

THE UNIVERSITY OF CHICAGO

ENGINEERING DIPOLAR INTERACTIONS IN WIDE BANDGAP
SEMICONDUCTORS USING DONOR-ACCEPTOR PAIRS

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To my grandparents

Crystals are like people, it is the defects in them which tend to make them interesting.

- Prof. Colin Humphreys.

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ABSTRACT

The control of dipolar interactions between quantum emitters in solid-state hosts is a central challenge for the development of scalable quantum information platforms and quantum-enabled devices. While atomic systems - such as trapped ions and Rydberg atoms - have long demonstrated tunable, long-range dipole coupling suitable for quantum logic, extending these concepts into the solid state requires identifying defect systems that combine strong intrinsic dipole moments with robust optical addressability and compatibility with nanophotonic architectures.

This thesis presents a series of first-principles investigations of donor-acceptor pairs (DAPs) and surface-defect pairs (SDPs) in wide-bandgap semiconductors, primarily focusing on diamond and silicon carbide (SiC), as candidate hosts for achieving coherent dipole-based coupling in scalable solid-state environments. Through systematic density functional theory (DFT) calculations, including constrained excited state simulations, phonon coupling analysis, and electric field response modeling, the thesis establish both the opportunities and the limitations of various defect architectures for realizing optically controllable dipolar networks.

In the first part of this work, I explore DAPs in bulk diamond and 3C-SiC, focusing on their electronic structure, charge transition levels, zero-phonon line (ZPL) energies, and their resulting photoluminescence spectra. The calculations reveal that certain substitutional donor-acceptor pairs exhibit large electric dipole moments - exceeding those of conventional point defects by orders of magnitude - and support narrow optical transitions with high Debye-Waller factors. Importantly, I demonstrate that the strength of dipolar coupling between DAPs can be systematically tuned by addressing donor-acceptor pairs with varying interatomic separation. These results establish a route toward engineering arrays of DAPs with interaction strengths suitable for implementing non-photonic two-qubit gates.

However, this initial study also highlights key limitations: in the bulk, the orientation

of DAP dipoles is random due to the lack of controlled positioning, and the dipoles are "on" in the ground state, and "off" in the excited state, which is opposite to conventional trapped atom Rydberg systems and complicates their control. Motivated by these challenges, the second part of this thesis extends the DAP framework to surfaces. Using *ab initio* calculations, I investigate the properties of DAPs and SDPs near hydrogen-terminated and hydroxyl-terminated SiC surfaces. I show that surface terminations can be exploited to engineer the electrostatic environment of near-surface defects, stabilizing configurations with highly aligned dipole moments. Unlike in the bulk, SDPs exhibit well-defined dipole orientations perpendicular to the surface plane, enabling deterministic control over coupling strengths and allowing for integration into planar photonic structures. I further compute polarization-resolved stimulated emission and photoionization cross sections for these systems, demonstrating that optical transitions can be selectively enhanced or suppressed via the polarization of incident light.

The final part of this thesis focuses on the field-induced response of the negatively charged germanium-vacancy (GeV) center, which belongs to the emerging class of Group IV-vacancy centers in diamond. This is a collaborative effort where I develop a second-order Stark shift model of the GeV's ZPL based on constrained DFT calculations, extracting the full polarizability tensor and constructing polar maps of spectral sensitivity to nearby fluctuating charges. This work resolves long-standing experimental observations of unexplained spectral jumps in GeV emission lines, demonstrating that the observed behavior can be fully accounted for by second-order Stark shifts induced by local charge fluctuations in the defect's environment. These insights also provide a predictive framework for mitigating spectral instability in GeV-based quantum devices.

Taking all these results together, this thesis advances the fundamental understanding of dipolar defect physics in wide-bandgap semiconductors and provides a roadmap for engineering optically controllable, dipole-coupled defect systems. The results demonstrate that

while bulk DAPs provide a rich playground for exploring dipolar interactions, their practical deployment will likely require surface-based architectures or hybrid schemes to overcome limitations of orientation randomness and dipole inversion. The surface-defect pairs developed here offer a concrete path towards integrating defect-based qubits into scalable, tunable quantum photonic platforms by building two-dimensional arrays of such systems and interfacing them with other nanophotonic control devices.

CHAPTER 1

INTRODUCTION

Wide-bandgap semiconductors have emerged as promising hosts for solid-state quantum systems thanks to their ability to accommodate point defects with optically addressable transitions and long-lived spin states [14, 15]. Unlike conventional semiconductors such as silicon or gallium arsenide, which often present limitations such as smaller bandgaps and more densely packed defect levels [16–18], wide-bandgap semiconductors offer large bandgaps (typically > 2.5 eV), enabling isolated defect states to remain well separated from conduction and valence bands. This energy separation may help with suppressing unwanted ionization and non-radiative recombination, allowing for stable charge states and sharp zero-phonon lines even at room temperature [19]. Materials like gallium nitride (GaN) [20–22], aluminum nitride (AlN) [23, 24], zinc oxide (ZnO) [25–27], and hexagonal boron nitride (hBN) [28–30] have been explored as point defect hosts. However, these systems still face challenges such as limited defect controllability, and, in some cases, poor photon emission rates [31]. In contrast, diamond and silicon carbide (SiC) have emerged as frontrunners due to their excellent crystal quality, mature fabrication methods, and crucially, their ability to host defects—such as nitrogen-vacancy (NV) centers in diamond and divacancies or transition-metal dopants in SiC—that exhibit both optically addressable transitions and spin coherence times extending into the millisecond regime under favorable conditions [32–34]. Spin coherence times (T_2) on the order of hundreds of microseconds to a few milliseconds have been routinely achieved at cryogenic temperatures using Hahn echo and dynamical decoupling sequences [32–34].

Yet, despite their strengths in single-qubit performance in these systems, robust mechanisms for establishing deterministic, coherent interactions between distant qubits are still lacking [35, 36]. Spin-spin interactions decay rapidly with distance, and becoming negligible beyond a few nanometers [15, 31, 35, 36]. This makes it difficult to implement two-qubit gates or correlated measurements between defects not placed with near-atomic precision. A num-

ber of strategies have been proposed to circumvent this limitation. For instance, embedding color centers in photonic waveguides or optomechanical cantilevers can, in principle, mediate indirect coupling through strain fields, guided photons, or localized vibrational modes [37,38]. Some efforts have focused on tuning local strain or electric fields to align optical transitions across multiple emitters, allowing for indistinguishable photon emission that enables probabilistic entanglement [39,40]. Others have proposed the use of magnons or acoustic phonons as carriers of quantum information between distant qubits, where defects are coupled to a shared vibrational or spin-wave mode of a nanomechanical resonator or magnetic substrate [41–43]. These methods offer exciting possibilities but face key challenges: photonic waveguides require precise spectral matching and high-quality nanofabrication; strain tuning requires individual tuning for each spin qubit and could be difficult to scale; phonon and magnon coupling mechanisms often suffer from thermal noise and limited coherence; and critically, many of these techniques require heralding or post-selection to confirm successful entanglement generation [37–43]. While these hybrid strategies extend the toolkit available for defect coupling, they do not yet offer a fully deterministic, scalable solution that integrates seamlessly with existing materials platforms.

