) for various quantum technologies, including quantum emitters, quantum memory, and quantum sensing. While all calculations utilized density functional theory and open quantum systems, they were benchmarked and compatible with experiments. This suggests the potential of applying the theoretical findings for the actual implementation of quantum technologies.

Quantum emitters or single photon sources are found feasible by hBN color centers. The pristine hBN possesses a wide bandgap of approximately 6 eV, which facilitates the localization of various defects within the in-gap region. As explored across the periodic table, there is no direct correlation between specific defects and emission wavelengths, necessitating individual characterization of each defect. This dissertation demonstrates that while the impurities from different elements in the periodic table primarily influence the number of defect states, they do not significantly alter the localization position within the bandgap. The wide range of potential defects is advantageous, offering multiple options for application. However, this diversity also poses challenges in accurately assigning the microscopic origins of the observed emissions. To address this issue, the dissertation proposes a methodology for comparing comprehensive properties to improve the accuracy of defect identification. Several defects have been benchmarked by experimental results, showing consistency with theoretical predictions. Despite the extensive calculations and data collection presented in this dissertation, which is available in an online database at <https://h-bn.info>, the characterization remains incomplete for some defects. Future work can potentially focus on extending these characterizations to encompass all relevant properties of hBN color centers and also revealing properties specific to each quantum technology. Apart from defect characterization, another noteworthy observation is the presence of temporal polarization at the initial stage before reaching saturation. This characteristic is particularly advantageous for quantum communication, as it can be utilized in polarization encoding. Future research should further explore and deepen the understanding of this phenomenon to enhance its applicability in quantum communication systems.

Regarding the quantum memory applications, Raman-based and nuclear-spin-based

protocols are investigated in this dissertation and show promise when applied to hBN color centers. For the Raman-based protocol, the current model is limited to a simplified case that neglects decay processes, leading to an idealized scenario where the writing efficiency is unity and equal to the reading efficiency. This differs from actual implementations, where decay must be accounted for. Future work should focus on refining this model by incorporating decay processes. Another avenue for development is exploring the relationship between efficiency and the quality factor of a cavity. The existing model fixes the efficiency and calculates the corresponding quality factors, with a photonic cavity potentially reaching a quality factor of up to 10^7 , as indicated by efficiencies exceeding 95%. However, further modeling could involve fixing the cavity's quality factor, for example, at a typical value in the order of 10^3 , and then estimating the resulting writing, reading, and total efficiencies. This would lead to a compatible model to experiment. Though the model can be improved, one of the outstanding intrinsic hBN properties found in this dissertation is compatibility with other quantum systems. This implies that there is possibly no need for hBN color centers to have the wavelength conversion; hence, it reduces additional noises.

Regarding the nuclear spin mechanism, the coupling between electron spin and nuclear spin has been elaborated in this dissertation with an ability for coherent control. A significant challenge, however, lies in the strong decoherence in hBN, which restricts the T_1 and T_2 times. Although purification methods have been proposed to mitigate this decoherence, the improvements observed are relatively modest when compared to other quantum systems. Thus, developing novel and efficient mechanisms to address decoherence remains an urgent priority, especially since coherent control and memory mechanisms have been shown to be feasible, paralleling those of NV-center quantum memory systems. Given that the current model can be performed in an experiment, another promising research direction is to advance toward simulating a quantum network that incorporates all realistic hBN parameters. Such a simulation would provide a comprehensive understanding of the macroscopic dynamics of quantum networks and, more importantly, assess the feasibility of implementing hBN-based quantum networks.

The final application examined in this dissertation is quantum sensing. It has been observed that hBN color centers suitable for quantum memory applications are also likely to be applicable to quantum sensing. This dual applicability arises from the electronic transitions that support both functionalities. However, the studies in this dissertation related to quantum sensing primarily focus on defect identification, as the electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) spectra reveal the intrinsic characteristics of a defect. Therefore, further investigation into specific defects for quantum sensing applications is necessary.

In conclusion, this dissertation establishes a robust theoretical foundation for the second generation quantum technology utilizing hBN color centers. Significant progress has been made in the development of quantum light sources, quantum memory, and quantum sensing; however, these advancements currently exist as individual components. The next ultimate objective of this research is to integrate these elements into a cohe-

sive hBN-based quantum network. For example, the quantum light source, supported by hBN color centers, could emit the desired wavelength, facilitating direct coupling with quantum memory at each quantum repeater node, thus circumventing the need for wavelength conversion. Although constructing such an hBN-based quantum network presents significant challenges, the promising properties of hBN defects make this a feasible long-term goal. This achievement would significantly advance optical quantum technologies, particularly through the implementation of “true” single photons.

Appendix A

Simplified Electronic Structures for Defects in Each Periodic Group

This appendix provides a summary of the electronic structures of hexagonal boron nitride (hBN) with various defects, categorized by periodic groups. The details of these structures are discussed in Chapter 4. Although the actual electronic band structures were plotted along the high-symmetry k -points Γ , M, K, and Γ , the following simplified electronic band structures are used for clarity. This simplification is valid because the defect states (both occupied and unoccupied) for all types of defects exhibit flat bands.

A.1 Properties of Defects in Each Periodic Group

As investigated in Chapter 4 for the electronic transition type, transition energy, wavelength, and lattice deformation, all properties of all defects are summarized and accessible via <https://doi.org/10.5281/zenodo.6826694>.

A.2 Simplified Electronic Structures in Each Periodic Group

The following presents the simplified electronic band structures for each periodic group. In these diagrams, VB and CB refer to the valence and conduction bands, respectively. The dashed green line denotes the Fermi energy. Spin-up and spin-down defect states are represented by blue and red bars, respectively, with filled and unfilled arrows indicating occupied and unoccupied electron states. The numerical value adjacent to the Fermi level represents the transition energy, which is the energy gap between the two-level quantum systems.

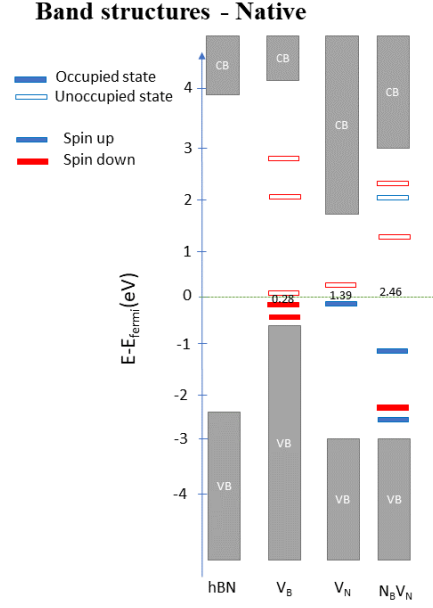


Figure A.1: Modified electronic band structures for native defects hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

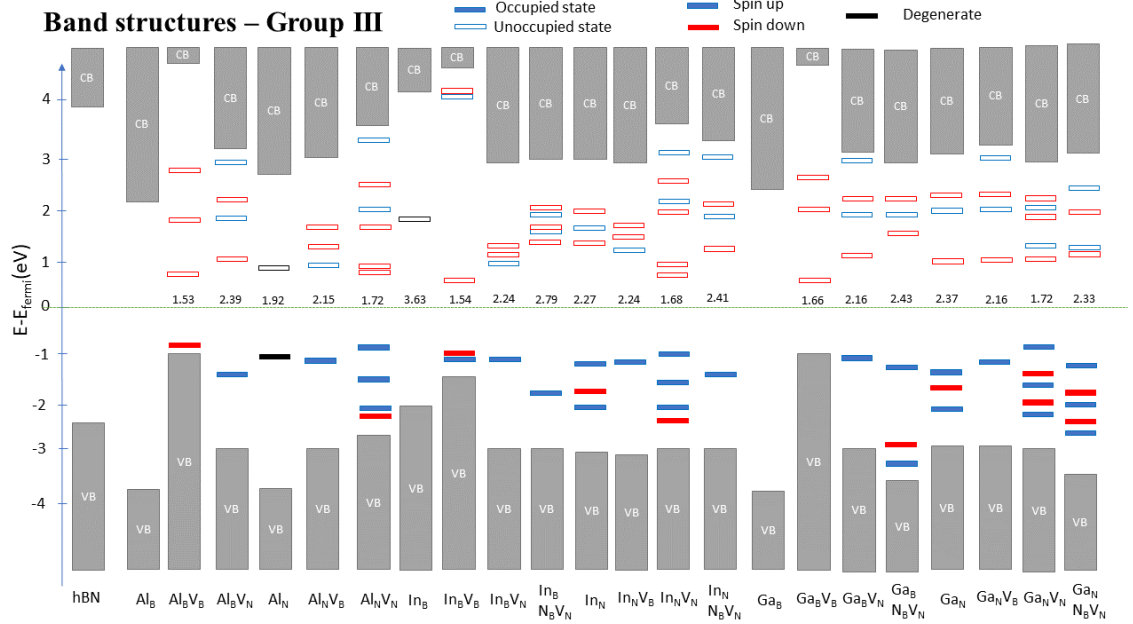


Figure A.2: Modified electronic band structures for defects from periodic group III hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