On the other hand, a parallel line of research has pursued long-distance quantum communication using optical links between spatially separated qubits. In systems such as NV centers in diamond or rare-earth ions in crystals, entanglement swapping is performed using photons emitted by each qubit and sent through optical fibers to interfere on a beam splitter [44,45]. If the photons are indistinguishable in energy, polarization, and temporal profile, a successful interference event—usually detected via a coincident photon detection—projects the distant qubits into an entangled state [46]. This process allows for qubits located meters or kilometers apart to become entangled, and forms the basis of most quantum repeater protocols [46]. However, such schemes rely on successful photon emission, low-loss transmission, and high-efficiency detection, each of which occurs with finite probability. Consequently, suc-

cess rates are typically low (10^{-4} to 10^{-2} per attempt), requiring many repeated trials, active stabilization, and long idle times between successful events [45, 46]. Moreover, many systems used with these protocols lack a built-in mechanism for deterministic two-qubit gates, since the entanglement resource is itself non-deterministic and must be heralded externally [47]. To improve performance, a number of hybrid systems have been proposed, where solid-state emitters are coupled to optical cavities, dielectric antennas, or photonic crystal waveguides. These structures enhance photon collection and emission rates through the Purcell effect or guided mode coupling [48, 49], and in some cases allow for faster, more directional photon emission. For example, quantum dots in photonic nanostructures have demonstrated on-demand photon emission with high indistinguishability [50], and trapped ions or neutral atoms in fiber-coupled cavities have enabled deterministic entangling gates via shared photons [51, 52]. Still, these hybrid platforms face considerable challenges: deterministic positioning of emitters relative to cavities, control over spectral diffusion, integration into scalable architectures, and loss in routing photons between nodes [19, 48]. While hybrid platforms represent an important step forward, they have not yet achieved the necessary combination of deterministic interaction, long coherence, and scalable device integration in a single solid-state platform.

Beyond point defects in diamond and SiC, several alternative approaches have been explored to bridge the gap between localized spin control and long-range, coherent interaction. Molecular dipolar systems, for instance, offer chemically tunable arrangements with fixed donor-acceptor distances and orientations, enabling precise control over dipole-mediated spin interactions [53, 54]. However, these systems are difficult to integrate into scalable devices due to their molecular nature and remain sensitive to vibrational and environmental noise. Meanwhile, solid-state realization of Rydberg physics—particularly Rydberg excitons in materials such as cuprous oxide—have been shown to exhibit strong dipole-dipole interactions due to their large spatial extent and high polarizability [55]. Yet, the production of

high-purity crystals that support these excitonic states remains technically challenging, and exceptionally high intrinsic exciton binding energies and low dielectric screening are required. Collectively, Rydberg platforms highlight promising directions but fall short of delivering a unifying solution that is simultaneously deterministic, scalable, and robust to decoherence.

In light of these limitations, an emerging direction in the search for scalable quantum architectures involves exploiting electric dipole-dipole interactions between optically active defects in the solid state. Inspired by the success of Rydberg-atom platforms, where strong, tunable interactions arise from large electric dipole moments between excited atomic states [52, 56, 57], there is growing interest in identifying analogous mechanisms in semiconductors. In principle, two defects with substantial, reconfigurable dipole moments could interact via a $1/R^3$ dipole-dipole coupling, where R is the spatial separation of the defects. If such dipolar systems can be engineered in solid-state hosts, they could mediate fast, coherent, tunable interactions over distances of ~ 100 nanometers—large enough to be compatible with photonic nanostructures, yet short enough to avoid unwanted cross-talk in a densely packed array of defects [48, 52]. The key challenge is to find defect platforms that combine large dipole moments, optical addressability, and stability under realistic device conditions.

One class of systems proposed to meet these criteria are donor-acceptor pairs (DAPs): pairs of oppositely charged impurities in a semiconductor, typically a donor and an acceptor, that form a bound electron-hole pair. These systems have long been studied in the context of impurity-related photoluminescence, with sharp emission lines attributed to recombination of an electron localized on the donor with a hole on the acceptor [58–62]. More recently, DAPs have been revisited as candidates for quantum applications [63–65], marking a stark departure from their applications in earlier decades [58–62]. First-principles calculations carried out in this thesis suggest that certain DAP configurations exhibit electric dipole moments large enough to yield coupling strengths in the ~ 100 MHz range over hundred nanometer scale separations [3]. Crucially, these dipoles may be optically switchable—that

is, they exist primarily in the electronic ground state and vanish upon excitation—opening the possibility of using light to turn dipolar interactions on and off. If realizable, this inversion of the conventional Rydberg paradigm could enable conditional quantum gates and state-selective entanglement protocols.

Despite this promise, several open questions remain. In bulk crystals, DAP dipoles are generally randomly oriented, leading to disordered and anisotropic interactions that are difficult to harness in a coherent and scalable way [3]. Moreover, the lifetime, photostability, and spectral stability of the excited states responsible for the dipole moment are not yet well characterized. It is unclear whether the dipolar states can be maintained for timescales compatible with quantum gate operations, or whether their emission lines are narrow and stable enough for high-fidelity optical control. Environmental effects such as strain, electric fields, or proximity to surfaces may further degrade the properties of these systems, introducing additional challenges for practical implementation.

To mitigate some of these issues, in a recent work we have proposed a new class of systems known as surface-defect pairs (SDPs). These configurations might have already been experimentally observed in hydrogen-terminated nanodiamonds [66]. While in DAPs the electron is bound to the donor and the hole to the acceptor, in SDPs, the hole is a surface state just above the valence band and the excited electron is localized on the defect. The resulting charge separation forms a dipole that is naturally aligned perpendicular to the surface, due to the geometric constraints imposed by the interface. This built-in alignment could overcome the orientation randomness problem in bulk DAPs, enabling more predictable and even stronger dipole-dipole interactions. In addition, surface-localized states are more accessible to nanofabricated photonic structures, offering opportunities for integration with waveguides, cavities, and electrodes [67].

However, SDPs remain a speculative proposal, supported primarily by computational predictions. Surface states are notoriously sensitive to reconstruction, surface termination and

chemistry, and environmental exposure, raising questions about the reproducibility and stability of SDP-based architectures. Furthermore, the coherence properties of surface-localized dipolar excitations are largely unknown, and it is not clear whether the presumed advantages of alignment and integration outweigh the risks of increased decoherence.

This thesis aims to critically evaluate the potential of both DAPs and SDPs in wide-bandgap semiconductors—particularly silicon carbide—as platforms for optically tunable, long-range dipolar coupling. Using first-principles simulations, we investigate their dipole moments, optical spectra, charge-state stability, and environmental sensitivity. We assess the robustness of these systems under realistic conditions, and aim to clarify whether DAP- and SDP-based architectures offer a viable pathway toward solid-state quantum technologies.

1.1 A Highly Dipolar System: Donor-Acceptor Pairs

The study of donor-acceptor pairs (DAPs) in semiconductors represents one of the earliest systematic inquiries into the microscopic behavior of charged impurities in crystalline solids. Initially investigated during the 1960s and 1970s, DAPs were central to understanding the electrical, thermal and optical properties of semiconductors under extrinsic doping [59, 62]. At the time, the primary motivation of studying DAPs was to elucidate the roles of shallow donors and acceptors in determining the conductivity, luminescence and carrier dynamics of emerging materials - such as silicon (Si) [60, 61], gallium phosphide (GaP) [58], and gallium nitride (GaN) [68] - in an effort to engineer more efficient electronic and optoelectronic devices.

In early landmark studies - such as those by Thomas, Gershenzon and Trumbore, in gallium phosphide [58] - DAPs were identified via sharp line emissions in photoluminescence (PL) experiments conducted at cryogenic temperatures. These sharp spectral features were found to originate from the radiative recombination of an electron bound to a donor with a hole bound to an acceptor, forming a neutral exciton-like object whose energy is determined

by the distance between the donor and the acceptor due to the Coulomb interaction between the two defects. The reproducibility and spectral richness of these emissions provided a new spectroscopic fingerprint for identifying dopants and their spatial configurations within the host lattice.

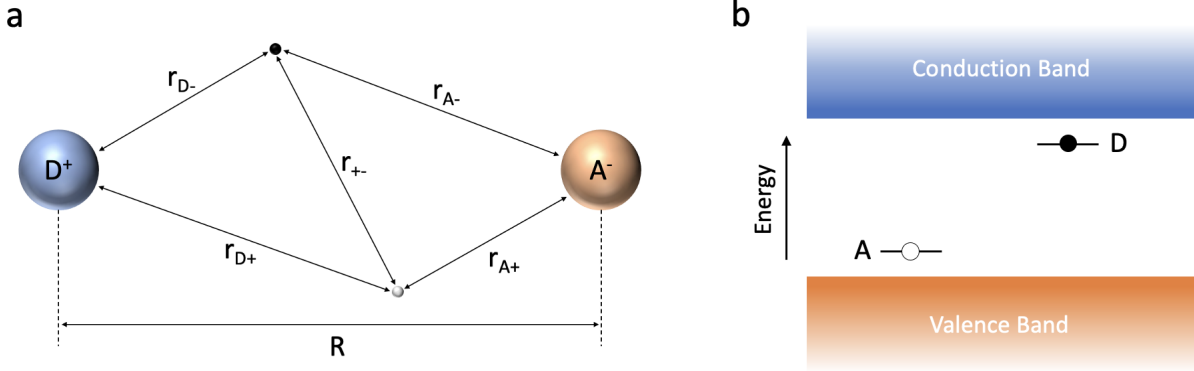


Figure 1.1: (a) Interparticle distances of a donor-acceptor pair (DAP), including a bound electron and hole. The interatomic distance R is fixed, and the distances between all other particles are labeled with subscripts. (b) Energy level diagram of a DAP in the excited state, with a bound hole and a bound electron at the acceptor and donor sites respectively.

1.1.1 Energy-level Derivation and Effective Mass Model

Microscopically, a donor-acceptor pair consists of two point defects in a host lattice: a donor D , typically donating an electron to the conduction band (or capturing a hole), and an acceptor A , capturing an electron (or donating a hole to the valence band). When both are present, an electron bound to the donor may recombine with a hole bound to the acceptor, resulting in photon emission. Crucially, this process occurs without the need for delocalized band states, meaning it can proceed even in insulating or highly compensated samples. The interparticle distances of a donor-acceptor pair, including a bound electron and hole, are together shown in Figure 1.1. The interatomic distance between the donor D and the

acceptor A is R . The coordinates of the electron and hole with respect to each other and with respect to the nuclei are shown by r with pairs of the subscripts $-$, $+$, D and A . The interatomic distance R is taken as fixed, and the coordinates of the electron and hole are described by a two-particle wavefunction $\Psi(+, -)$. The system can be described as an exciton bound in the field of a finite dipole. The qualitative energy level structure of an associated donor-acceptor pair is illustrated in Figure 1.1

The emission energy of a donor-acceptor pair as illustrated in Figure 1.1 can be derived by considering the total energies of the entire system in the ground and excited states respectively. The Hamiltonian operator for the donor-acceptor pair system is:

$$\hat{H} = -\frac{\hbar^2}{2} \left(\frac{\nabla_e^2}{m_e^*} + \frac{\nabla_h^2}{m_h^*} \right) + \frac{e^2}{4\pi\epsilon_r\epsilon_0} \left(-\frac{1}{r_{A+}} - \frac{1}{r_{D-}} + \frac{1}{r_{A-}} + \frac{1}{r_{D+}} - \frac{1}{r_{+-}} - \frac{1}{R} \right) \quad (1.1)$$

where m_e^* and m_h^* are the effective masses of the electron and the hole, respectively. We write the two-particle wavefunction as a single product function of the separated donor D and acceptor A one-particle wavefunctions:

$$\Psi(+, -) = \psi_D(-)\psi_A(+) \quad (1.2)$$

where $+$ and $-$ indicate the hole and electron respectively. Note that the permuted product $\psi_D(+)\psi_A(+)$ is not part of the bound exciton state, as electrons and holes are distinguishable particles, and this product refers to a configuration of a different energy. The total energy of the donor-acceptor pair is:

$$E = \frac{\iint \Psi^*(+, -) \hat{H} \Psi(+, -) dv_+ dv_-}{\iint \Psi^*(+, -) \Psi(+, -) dv_+ dv_-} \quad (1.3)$$

Upon substituting Equation 1.1 and Equation 1.2 into Equation 1.3 and normalizing $\psi_D(-)$ and $\psi_A(+)$, we obtain:

$$E = \iint \psi_D^*(-) \psi_A^*(+) \left[-\frac{\hbar^2}{2} \left(\frac{\nabla_e^2}{m_e^*} + \frac{\nabla_h^2}{m_h^*} \right) + \frac{e^2}{4\pi\epsilon_r\epsilon_0} \left(-\frac{1}{r_{A+}} - \frac{1}{r_{D-}} + \frac{1}{r_{A-}} + \frac{1}{r_{D+}} - \frac{1}{r_{+-}} - \frac{1}{R} \right) \right] \psi_D(-) \psi_A(+) dv_+ dv_- \quad (1.4)$$

The kinetic energy terms together with the first two potential energy terms can be identified as the energies of the separated donor and acceptor, E_D and E_A respectively. Then the total energy E becomes:

$$E = E_D + E_A + \frac{e^2}{4\pi\epsilon_r\epsilon_0} \iint \psi_D^*(-) \psi_A^*(+) \left[\frac{1}{r_{A-}} + \frac{1}{r_{D+}} - \frac{1}{r_{+-}} - \frac{1}{R} \right] \psi_D(-) \psi_A(+) dv_+ dv_-$$

$$E = E_D + E_A + J(R) \quad (1.5)$$

where the remaining four Coulomb integrals define the term $J(R)$, a correction energy that is significant when the distance R is comparable to the Bohr radii of the electron and hole wavefunctions and then vanishes when R increases.

Within the effective mass approximation, the one-particle 1s-type wavefunctions and the energies for an electron bound to a donor and an acceptor bound to a hole can be written as:

$$\psi_{e(h)}(r) = \frac{1}{\sqrt{\pi a_{e(h)}^3}} e^{-r/a_{e(h)}}, \quad E_{D(A)} = -\frac{\hbar^2}{2m_{e(h)}^* a_{e(h)}^2}, \quad \text{where} \quad a_{e(h)} = \frac{4\pi\epsilon_r\epsilon_0\hbar^2}{m_{e(h)}^* e^2} \quad (1.6)$$

The total energy E_I to ionize both the electron and the hole to their respective conduction bands becomes:

$$E_I = E_D + E_A + J(R) + \frac{e^2}{4\pi\epsilon_r\epsilon_0 R} \quad (1.7)$$

where the last term describes the interaction of the D - A pair in its electronic ground state.

Keeping in mind that binding energies are referenced with respect to their respective band edges, the photon emission energy that results from radiative recombination of the hole and the electron is:

$$\hbar\omega = E_g + E_I = E_g + E_D + E_A + J(R) + \frac{e^2}{4\pi\epsilon_r\epsilon_0 R} \quad (1.8)$$

where the binding energies E_D and E_A are negative by convention, as can be seen from Equation 1.6. However, it is also common practice to define the binding energies as positive and write the energy of emission as:

$$\hbar\omega_m = E_g - (E_D + E_A) + J(R) + \frac{e^2}{4\pi\epsilon_r\epsilon_0 R_m} \quad (1.9)$$

Equation 1.9 describes the emission energy of electron-hole recombination from donor-acceptor pairs. Because the lattice is periodic, donors and acceptors can only occupy certain allowed separations — not a continuous range — and these separations are grouped into shells based on the number of lattice steps (nearest neighbor distances) between them. The first shell corresponds to the nearest-neighbor donor-acceptor pairs, the second shell to the next-nearest neighbors, and so on. Each shell number thus determines a characteristic donor-acceptor distance R_m , which in turn sets the Coulomb interaction strength and leads to a series of distinct emission lines in DAP photoluminescence spectra, with higher shell numbers corresponding to larger separations and lower Coulomb shifts. Some examples of typical DAP spectra are shown in Figure 1.2, where shells from $m = 3$ to $m = 26$ are labeled. Both Type I (P-Al) and Type II (N-Ga and N-Al) DAP spectra in 3C-SiC are shown, and multipole splittings for smaller shell numbers $m \sim 4 - 8$ are marked in red.