A.2 Simplified Electronic Structures in Each Periodic Group

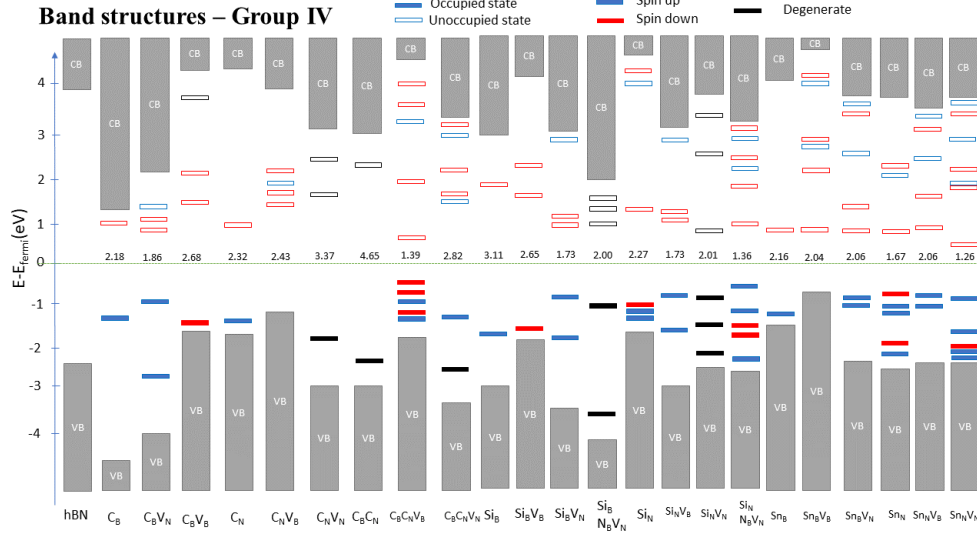


Figure A.3: Modified electronic band structures for defects from periodic group IV hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

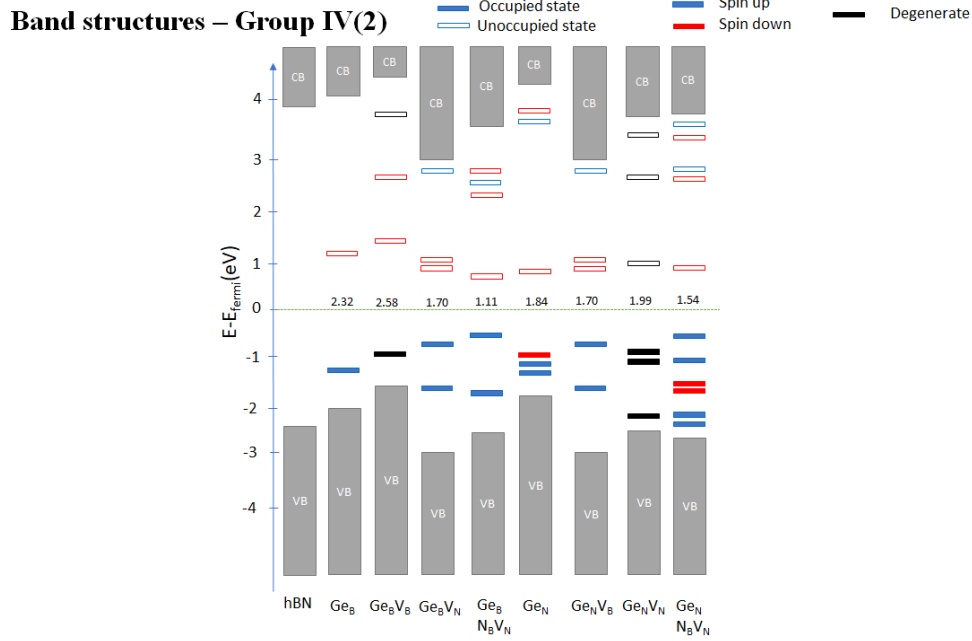


Figure A.4: Modified electronic band structures for defects from periodic group IV(2) hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

Appendix A Simplified Electronic Structures for Defects in Each Periodic Group

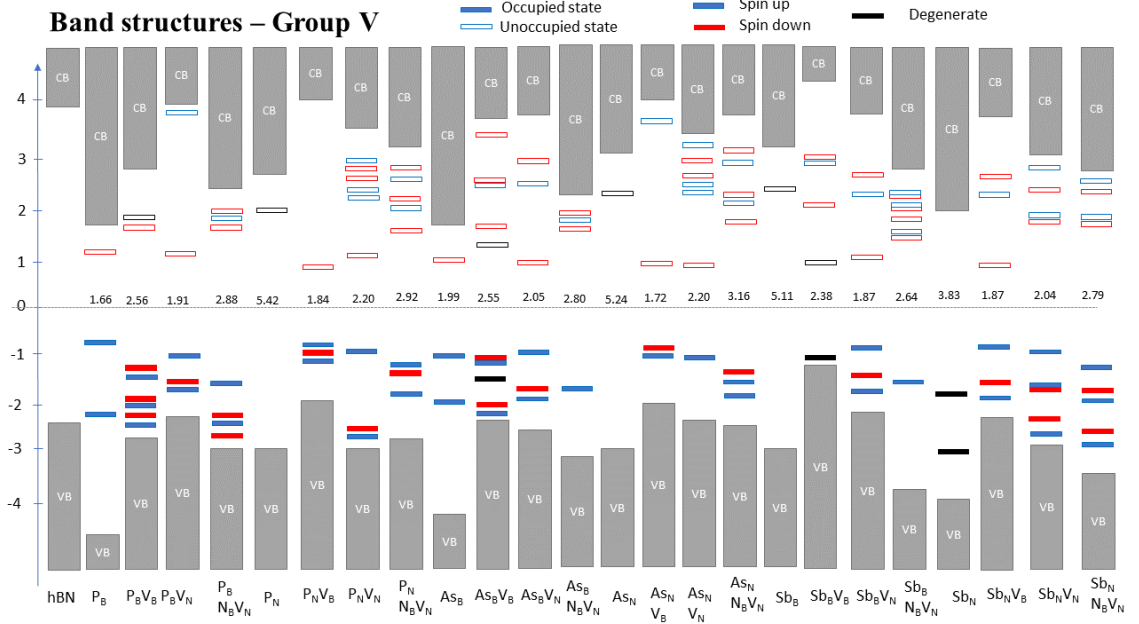


Figure A.5: Modified electronic band structures for defects from periodic group V hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

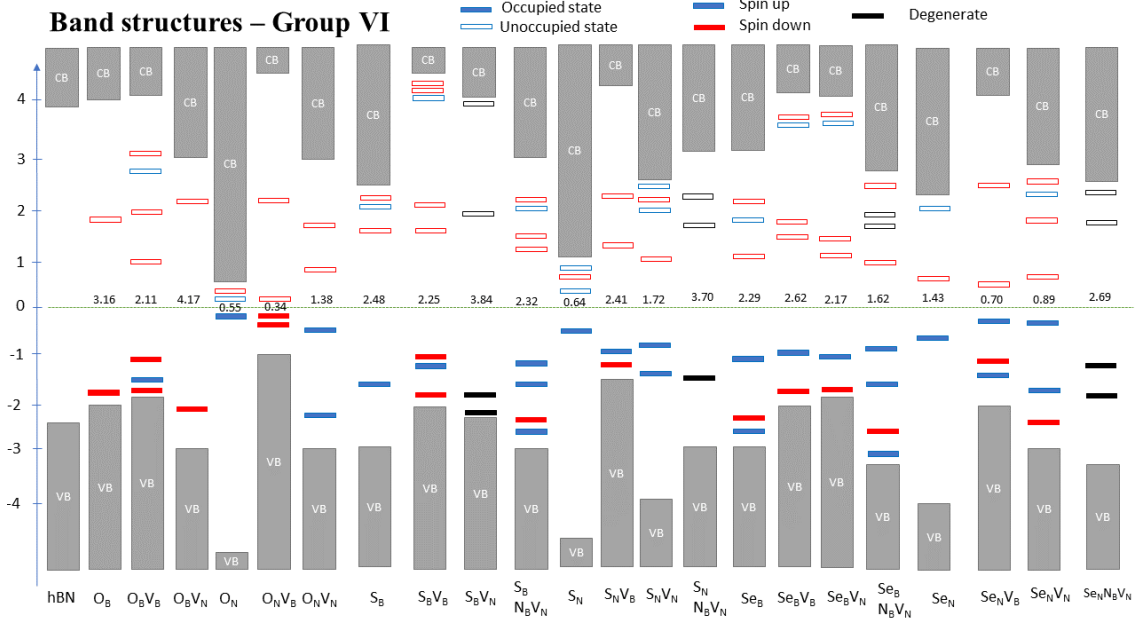


Figure A.6: Modified electronic band structures for defects from periodic group VI hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

A.3 Effects of Strain on Electronic Band Structures of hBN Defects

This section summarizes the effects of strain on the electronic band structures. As discussed in Chapter 4, strain is applied in bi-axial directions.