1.1.2 Shell Structure and Lattice Geometry (Type I / Type II)

Donors and acceptors in the crystal may in principle occupy substitutional or interstitial sites. In compound semiconductors two types of spectra resulting from substitutional defects are possible: Type I when both the impurities are on the same sublattice, and Type II when the two impurities are on different sublattices (*e.g.* Si-C in 3C-SiC). Atoms on interstitial sites (of which there are two kinds) may give rise to Type I or II arrangements, in addition to a Type

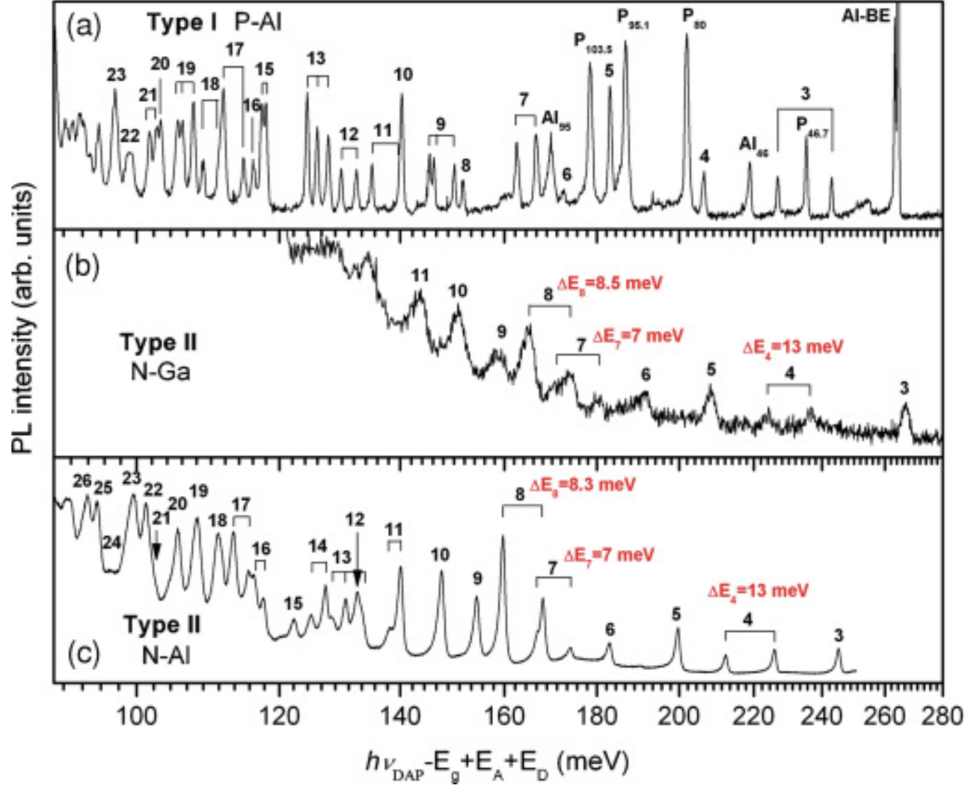


Figure 1.2: Low-temperature photoluminescence spectra of Type I (P-Al) and Type II (N-Al, N-Ga) spectra in 3C-SiC. The shell numbers m are also given for each shell. As examples, the multipole splitting energies for $m = 4, 7, 8$ are given by $\Delta E_4 = 13$, $\Delta E_7 = 7$, $\Delta E_8 = 8.3$ meV for both N-Al and N-Ga spectra, respectively. Figure and caption reproduced from [1].

III array with one impurity at an interstitial site and one at a particular substitutional site. In this thesis, we restrict ourselves to Type I and II spectra resulting from substitutional impurities; however, treatments similar to those presented here for Type I and Type II spectra are also possible for interstitial defects involving Type III spectra. For a given host material, we can write the distance-type relationship:

$$R_{\text{Type I}}^2 = a^2 h^2 + b^2 k^2 + c^2 l^2 + 2abhk \cos \gamma + 2achl \cos \beta + 2bckl \cos \alpha \quad (1.10)$$

$$R_{\text{Type II}}^2 = a^2 (h + \delta_h)^2 + b^2 (k + \delta_k)^2 + c^2 (l + \delta_l)^2 + 2ab(h + \delta_h)(k + \delta_k) \cos \gamma \\ + 2ac(h + \delta_h)(l + \delta_l) \cos \beta + 2bc(k + \delta_k)(l + \delta_l) \cos \alpha \quad (1.11)$$

where a, b, c are the lattice constants, (h, k, l) is the displacement vector between the donor and the acceptor in units of the lattice constants, α, β, γ are the angles between the lattice axes, and $(\delta_h, \delta_k, \delta_l)$ are the fractional shifts due to the basis between the donor and acceptor sublattices (*e.g.* for the zinc-blende structure, $\delta_h = \delta_k = \delta_l = 1/4$). For a cubic lattice where $a = b = c$ and $\alpha = \beta = \gamma = 90$, these expressions simplify to:

$$R_{\text{Type I}} = a_0 \sqrt{h^2 + k^2 + l^2} \quad (1.12)$$

$$R_{\text{Type II}} = a_0 \sqrt{(h + \delta_h)^2 + (k + \delta_k)^2 + (l + \delta_l)^2} \quad (1.13)$$

As mentioned briefly at the end of Section 1.1.1, each distinct crystallographic separation between donor and acceptor defines a discrete shell labeled by an index m , corresponding to a unique $D - A$ pair distance R_m . For a given lattice structure, the shell number increases with increasing distance, not necessarily linearly. In simple cubic or zinc-blende crystals, the shell number is loosely proportional to the squared displacement, and can be expressed as:

$$R_m \sim a_0 \sqrt{c_m}, \quad \text{where } c_m = (h + \delta_h)^2 + (k + \delta_k)^2 + (l + \delta_l)^2 \quad (1.14)$$

with $m \sim c_m$. The smallest Type I case is with $(h, k, l) = (\frac{1}{2}, \frac{1}{2}, 0)$ and its permutations, which gives $R_1^{\text{Type I}} = a_0 \frac{\sqrt{2}}{2}$. In the Type II case, the shortest distance corresponds to the nearest neighbor pairs with $(h, k, l) = (0, 0, 0)$ and $(\delta_h, \delta_k, \delta_l) = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The smallest shell is therefore given by $R_1^{\text{Type II}} = a_0 \frac{\sqrt{3}}{4}$. In order to clarify which shell numbers correspond to what kinds of distances, we provide in Table 1.1 the distances that correspond to the first ten shell numbers in both diamond and 3C-SiC.

1.1.3 Electric Dipole Moments And Optical Switching

Donor-acceptor pairs (DAPs) naturally possess electric dipole moments due to the spatial separation between the positively charged donor ion and the negatively charged acceptor ion

Table 1.1: The inter-defect distances (in Å) that correspond to the first 10 shell numbers in diamond and 3C-SiC.

Shell #	Distance (Å)	
	Diamond	3C-SiC
m1	1.55	1.90
m2	2.52	3.10
m3	2.96	3.63
m4	3.57	4.38
m5	3.89	4.77
m6	4.37	5.37
m7	4.64	5.69
m8	5.05	6.20
m9	5.28	6.48
m10	5.64	6.93

in the ground state. These dipole moments originate from the static charge configuration that arises when the donor atom donates an electron to the acceptor. The donor becomes a positively charged ion (D^+), and the acceptor becomes negatively charged (A^-), forming a fixed ionic dipole. Here we explore the physical origin, magnitude, orientation, and tunability of these dipoles, and how their behavior changes under optical excitation. The electric dipole moment $\vec{\mu}$ of a DAP in its ground state is given by:

$$\vec{\mu}_{\text{ground}} = e \cdot \vec{R}_{AD} \quad (1.15)$$

where e is the elementary charge and $\vec{R}_{AD}$ is the displacement vector from the acceptor site to the donor site.

Since $|\vec{\mu}| \propto |\vec{R}_{AD}|$, even modest separations on the order of 1 nm result in dipole moments in the range of 50 Debye, and larger separations can yield dipoles exceeding 200 Debye. This large, fixed dipole is aligned along the acceptor-to-donor vector, and its direction depends

on the crystallographic orientation and sublattice occupancy of the donor and the acceptor.

When a DAP absorbs a photon and transitions to an electronic excited state, the electron that was initially donated from the donor to the acceptor is promoted back from the acceptor to the donor site. This results in a configuration where both the donor and the acceptor are electrically neutral ($D^0 - A^0$), eliminating the static charge separation:

$$\vec{\mu}_{\text{excited}} = 0 \quad (1.16)$$

This process amounts to an optical switching of the dipole moment, where the dipole is "turned off" via photoexcitation. When the system subsequently recombines radiatively, the system goes to the ionic $D^+ - A^-$ configuration of the ground state and the dipole is non-zero again.