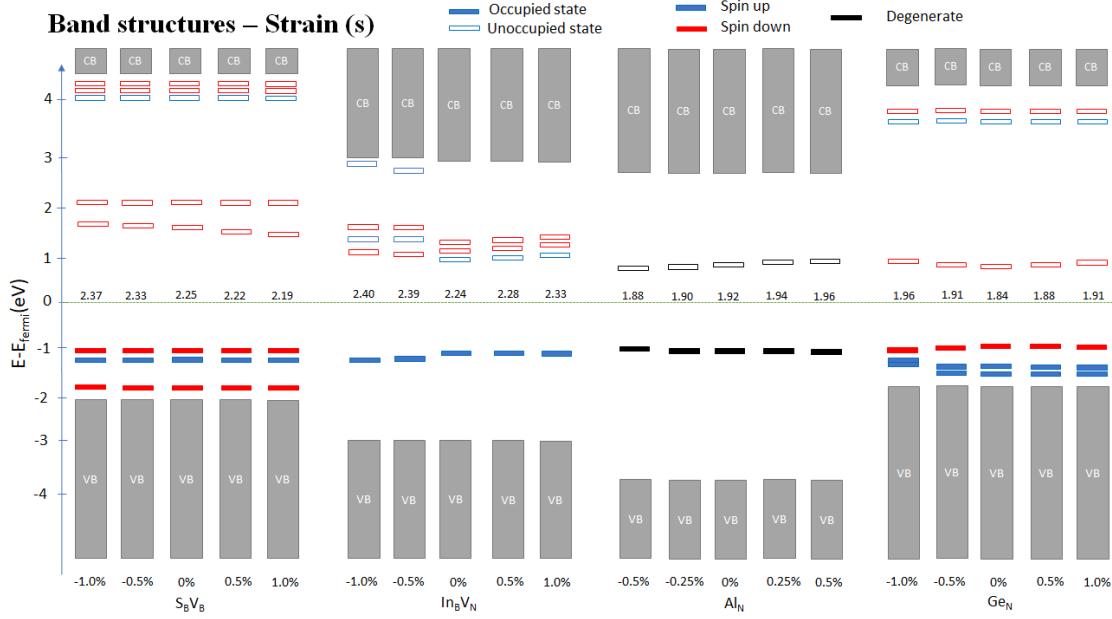


Figure A.11: Modified electronic band structures of defects affected by bi-axial strain. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

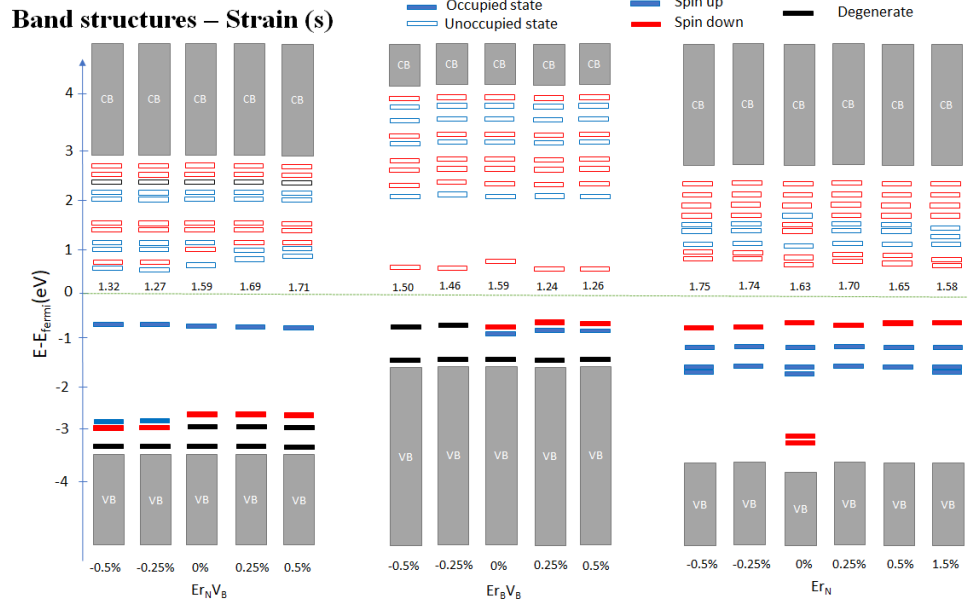


Figure A.12: Modified electronic band structures of defects affected by bi-axial strain. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

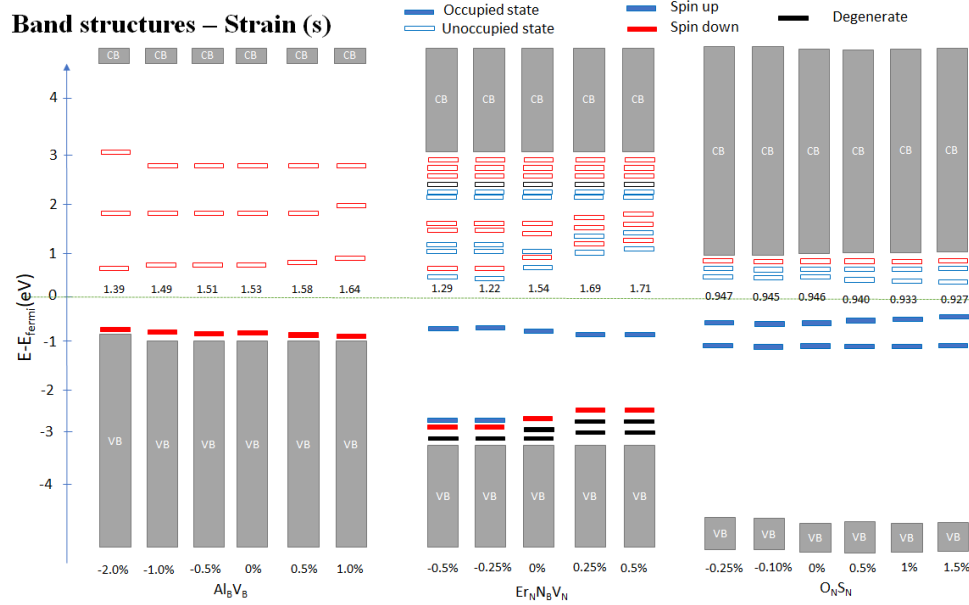


Figure A.13: Modified electronic band structures of defects affected by bi-axial strain. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

A.4 Effects of Charge on Electronic Band Structures of hBN Defects

This section summarizes the effects of charge states on the electronic band structures. As discussed in Chapter 4, charge-state defects are regarded as novel due to their emission wavelengths, which are uncorrelated with those of neutral defects.

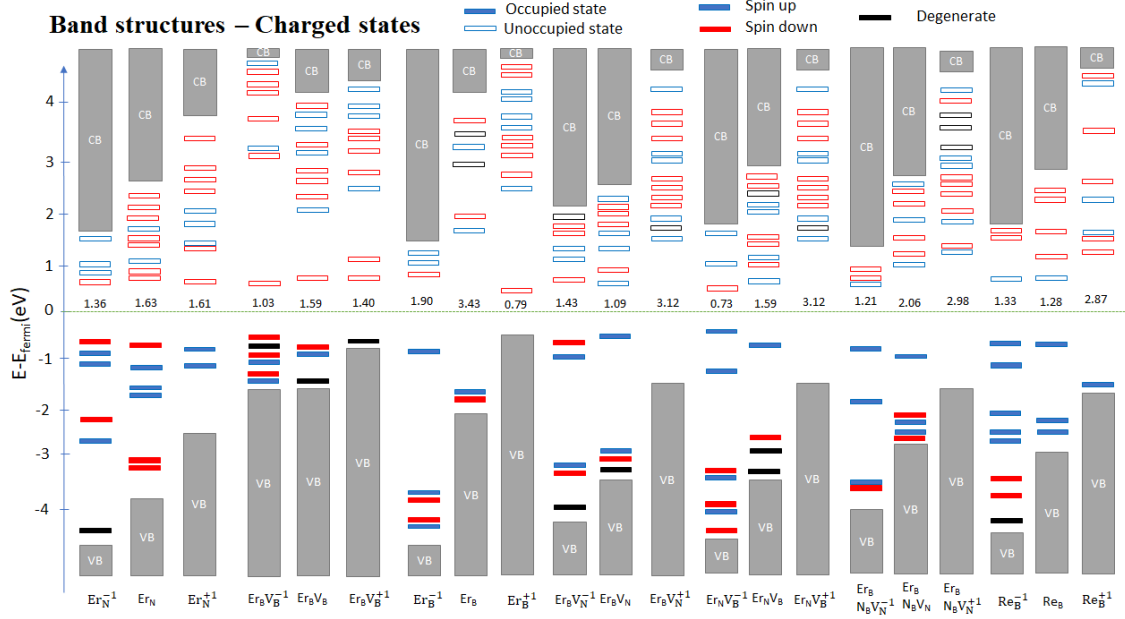


Figure A.14: Modified electronic band structures for charged-state defects hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

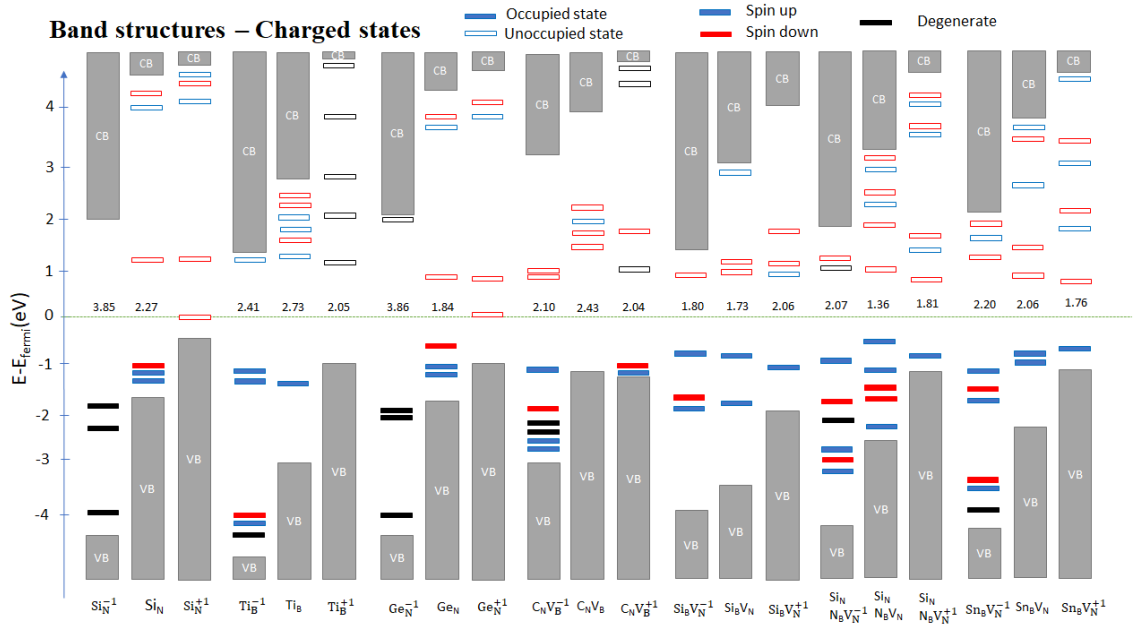


Figure A.15: Modified electronic band structures for charged-state defects hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

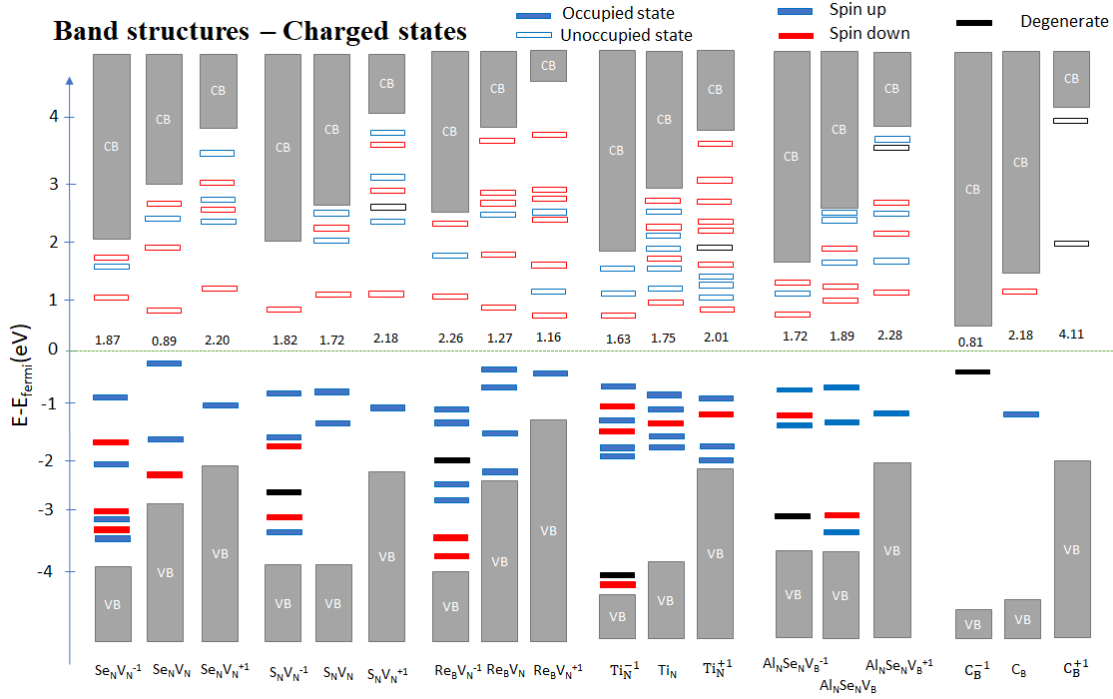


Figure A.16: Modified electronic band structures for charged-state defects hosted by hBN. The figure is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

Table A.1: Charged-state defects with transition types. E_T , λ , and $\downarrow\text{-}\uparrow$ denote the transition energy, wavelength, and the spin-flipping transition, respectively. Transitions from valence band (VB) to conduction band (CB), or between generate states (deg) are also listed. Radiative transitions are shaded in gray. The table is adapted from Ref. [90] available under a [CC-BY 4.0 license](#). Copyright 2022 Cholsuk *et al.*

Defect	Charge -1			Neutral charge			Charge +1		
	E_T (eV)	λ (nm)	Transition	E_T (eV)	λ (nm)	Transition	E_T (eV)	λ (nm)	Transition
Er _N	1.361	911.1	$\downarrow - \downarrow$	1.634	758.7	$\downarrow - \downarrow$	1.607	771.6	$\uparrow - \downarrow$
Er _B V _B	1.030	1204.3	$\downarrow - \downarrow$	1.592	778.7	$\downarrow - \downarrow$	1.398	886.9	deg - $\downarrow$
Si _N	3.852	321.9	deg - CB	2.268	546.8	$\downarrow - \downarrow$	-	-	-
Ti _B	2.410	514.5	$\uparrow - \uparrow$	2.733	453.6	$\uparrow - \uparrow$	2.053	604.1	VB - deg
Re _B	1.331	931.5	$\uparrow - \uparrow$	1.277	971.4	$\uparrow - \uparrow$	2.869	432.3	$\uparrow - \downarrow$
Er _B	1.898	653.3	$\uparrow - \downarrow$	3.433	361.2	$\uparrow - \uparrow$	0.789	1572.3	VB - $\downarrow$
Er _B N _B V _N	1.205	1028.7	$\uparrow - \uparrow$	2.063	601.1	$\uparrow - \uparrow$	2.980	416.1	VB - $\uparrow$
Er _N V _B	0.734	1690.2	$\uparrow - \downarrow$	1.590	779.6	$\uparrow - \uparrow$	3.122	397.2	VB - $\uparrow$
Er _B V _N	1.427	869.0	$\downarrow - \downarrow$	1.089	1138.7	$\uparrow - \uparrow$	3.124	396.9	VB - $\uparrow$
C _N V _B	2.100	590.4	$\uparrow - \downarrow$	2.433	509.8	VB - $\downarrow$	2.042	607.1	$\downarrow$ - deg
As _N	1.131	1096.4	$\uparrow - \downarrow$	5.24	236.6	deg - deg	4.813	257.6	$\downarrow$ - deg
Si _B V _N	1.796	690.4	$\uparrow - \downarrow$	1.734	715.2	$\uparrow - \downarrow$	2.058	602.4	$\uparrow - \uparrow$
Si _N N _B V _N	2.070	599.2	$\uparrow$ - deg	1.360	912.0	$\uparrow - \downarrow$	1.808	685.8	$\uparrow - \downarrow$
Sn _B V _N	2.198	564.1	$\uparrow - \downarrow$	2.057	602.7	$\uparrow - \downarrow$	1.760	704.5	$\uparrow - \downarrow$
Al _N V _N	1.715	723.2	$\uparrow - \downarrow$	1.72	721.3	$\uparrow - \downarrow$	2.248	551.6	$\uparrow - \downarrow$
In _N	-	-	-	2.27	547.3	$\uparrow - \downarrow$	-	-	-
Ga _B V _N	2.870	432.1	deg - CB	2.16	574.3	$\uparrow - \downarrow$	3.395	365.2	VB - deg
P _B	0.312	3976.0	$\downarrow$ - CB	1.66	748.8	$\uparrow - \downarrow$	2.272	545.9	VB - $\downarrow$
Sb _N V _B	2.977	416.6	deg - CB	1.87	661.5	$\uparrow - \downarrow$	0.829	1495.3	$\uparrow - \downarrow$
O _N V _N	1.882	659.0	$\uparrow - \downarrow$	1.38	896.6	$\uparrow - \downarrow$	2.105	588.9	$\uparrow - \downarrow$
Se _N V _N	1.868	663.8	$\uparrow - \downarrow$	0.89	1392.4	$\uparrow - \downarrow$	2.202	563.1	$\uparrow - \downarrow$
S _N V _N	1.823	680.3	$\uparrow - \downarrow$	1.72	720.1	$\uparrow - \downarrow$	2.182	568.2	$\uparrow - \downarrow$
Re _B V _N	2.261	548.4	$\uparrow - \downarrow$	1.265	979.7	$\uparrow - \downarrow$	1.158	1070.4	$\uparrow - \downarrow$
Ti _N	1.629	761.3	$\uparrow - \downarrow$	1.7535	707.2	$\uparrow - \downarrow$	2.014	615.7	$\uparrow - \downarrow$
Al _N Se _N V _B	1.719	721.5	$\uparrow - \downarrow$	1.886	657.5	$\uparrow - \downarrow$	2.284	542.9	$\uparrow - \downarrow$
C _B	0.814	1523.0	deg - CB	2.18	568.7	$\uparrow - \downarrow$	4.112	301.6	VB - deg