This reversible switching process is analogous to a two-level optical dipole system, in which dipolar interactions can be modulated through optical control. Unlike Rydberg systems, where moments emerge only in the excited state, DAPs exhibit dipoles in the ground state, that are switched off when the DAP is optically excited. This inversion of the conventional Rydberg paradigm has consequences for the implementation of quantum gates and state-selective entanglement schemes.

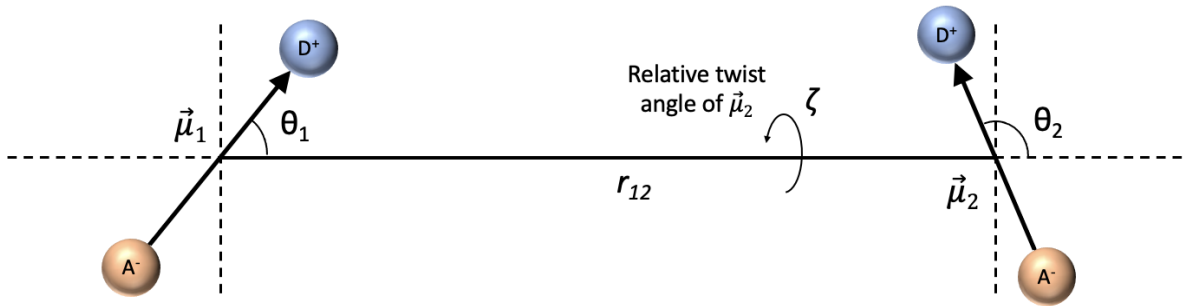


Figure 1.3: Coordinate diagram defining the dipolar interaction between two donor-acceptor pairs. θ_1 and θ_2 are the angles between each dipole moment and the vector $\vec{r}_{12}$ connecting the center points of the two dipoles. ζ is the relative twist angle of $\vec{\mu}_2$ with respect to $\vec{\mu}_1$.

The interaction between two DAPs is governed by the classical dipole-dipole potential, which depends not only on the magnitudes of the dipole moments but also on their orientations and relative positions. This interaction is given by:

$$U_{dd} = \frac{1}{4\pi\epsilon_r\epsilon_0} \frac{|\vec{\mu}_1||\vec{\mu}_2|}{r_{12}^3} f(\theta_1, \theta_2, \zeta) \quad (1.17)$$

where r_{12} is the center-to-center distance between the two dipoles, and the angular term $f(\theta_1, \theta_2, \zeta)$ captures the relative orientations:

$$f(\theta_1, \theta_2, \zeta) = -2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \zeta \quad (1.18)$$

Here, θ_1 and θ_2 are the angles between each dipole moment and the separation vector $\vec{r}_{12}$ between the dipoles, and ζ is the relative twist angle of $\vec{\mu}_2$ with respect to $\vec{\mu}_1$ as shown in Figure 1.3. This function is bound in range: $-2 \leq f(\theta_1, \theta_2, \zeta) \leq 2$, meaning the interaction energy can be either attractive or repulsive depending on the geometry.

Just like how the discrete nature of the atomic positions in the host crystal gives rise to Type I and Type II spectra coming from DAPs, the same principle also leads to discrete directions for DAPs' dipoles. Hence, only a finite set of angular configurations appears in practice, with significant implications for the spatial pattern and magnitude of the dipole-dipole interactions. Moreover, external fields can perturb these configurations. Under the influence of an applied electric field $\vec{E}$, the energy of a DAP experiences a Stark shift given by:

$$\Delta U = -\vec{\mu} \cdot \vec{E} = -|\vec{\mu}||\vec{E}| \cos \theta \quad (1.19)$$

where θ is the angle between the dipole moment and the applied field. As DAPs occupy quantized directions in the lattice, discrete set of Stark shifts depending on the orientation may arise. Thus, under a sufficiently strong electric field, PL spectra from a single shell can split into multiple peaks, each corresponding to a distinct dipole orientation. This effect

provides a spectroscopic means of resolving otherwise degenerate DAPs within the same shell.

Among other knobs that provide some optical addressability for DAPs is the wavelength-selective resonant excitation to target specific donor-acceptor separations, due to the relationship between separation and emission energy as outline by Equation 1.9. Additionally, polarization-resolved PL can also probe the angular dependence of absorption or emission, which is governed by optical transition dipole moment selection rules. Only those DAPs with optical transition dipole moments aligned with the optical field vector $\vec{E}_{\text{light}}$ contribute to absorption or emission, with the coupling strength scaling as $|\vec{\mu}_{\text{optical}} \cdot \vec{E}_{\text{light}}|^2$. Finally, external electric fields can be used to tune the energy levels of DAPs through the Stark effect, selectively enhancing or suppressing certain orientations. These mechanisms, used individually or in combination, offer fine-grained control over the population and emission of DAPs, enabling construction of optically tunable dipolar lattices and spatially addressable qubit architectures.

1.1.4 Radiative Lifetimes and Transition Dynamics

DAPs in semiconductors exhibit radiative recombination processes wherein the electron bound to the donor recombines with a hole bound to the acceptor, emitting a photon in the process. This transition is governed by several factors including the donor-acceptor separation, the overlap of their respective wavefunctions, and the energy of the emitted photon. Here, we examine the radiative lifetime of DAPs, its dependence on physical and electronic properties of the host material and defect species, and how it can be modulated or interpreted in the context of quantum information and device applications.

The radiative lifetime τ_r of a DAP is often evaluated using Fermi's Golden Rule, which provides spontaneous emission rate Γ_r as:

$$\Gamma_r = \frac{1}{\tau_r} = \frac{2\pi}{\hbar} |\langle f | \hat{H}_{\text{int}} | i \rangle|^2 \rho(\hbar\omega) \quad (1.20)$$

where $|i\rangle$ and $|f\rangle$ denote the initial (excited) and final (ground) electronic states of the donor-acceptor system respectively, and $\rho(\hbar\omega)$ is the density of photon states at the emission energy. The interaction Hamiltonian $\hat{H}_{\text{int}}$ describes the coupling between the electronic system and the perturbing electromagnetic field. For optical transitions, this interaction takes the form:

$$\hat{H}_{\text{int}} = -\hat{d} \cdot \vec{E} \quad (1.21)$$

where $\hat{d} = e\hat{r}$ is the electric dipole operator, $\hat{r}$ is the position operator acting on the electron's wavefunction, and $\vec{E}$ is the electric field of the radiation. It can be shown that expressions for τ_r obtained from Fermi's Golden Rule and Wigner-Weisskopf theory of luminescence are equivalent in the weak-coupling regime, and can be calculated as:

$$\tau_r = \frac{3\epsilon_0\hbar c^3}{2n_r\omega^3|\mu|^2}, \quad \text{where } \mu = \langle\psi_f|e\hat{r}|\psi_i\rangle \quad (1.22)$$

where μ is the optical transition dipole moment, n_r is the refractive index of the host material, and ω is the angular frequency of the optical transition.

Since the DAP transition involves spatially separated orbitals, the radiative rate depends exponentially on the donor-acceptor separation. In a simplified model, assuming Hydrogenic wavefunctions for the donor and acceptor, the radiative transition probability is proportional to the squared overlap integral between the two localized wavefunctions:

$$\Gamma_r(R) \propto |\langle\psi_A|\psi_D\rangle|^2 \propto e^{-2R/a^*} \quad (1.23)$$

where R is the donor-acceptor distance and a^* is the effective Bohr radius determined by the dielectric constant and effective masses:

$$a^* = \frac{4\pi\epsilon_r\epsilon_0\hbar^2}{\mu e^2} \quad (1.24)$$

Here μ is the reduced mass of the electron-hole system. This exponential scaling implies that recombination is sharply suppressed at large distances, leading to longer radiative lifetimes.