Appendix B

Structural Configurations of $C_B C_N C_B C_N$ Defects

This appendix visualizes the lattice configurations of $C_B C_N C_B C_N$ defect (or $C_2 C_2$ defect), following from Sec. 4.5.2 in Chapter 4,

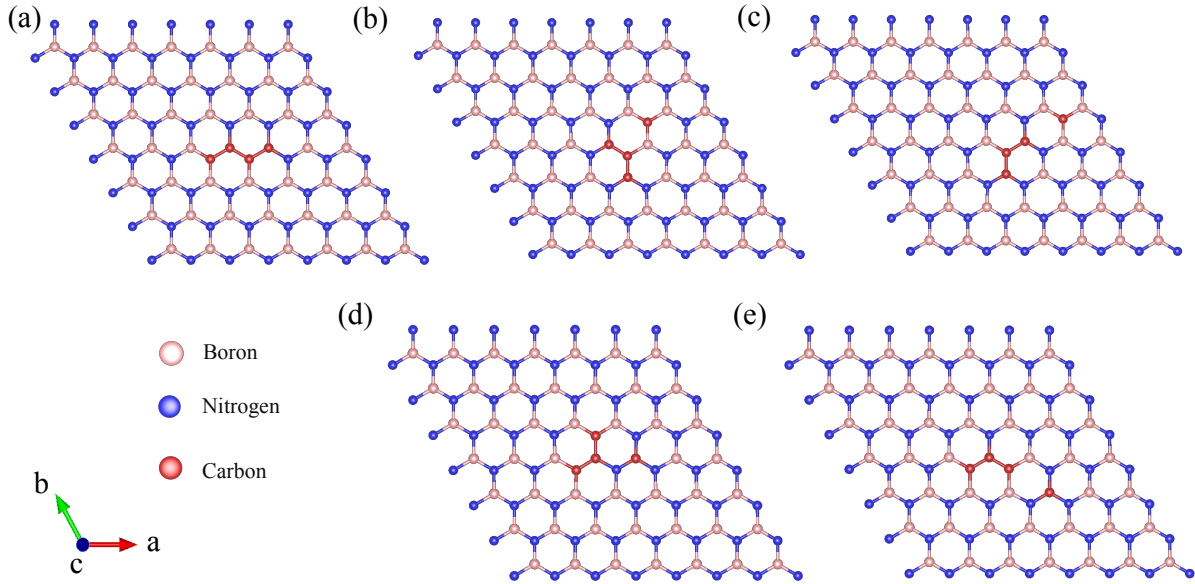


Figure B.1: Structural configurations of $C_B C_N C_B C_N$ defects where (a) four carbons are bonded together ($C_B C_N C_B C_N$ -1), (b) three carbons are bonded but one carbon is isolated under boron environment ($C_B C_N C_B C_N$ -2), (c) is similar to (b), but with different orientation ($C_B C_N C_B C_N$ -3), (d) three carbons are bonded but one carbon is isolated under nitrogen environment ($C_B C_N C_B C_N$ -4), (e) is similar to (d), but with different orientation ($C_B C_N C_B C_N$ -5). The figure is adapted from Ref. [179] available under a [CC-BY 4.0 license](#). Copyright 2023 Kumar *et al.*

Appendix C

Photophysical Properties of hBN Color Centers

This appendix provides additional details on hBN color centers, covering over 126 defects examined in relation to yellow emitters, the Purcell effect, and other properties relevant to defects proposed for various quantum applications, as discussed in Chapter 4.

C.1 Further Analysis of hBN Yellow Emitters

Following Sec. 4.5.2 in Chapter 4, the dipole orientation can take place via four transition pathways. In this section, the pathways from point 3 to point 1 and from point 4 to point 1 are investigated.

C.1.1 Additional Transition Pathways for Dipole Orientation

The findings for the $C_B C_N C_B C_N$ -3 defect are presented in Chapter 4. As illustrated in Fig. 4.10 in Chapter 4, the emission from point 3 can proceed either directly to the ground state (point 1) or through an intermediate phonon mode (point 4). When we computed the transition dipole moments for both the ZPL (3–1 transition) and a randomly selected phonon mode within the PSB (3–4 transition), we found minimal differences in the relative angles (less than 1°), as detailed in Tab. C.1 below. Consequently, we focus our analysis of the emission dipole only on the ZPL transition (from point 3 to point 1).

Table C.1: Emission decay pathway of $C_B C_N C_B C_N$ -3

Properties	Points 3 to 1	Points 3 to 4
Emission wavelength (nm)	573	708
Emission dipole ($^\circ$)	17.9	18.6
Emission polarization ($^\circ$)	12.1	11.4
Dipole misalignment ($^\circ$)	1.1	0.3
Polarization misalignment ($^\circ$)	1.0	0.3

C.1.2 Dipoles of Yellow Emitter's Candidates

Out of the 126 defects examined, we identified two additional promising candidates: $C_N V_N$ (illustrated in Fig. C.1) and $C_B C_N C_B C_N$ -5 (shown in Fig. C.2). However, integrating all the data, we believe the $C_B C_N C_B C_N$ -3 defect to be the most likely candidate. The comprehensive results for all 126 defects are compiled in the accompanying Excel spreadsheet, accessible at <https://doi.org/10.5281/zenodo.10288562>.

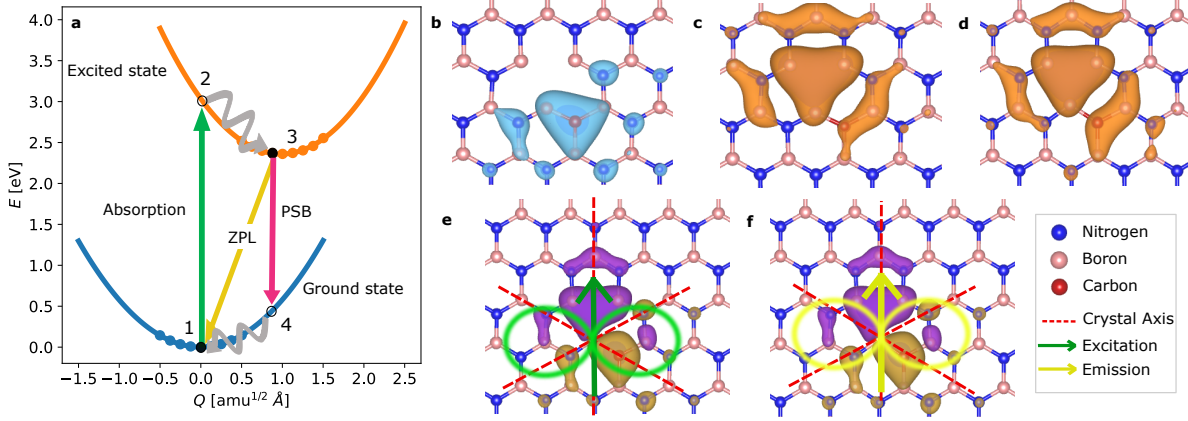


Figure C.1: Theoretical characterization of the neutral-charged $C_N V_N$ defect without strain. (a) Potential energy surface, illustrating the full excitation and emission process. This includes absorption (green line), the zero-phonon line (ZPL, yellow line at 525 nm), and the phonon sideband (PSB, magenta line). (b)-(d) Probability density $|\psi|^2$ of electron occupations: (b) in the ground state at point 1, and (c, d) in excited states at points 2 and 3, respectively. (e) Charge difference between points 1 and 2, visualized by isosurfaces, with the green arrow indicating the excitation dipole axis, aligned with light radiation shown in green. The excitation axis is tilted 29.8° relative to the crystal axis (red dashed line). (f) Charge difference between points 1 and 3, with the yellow arrow showing the emission dipole axis, aligned with light radiation in yellow. The emission axis is tilted 28.1° relative to the crystal axis. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