As a results, DAPs exhibit a distribution of lifetimes that maps onto their spatial separation, and thereby onto their emission energies.

However, in practice radiative recombination competes with non-radiative processes such as multi-phonon assisted emission or Auger recombination. The observed (effective) lifetime τ_{eff} is determined by both channels:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (1.25)$$

The non-radiative lifetime τ_{nr} is highly sensitive to temperature and local environment. At elevated temperatures, thermal ionization or phonon-assisted escape of carriers can significantly quench radiative recombination. The balance between τ_r and τ_{nr} determines the quantum efficiency of DAP emission and limits its usability in photonic devices.

The exponential dependence of the radiative lifetime on spatial separation makes DAPs particularly interesting for quantum optical architectures. For closely separated DAPs with $R < a^*$, lifetimes can be in the nanoseconds regime, enabling fast emission and acting as highly bright single photon sources. Conversely, widely spaced pairs yield long-lives states, potentially usable for storage or delayed emission applications. Additionally, DAPs offer the possibility of engineered decay dynamics by selecting specific shells or orientations via optical or electric control. This configurational control can be exploited in protocols where conditional emission, indistinguishability, or temporal gating are required.

Finally, a further consequence of spatial variability is the inhomogeneous broadening of lifetime distributions even within a single shell. Strain, local charge fluctuations, and surface effects all introduce variations in the local potential that affect wavefunction overlap. This leads to spectral diffusion and linewidth broadening, which, though undesirable for coherence, can be useful for probing environmental fluctuations.

CHAPTER 2

FIRST-PRINCIPLES CALCULATIONS

This chapter introduces the theoretical foundations for the computational methods used throughout this thesis. At the core of these methods lies density functional theory (DFT), a quantum mechanical framework that allows tractable calculations of the electronic structure of atoms, molecules, and solids. We begin by establishing the many-body Schrödinger equation, the fundamental equation governing all quantum systems composed of interacting electrons and nuclei. Since solving the full equation directly is computationally intractable for meaningfully large systems, we introduce the Born-Oppenheimer approximation, which separates electronic and nuclear motion. This reduction enables the use of DFT and other first-principles methods, which are presented later in the chapter along with key approximations, such as approximations to exchange-correlation functionals, and practical implementation strategies involving pseudopotentials and periodic boundary conditions.

2.1 From the Many-Body Problem to the Born-Oppenheimer Approximation

The accurate theoretical description of matter at the atomic scale begins with quantum mechanics. For a general system consisting of interacting electrons and atomic nuclei, the non-relativistic time-independent Schrödinger equation governs all observable properties:

$$\hat{H}\Psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) = E\Psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) \quad (2.1)$$

Here Ψ is the many-body wavefunction describing all N_e electrons and N_n nuclei, each at position $\vec{r}_i$ and $\vec{R}_I$ respectively. The system's Hamiltonian $\hat{H}$ consists of kinetic and potential energy operators:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en} \quad (2.2)$$

where the individual terms are defined as:

- Electronic kinetic energy:

$$\hat{T}_e = - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_{\vec{r}_i}^2 \quad (2.3)$$

- Nuclear kinetic energy:

$$\hat{T}_n = - \sum_{I=1}^{N_n} \frac{1}{2M_I} \nabla_{\vec{R}_I}^2 \quad (2.4)$$

- Electron-electron Coulomb interaction:

$$\hat{V}_{ee} = \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (2.5)$$

- Nucleus-nucleus repulsion:

$$\hat{V}_{nn} = \sum_{I < J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (2.6)$$

- Electron-nucleus attraction

$$\hat{V}_{en} = - \sum_{i=1}^{N_e} \sum_{I=1}^{N_n} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \quad (2.7)$$

where M_I represents the mass of the I -th nucleus and Z_I its charge. In principle, solving this equation yields complete knowledge of the system's structure and dynamics. However, even for modest system sizes - *e.g.* a water molecule with 10 electrons and 3 nuclei - exact diagonalization of the Hamiltonian would require working with a 39 dimensional (13 particles $\times$ 3 dimensions) wavefunction, and is computationally infeasible. Therefore, to make practical progress, one seeks physically justified approximations.

The central observation that underpins many quantum mechanical approximations in chemistry and materials science is the mass disparity between electrons and nuclei. The rest mass of a proton is approximately 1800 times greater than that of an electron. This means

that nuclei move significantly slower than electrons do. Consequently, in many physical systems, the electrons adjust almost instantaneously to changes in nuclear positions. This physical intuition leads to the Born-Oppenheimer (BO) approximation, which approximates the total wavefunction as follows:

$$\Psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) \approx \psi_{el}(\vec{r}_1, \dots, \vec{r}_{N_e}; \{\vec{R}_I\}) \cdot \chi(\vec{R}_1, \dots, \vec{R}_{N_n}) \quad (2.8)$$

where ψ_{el} is the electronic wavefunction for a set of fixed nuclear positions, and χ describes the quantum state of the nuclei evolving on a potential energy surface defined by the electronic energy.

Let us consider expanding the full wavefunction Ψ as a linear combination of electronic eigenstates ψ_n , each associated with a different potential energy surface:

$$\Psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) = \sum_n \chi_n(\vec{R}_1, \dots, \vec{R}_{N_n}) \psi_n(\vec{r}_1, \dots, \vec{r}_{N_e}; \{\vec{R}_I\}) \quad (2.9)$$

In this expression, the index n labels discrete electronic eigenstates, including the ground state ($n = 0$). Each $\psi_n(\{\vec{r}_i\}; \{\vec{R}_I\})$ is an eigenfunction of the electronic Hamiltonian for a fixed set of nuclear configurations $\{\vec{R}_I\}$ (Note that we are using $\{\}$ to indicate the set of all coordinates). These wavefunctions form a complete set of orthonormal states for the electronic problem at each $\{\vec{R}_I\}$:

$$\hat{H}_{el}(\{\vec{R}_I\}) \psi_n(\{\vec{r}_i\}; \{\vec{R}_I\}) = E_n(\{\vec{R}_I\}) \psi_n(\{\vec{r}_i\}; \{\vec{R}_I\}) \quad (2.10)$$

where $\hat{H}_{el} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en}$ is the electronic Hamiltonian, and $E_n(\{\vec{R}_I\})$ is the corresponding eigenvalue - *i.e.* the potential energy of state n for fixed nuclei. Finally, the coefficients $\chi_n(\{\vec{R}_I\})$ are nuclear wavefunctions, each associated with the nuclear motion of the n^{th} electronic energy surface. This expansion expresses the total wavefunction as a superposition of different electronic configurations, each weighted by a nuclear wavefunction that determines how the nuclei move on that surface. This is what is called the

Born-Oppenheimer expansion [69]. The nuclear wavefunctions $\chi(\{\vec{R}_I\})$ can be computed by solving the eigenvalue equation:

$$\left[\hat{T}_n + E_m(\{\vec{R}_I\})\right]\chi_m(\{\vec{R}_I\}) + \sum_{m \neq n} \hat{\Lambda}_{mn}(\{\vec{R}_I\})\chi_n(\{\vec{R}_I\}) = E\chi(\{\vec{R}_I\}) \quad (2.11)$$

where $E_m(\{\vec{R}_I\})$ is the potential energy surface corresponding to the m^{th} electronic state and the second term on the left-hand side involves the non-adiabatic coupling operator $\hat{\Lambda}_{mn}(\{\vec{R}_I\})$, which captures the interaction between different electronic states as the nuclei move.

The full set of equations derived above is exact, but still quite difficult to solve due to the off-diagonal terms $\hat{\Lambda}_{mn}(\{\vec{R}_I\})$. The Born-Oppenheimer approximation consists of neglecting all non-adiabatic couplings:

$$\hat{\Lambda}_{mn}(\{\vec{R}_I\}) \approx 0 \quad \text{for } m \neq n \quad (2.12)$$

Under this assumption, the equation for each χ_m decouples:

$$\left[\hat{T}_n + E_m(\{\vec{R}_I\})\right]\chi_m(\{\vec{R}_I\}) = E\chi_m(\{\vec{R}_I\}) \quad (2.13)$$

This says that the nuclear wavefunction $\chi_m(\{\vec{R}_I\})$ evolves under the influence of a potential energy surface $E_m(\{\vec{R}_I\})$, which comes from solving the electronic problem at a fixed nuclear geometry. Each nuclear wavefunction evolves independently, and the system stays on a single electronic state as the nuclei move. In practice, nearly all ground-state calculations assume $m = 0$, the lowest energy surface, corresponding to the electronic ground state. Excited state dynamics and transitions between surfaces require restoring the non-adiabatic coupling terms.