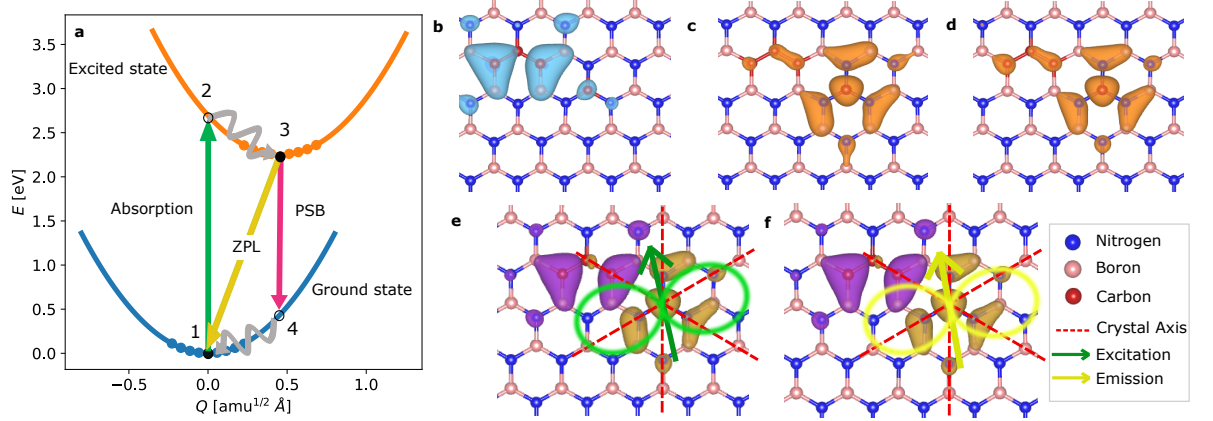


Figure C.2: Theoretical characterization of the neutral-charged $C_B C_N C_B C_N-5$ defect without strain. (a) Potential energy surface, illustrating the full excitation and emission process. This includes absorption (green line), the zero-phonon line (ZPL, yellow line at 562 nm), and the phonon sideband (PSB, magenta line). (b)-(d) Probability density $|\psi|^2$ of electron occupations: (b) in the ground state at point 1, and (c, d) in excited states at points 2 and 3, respectively. (e) Charge difference between points 1 and 2, visualized by isosurfaces, with the green arrow indicating the excitation dipole axis, aligned with light radiation shown in green. The excitation axis is tilted 12.3° relative to the crystal axis (red dashed line). (f) Charge difference between points 1 and 3, with the yellow arrow showing the emission dipole axis, aligned with light radiation in yellow. The emission axis is tilted 13.7° relative to the crystal axis. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

C.1.3 Charged-State Defects

In this section, we analyze the angles between the excitation/emission dipoles and the nearest crystal axis, regardless of their charge-state stability (refer to Figs. C.3, C.4, and C.5). Our primary objective is to identify defects that match the excitation and emission characteristics observed in experimental results. Subsequently, we exclude certain defects based on criteria such as the zero-phonon line, dipole orientation alignment, and linear in-plane polarization visibility, as detailed in Chapter 4. The full dataset is available in an Excel spreadsheet, accessible at the following link: <https://doi.org/10.5281/zenodo.10288562>.

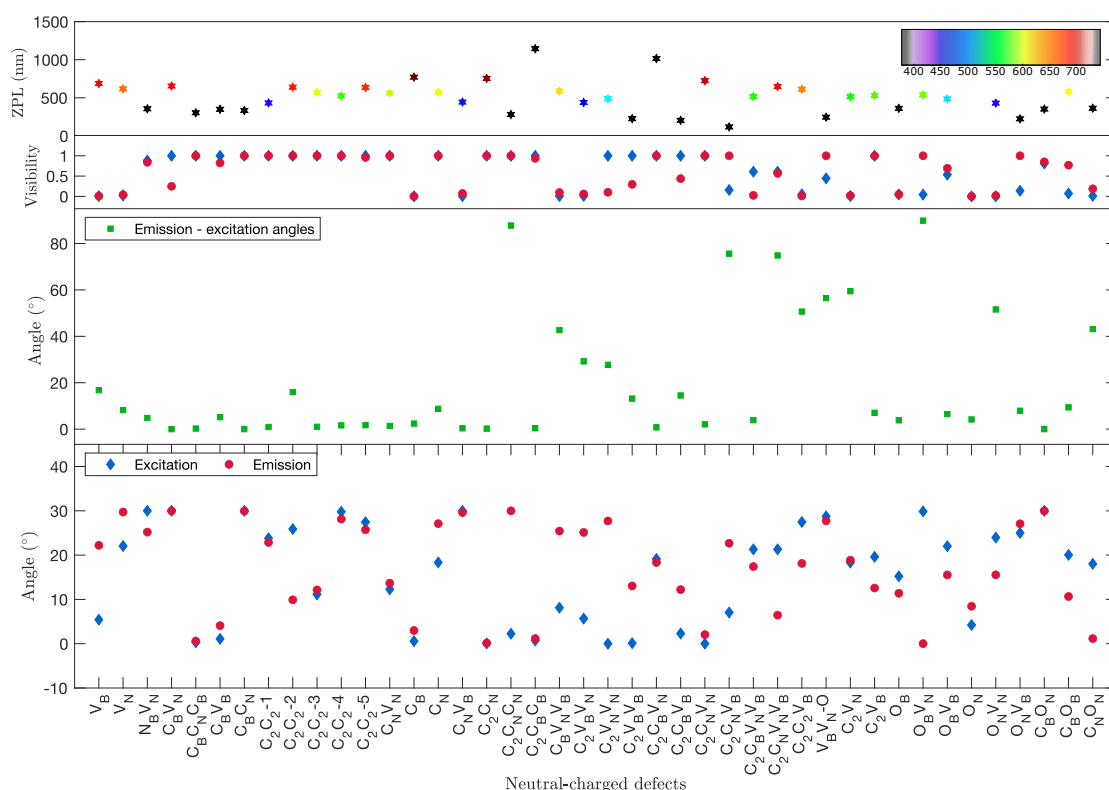


Figure C.3: Theoretical characterization of 42 neutral-charged defects, where the top-most panel indicates the zero phonon line (ZPL) represented by the color. The black dots represent the ZPLs which are out of visible range. The second top panel depicts the linear in-plane polarization visibility of excitation (blue) and emission (red); the middle panel illustrates the misalignment between excitation and emission; and the bottom panel shows the angle of excitation (blue) and emission (red) with respect to the nearest crystal axis. Some sub-figures are adapted from Ref. [61] available under a [CC-BY 4.0 license](#). Copyright 2024 Kumar *et al.*

C.2 Effect of Purcell Factor on Lifetime

The finite-difference time-domain (FDTD) simulation was conducted using Lumerical FDTD Solutions. To investigate the Purcell enhancement, an in-plane dipole emitter was positioned at the center of an hBN layer (the light blue region in Fig. C.6) with a refractive index of 1.85 at 532 nm and a thickness of 20 nm. This hBN slab was placed atop a SiO₂ substrate with a thickness of 200 nm (the gray region in Fig. C.6). The Purcell enhancement and the electric field mode profile were recorded for each layer.

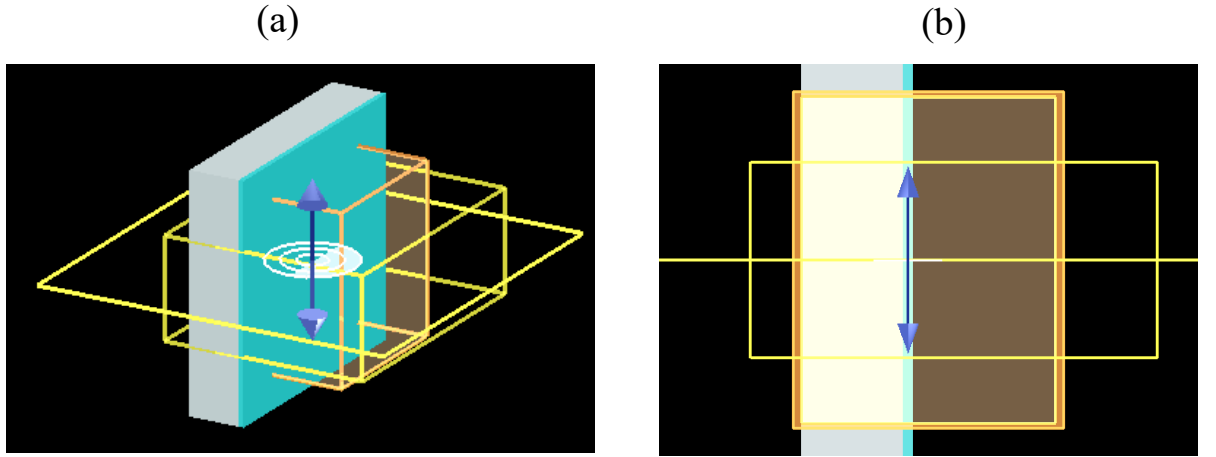


Figure C.6: Finite-difference time-domain (FDTD) simulation where the blue and gray regions represent the 20-nm hBN layer and 200-nm SiO₂ layer. The arrow indicates an in-plane dipole from an emitter.

The lifetime (τ) depends on Purcell factor $\mathcal{F}$ by the following relation,

$$\tau_{Purcell} = \frac{\tau}{\mathcal{F}} \quad (C.1)$$

From our FDTD simulation, we found that the Purcell factors at 572.61 nm, 681.81 nm, and 673.36 nm are 0.835, 0.829, and 0.831, respectively (see Fig. C.7). Consequently, the lifetimes for C₂C₂, Al_N, and P_NV_B, including the Purcell factor ($\tau_{Purcell}$), are 20.31 ns, 2.55 ms, and 0.71 μ s, respectively.

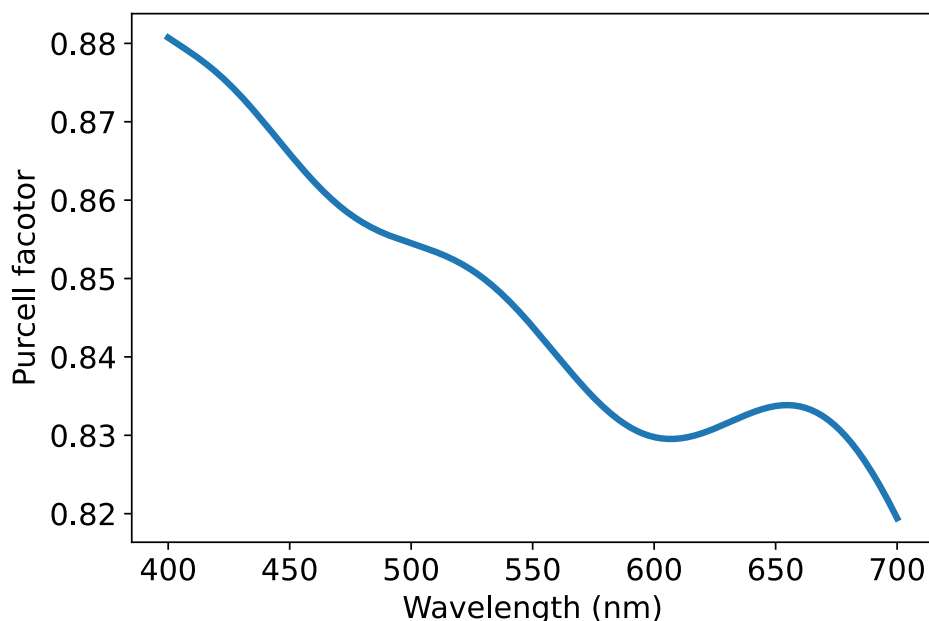


Figure C.7: Purcell factor as a function of wavelength where an in-plane dipole is situated at the middle of hBN placed on top of a SiO₂ substrate. The figure is adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

C.3 Convergence Test of Photoluminescence Spectrum

Fig. C.8 presents the convergence test of PL spectra across four different supercell sizes. The results indicate that a supercell size of $5 \times 5 \times 1$ is likely too small for all defects, as evidenced by significantly distinct PSB and ZPL compared to other sizes. A supercell size of $7 \times 7 \times 1$ offers a good balance, providing consistent spectra with larger sizes while not requiring excessively expensive computational resources. It is important to note that we did not test the C₂C_N defect, as it has been demonstrated by Ref. [175] that $7 \times 7 \times 1$ is a sufficient size.

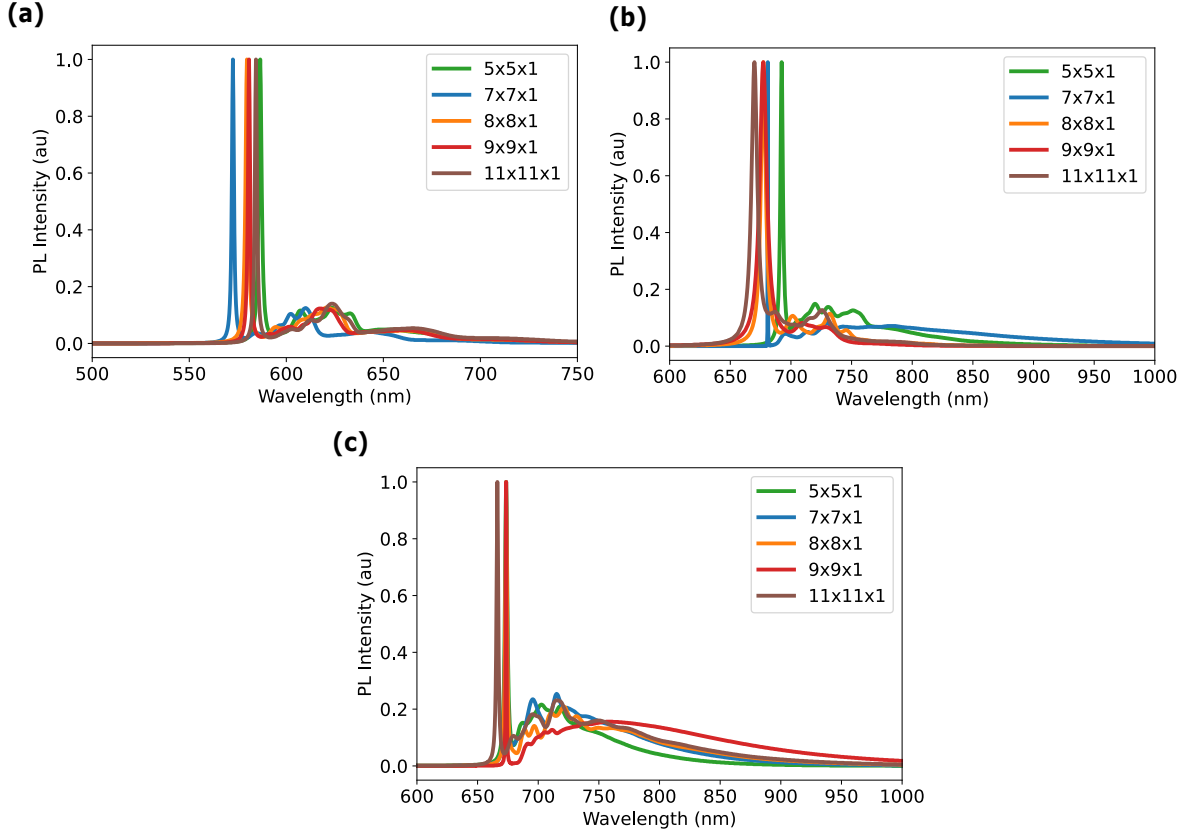


Figure C.8: Convergence test of photoluminescence spectra by varying supercell sizes where (a) is for C_2C_2 , (b) is for Al_N , and (c) is for P_NV_B . This figure is adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

C.4 Stability Investigation of Al_N and P_NV_B Defects

Here, we evaluate the charge states from -2 to $+2$ of Al_N and P_NV_B and consider the one with the lowest defect formation energy to form a stable charge state defect (see Fig. C.9).