2.2 Foundations of Density Functional Theory

Following the Born-Oppenheimer approximation, the electronic structure of a many-electron system is governed by the time-independent Schrödinger equation with the nuclei treated as fixed classical sources of an external potential. Solving this many-body problem directly is intractable for large systems due to the exponential scaling of the wavefunction. Density functional theory (DFT) offers an elegant reformulation, in which the central variable is not the many-body wavefunction but rather the electron density, a function of only three spatial coordinates.

2.2.1 The Hohenberg-Kohn Theorems

In 1964, Hohenberg and Kohn provided the theoretical foundation for DFT through two theorems:

- For a system of interacting electrons under an external potential $V_{ext}(\vec{r})$, the ground state electron density $\rho_0(\vec{r})$ uniquely determines $V_{ext}(\vec{r})$, up to a constant. Since the full Hamiltonian is then determined, all properties of the system, including those of excited states, are functionals of the ground state density $\rho_0(\vec{r})$.
- The functional that delivers the ground state energy of the system gives the lowest energy if and only if the input density is the true ground state density. In other words, there exists a universal functional $F[\rho]$, independent of the external potential, such that the total energy of the system can be written as:

$$E[\rho] = F[\rho] + \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r} \quad (2.14)$$

Minimizing this energy functional with respect to $\rho(\vec{r})$ yields the exact ground state energy and the density of the system.

The universal functional $F[\rho]$ contains the internal kinetic and interaction energy:

$$F[\rho] = T[\rho] + V_{ee}[\rho] \quad (2.15)$$

However, both components are highly nontrivial to express as functionals of the density, especially the kinetic energy $T[\rho]$ of an interacting many electron system.

2.2.2 The Kohn-Sham Ansatz

To make the Hohenberg-Kohn theorems practical, Kohn and Sham introduced a powerful approximation in 1965. They proposed a fictitious system of non-interacting electrons that yields the same ground state density as the interacting system. This allowed them to write the total energy as:

$$E[\rho] = T_s[\rho] + \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + E_H[\rho] + E_{xc}[\rho] \quad (2.16)$$

where:

- $T_s[\rho]$ is the kinetic energy of the non-interacting reference system,
- $E_H[\rho]$ is the classical electrostatic (Hartree) energy:

$$E_H[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' \quad (2.17)$$

- $E_{xc}[\rho]$ is the exchange-correlation energy functional, which captures all many-body effects not included in T_s or E_H , including exchange, correlation, and the correction to the true kinetic energy.

The key idea is that while the full interacting kinetic energy is unknown, T_s can be computed exactly from the Kohn-Sham orbitals $\{\phi(\vec{r})\}$, which are solutions to the single-particle Kohn-Sham equations:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}[\rho](\vec{r})\right)\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \quad (2.18)$$

with:

$$V_{eff}[\rho](\vec{r}) = V_{ext}(\vec{r}) + V_H[\rho](\vec{r}) + V_{xc}[\rho](\vec{r}) \quad (2.19)$$

where:

- $V_H[\rho](\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'$ is the Hartree potential
- $V_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$ is the exchange-correlation potential, which is the functional derivative of the exchange-correlation energy.

And the density $\rho(\vec{r})$ is reconstructed from the Kohn-Sham orbitals as:

$$\rho(\vec{r}) = \sum_{i=1}^{N_e} |\phi_i(\vec{r})|^2 \quad (2.20)$$

The problem is now simplified significantly, but it is still far from simple. The next hurdle is figuring out the exact expression for the exchange-correlation energy $E_{cx}[\rho]$, and there are no known solutions for this problem to this day. Thus, proper approximations have to be made to make progress with practical calculations. The approximations for the exchange-correlation energy $E_{xc}[\rho]$ are discussed in Section 2.3, but before we do that, we briefly discuss the self-consistent procedure for solving the Kohn-Sham eigenvalue equations.

Since V_{eff} depends on the density $\rho(\vec{r})$, and the density in turn depends on the orbitals ϕ_i , it's necessary to solve the Kohn-Sham equations self-consistently. The steps of this procedure are laid out below, and depicted in Figure 2.1:

- Guess an initial density $\rho^{(0)}(\vec{r})$,
- Construct the effective potential $V_{eff}^{(0)}[\rho](\vec{r})$,

- Solve the Kohn-Sham equations to obtain the orbitals $\phi_i^{(0)}$,
- With the obtained orbitals, compute the new density:

$$\rho^{(1)}(\vec{r}) = \sum_{i=1}^{N_e} |\phi_i^{(0)}(\vec{r})|^2 \quad (2.21)$$

- Use a linear combination of $\rho^{(1)}(\vec{r})$ and $\rho^{(0)}(\vec{r})$ as the next guess, and repeat until self-consistency is attained.

This procedure defines the self-consistent field (SCF) cycle. Once converged, the total energy is evaluated from:

$$E[\rho] = \sum_i^{occ} \varepsilon_i - E_H[\rho] + E_{xc}[\rho] - \int V_{xc}(\vec{r})\rho(\vec{r})d\vec{r} \quad (2.22)$$

Here, corrections are needed because the eigenvalues ε_i include contributions from V_H and V_{xc} , which must not be double counted.

2.3 Exchange-Correlation Functionals

In the Kohn-Sham formulation of DFT, the only uncontrolled approximation lies in the exchange-correlation (XC) functional $E_{xc}[\rho]$. This term must encapsulate the many-body effects of electron exchange and correlation, as well as the difference between the true interacting kinetic energy $T[\rho]$ and the non-interacting kinetic energy $T_s[\rho]$. As such, it is a compact but rich object that governs the success or failure of any DFT calculation.

The expression for the total energy is given in Equation 2.16. In this expression, the first three terms - non-interacting kinetic energy, external potential energy, and the Hartree energy - are either known or easily computable from the electron density and the Kohn-Sham orbitals. However, $E_{xc}[\rho]$ contains:

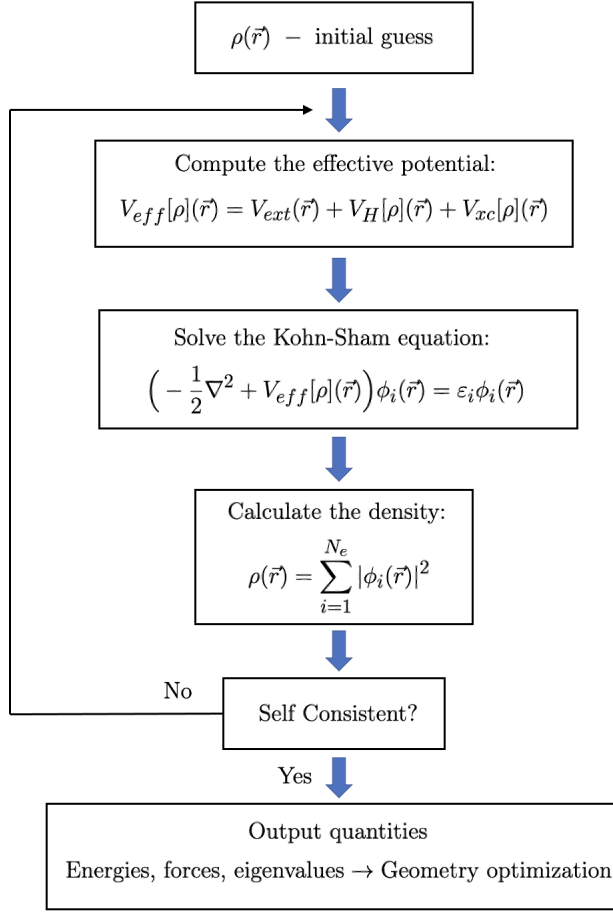


Figure 2.1: Schematic representation of the self-consistent field (SCF) cycle in Kohn-Sham density functional theory calculations. The arrow pointing back to the start is a representation of the force and energy convergence criteria implemented in first-principles calculations.