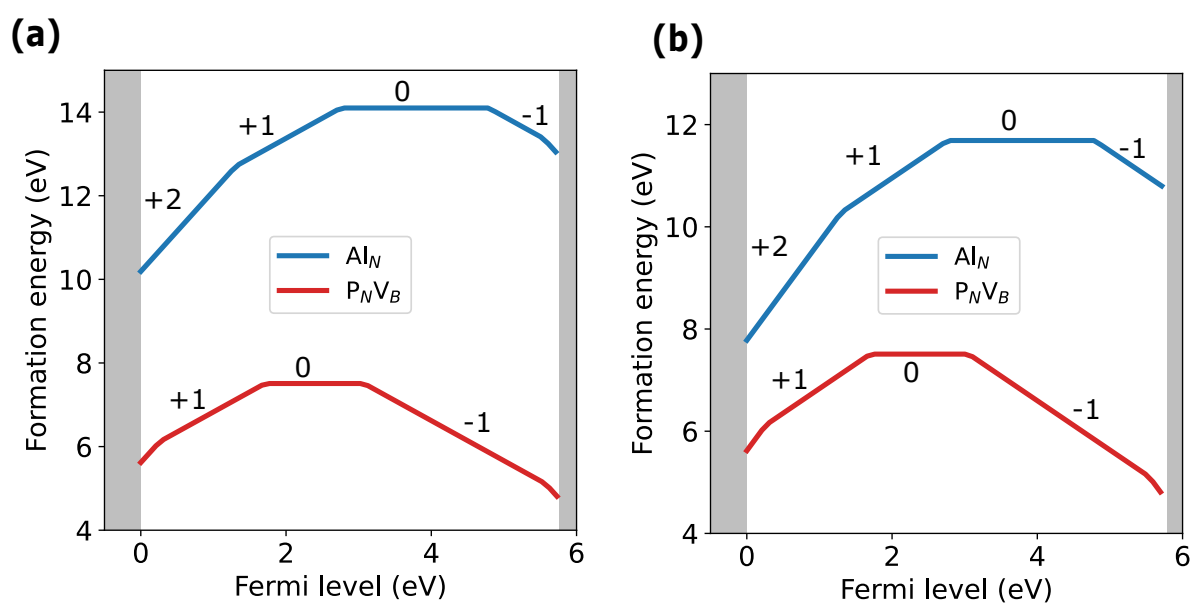


Figure C.9: Defect formation energy where (a) is under N-rich condition whereas (b) is under N-poor condition. This figure is adapted with permission from Ref. [136]. Copyright 2023 American Chemical Society.

Appendix D

Additional Electronic Transitions of Defects for Raman-based Quantum Memory

Supplementing Tab. 5.1 in Chapter 5, the electronic transitions of the selected defects were depicted in Figs. D.1, D.2, and D.3.

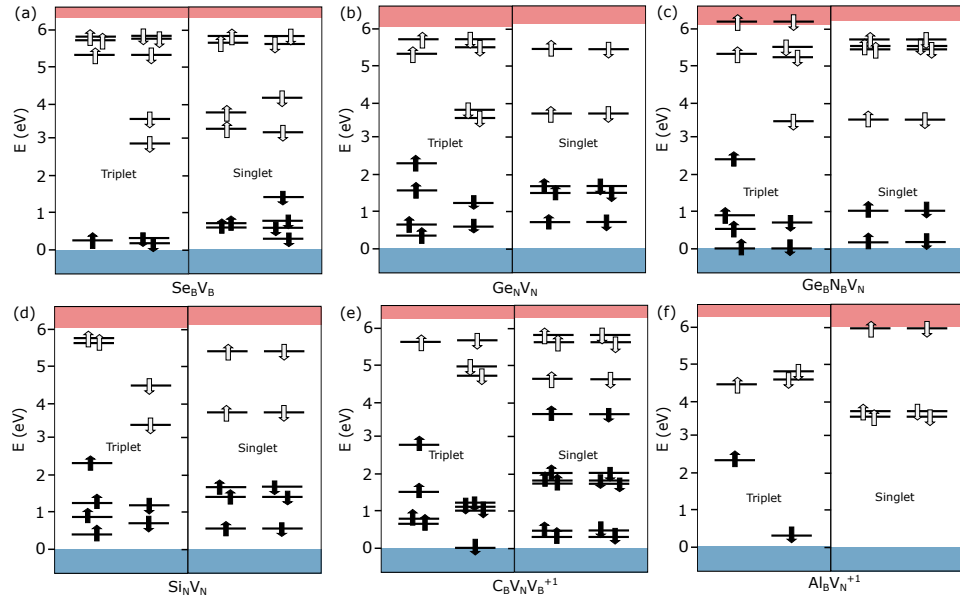


Figure D.1: Kohn-Sham electronic transitions, where filled and unfilled arrows represent occupied and unoccupied defect states, respectively, and up and down arrows denote spin-up and spin-down polarizations. (a) $O_B V_B$, (b) $Ge_N V_N$, (c) $Ge_B N_B V_N$, (d) $Si_N V_N$, (e) $C_B V_N V_B^{+1}$, and (f) $Al_B V_N^{+1}$. The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

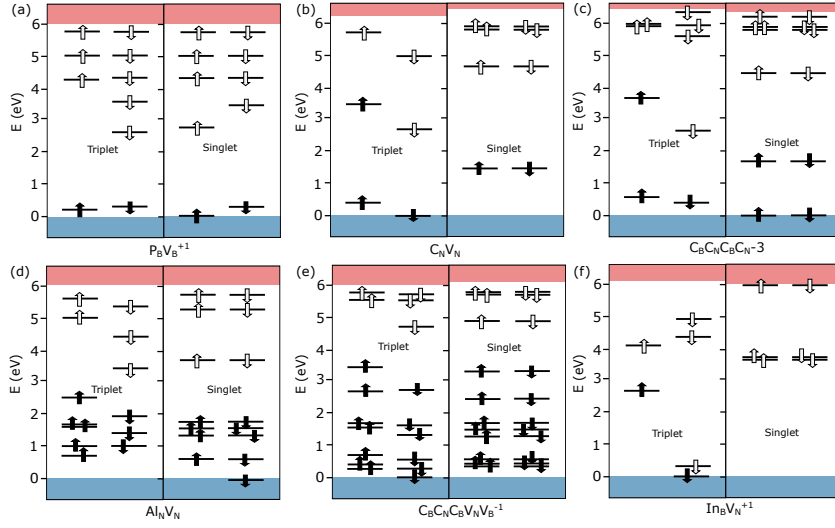


Figure D.2: Kohn-Sham electronic transitions, where filled and unfilled arrows represent occupied and unoccupied defect states, respectively, and up and down arrows denote spin-up and spin-down polarizations, respectively. (a) $P_B V_B^{+1}$, (b) $C_N V_N$, (c) $C_B C_N C_B C_N^{-3}$, (d) $Al_N V_N$, (e) $C_B C_N C_B V_N V_B^{-1}$, and (f) $In_B V_N^{+1}$. The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

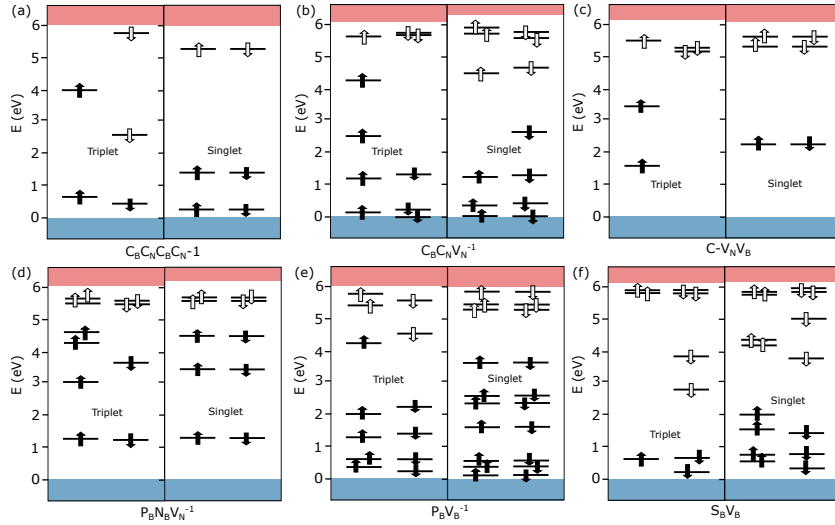


Figure D.3: Kohn-Sham electronic transitions, where filled and unfilled arrows represent occupied and unoccupied defect states, respectively, and up and down arrows denote spin-up and spin-down polarizations, respectively. (a) $C_B C_N C_B C_N^{-1}$, (b) $C_B C_N V_N^{-1}$, (c) $C-V_N V_B$, (d) $P_B N_B V_N^{-1}$, (e) $P_B V_B^{-1}$, and (f) $S_B V_B$. The figure is adapted from Ref. [217] available under a [CC-BY 4.0 license](#). Copyright 2024 Cholsuk *et al.*

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