- The remainder of the true kinetic energy: $T[\rho] - T_s[\rho]$,
- The difference between the true Coulomb interaction energy and the classical Hartree term,
- All quantum exchange and correlation effects.

Since the exact form of $E_{xc}[\rho]$ is unknown, a variety of approximations have been developed. These approximations are usually categorized based on a hierarchy of complexity, from local to semi-local to non-local functionals. Each level of complexity aims to improve

certain aspects (*e.g.* bandgap prediction, structural accuracy) but usually at an increased computational cost.

2.3.1 Local and Semi-local Approximations: LDA and GGA

The simplest exchange-correlation approximations assume that the exchange-correlation energy density at a point depends only on the local density $\rho(\vec{r})$, or its local gradients. These are called local and semi-local functionals.

Local Density Approximation (LDA)

The local density approximation (LDA) is based on the exact solution to the homogeneous electron gas [70–73], in which electrons move in a uniform positive background. In LDA, the exchange-correlation energy is written as:

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})) d\vec{r} \quad (2.23)$$

Here, $\varepsilon_{xc}(\rho)$ is the exchange-correlation energy per particle of the uniform electron gas at density ρ . Several parametrizations exist (*e.g.* Perdew-Zunger [72], Vosko-Wilk-Nusair [74]), obtained from quantum Monte Carlo simulations of the homogeneous gas.

LDA tends to overbind atoms and molecules, slightly underestimate lattice constants, and underestimate bandgaps in insulators and semiconductors. However, it often yields surprisingly good results for close-packed solids.

Generalized Gradient Approximation (GGA)

The generalized gradient approximation (GGA) improves on LDA by incorporating information about the local gradient of the density:

$$E_{xc}^{GGA}[\rho] = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r}), \nabla \rho(\vec{r})) d\vec{r} \quad (2.24)$$

The most widely used GGA functional is the Perdew-Burke-Ernzerhof (PBE) functional [10], also used in this thesis. Other GGAs (*e.g.* PW91 [73]) exist, but PBE has become the standard for many materials applications.

GGA tends to correct LDA’s overbinding, giving better structural parameters and energetics for molecules and solids. However, like LDA, it fails to predict accurate electronic bandgaps and can struggle in systems with strong self-interaction errors or dispersion forces. Yet, it’s still considered very practical, and it remains the default choice for large-scale optimization and initial screening of defects in materials.

2.3.2 Hybrid Functionals: PBE0, HSE, and Dielectric-Dependent Hybrids

While LDA and GGA are useful, they suffer from systematic underestimation of bandgaps and sometimes poor description of localized electronic states due to the lack of exact exchange and the presence of self-interaction errors. Hybrid functionals address these problems by mixing a fraction of exact exchange from Hartree-Fock (HF) theory into the XC functional. The general form of a hybrid functional is:

$$E_{xc}^{\text{hyb}} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{GGA}} + E_c^{\text{GGA}} \quad (2.25)$$

where E_x^{HF} is the exact exchange energy calculated from the Kohn-Sham orbitals, E_x^{GGA} and E_c^{GGA} are the GGA exchange and correlation energies respectively, and α is a mixing parameter, often chosen empirically. For example, the PBE0 functional [75] mixes 25% exact exchange with 75% PBE exchange, along with full PBE correlation:

$$E_{xc}^{\text{PBE0}} = \frac{1}{4} E_x^{\text{HF}} + \frac{3}{4} E_x^{\text{PBE}} + E_c^{\text{PBE}} \quad (2.26)$$

PBE0 is non-empirical and often yields improved results for molecular systems and insulators, with better bandgaps and reaction energies than GGA.

The Heyd-Scuseria-Ernzerhof (HSE) [76] functional modifies PBE0 by screening the

Coulomb potential in the exchange term. It replaces the long-range part of exact exchange with a screened form, controlled by a screening parameter ω , which separates the exchange interaction into short and long-range terms:

$$E_x^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) \quad (2.27)$$

where α is again chosen as $\frac{1}{4}$. ω is often chosen as 0.11 Bohr^{-1} , which is commonly referred as the HSE06 functional [11]. HSE is widely used in solid-state physics and often gives accurate lattice parameters and bandgaps across a wide range of materials.

Another class of hybrid functionals is the dielectric-dependent hybrid (DDH) functionals [12, 77]. DDH generalizes the hybrid mixing fraction α by tying it to the inverse dielectric constant of the material:

$$\alpha = \frac{1}{\epsilon_\infty} \quad (2.28)$$

This is motivated by the idea that the degree of screening in a material should govern the strength of exchange. DDH functionals can significantly improve bandgap predictions and optical properties, especially for materials with intermediate screening [13, 78]. They also avoid the use of empirical parameters, offering a systematically tunable alternative to PBE0 and HSE.

2.4 Practical Implementation of First-Principles Calculations

2.4.1 Plane-Wave Basis Sets and Convergence Behavior

In this thesis, all DFT calculations were performed using a plane-wave basis set, a natural choice for periodic systems such as crystals, slabs and supercells. Plane-waves form a complete, orthonormal set of eigenfunctions of the Laplacian operator under periodic boundary conditions, making them ideally suited for systems that exploit translational symmetry.

Their key advantage lies in their computational simplicity and systematic convergence: the accuracy of a plane-wave expansion is controlled by a single global parameter - the kinetic energy cutoff, E_{cut} .

Each Kohn-Sham orbital $\phi_{nk}(\vec{r})$ is expanded as a Fourier series over reciprocal lattice vectors $\vec{G}$, shifted by a crystal momentum $\vec{k}$:

$$\phi_{nk}(\vec{r}) = \sum_{\vec{G}} c_{nk}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad (2.29)$$

The plane-wave expansion is truncated by enforcing $\frac{1}{2}|\vec{k} + \vec{G}|^2 < E_{\text{cut}}$. This truncation introduces a variational error in total energy and derived quantities such as forces, stress tensors, and phonon frequencies. Importantly, convergence of the total energy alone is not always sufficient: forces and defect-level positions may converge more slowly and require higher cutoffs.

In practice, the choice of E_{cut} is guided by the hardness of the pseudopotentials and the nature of the atoms in the system. For example, light atoms with compact valence orbitals, such as C, N, and O often require higher cutoffs than heavier elements like Si or Al. In this thesis, cutoff energies between 80-90 Ry were used for plane-wave expansions in all calculations performed using the Quantum ESPRESSO and [79–81] WEST packages [8,9]. These values are relatively high by conventional standards but were chosen to ensure convergence of key physical quantities relevant to defect energetics and optical transitions, especially for hybrid functionals. To ensure accuracy, convergence tests were performed on key observables such as total energy differences. Convergence was deemed acceptable when the differences in total energy were less than 1 meV per atom upon increasing the cutoff energy by 10 Ry.

Another subtle issue is the treatment of vacuum regions during slab calculations when trying to understand behavior of defects near surfaces. Since vacuum is a region of low density, it may initially seem that fewer plane waves are needed to describe it. However,

in practice, ensuring an accurate description of the electrostatic potential in the vacuum requires retaining high-frequency components to capture local field variations and surface dipoles. As a result, convergence behavior in slab geometries may differ from that in bulk, and cutoff values used for surface calculations were generally maintained at the higher end of the tested range.

The choice of plane-wave basis also facilitates efficient evaluation of forces and stresses via analytic derivatives of the total energy, making them ideal for structural optimization of defects and relaxation of surface geometries. In all calculations presented in this work, structural relaxations were performed using either conjugate-gradient or quasi-Newton methods until the maximum atomic force fell below $10 \text{ meV}/\text{\AA}$, ensuring tight convergence in defect geometries.

Finally, we note that while localized basis sets (*e.g.* Gaussian orbitals, numeric atomic orbitals) are often used in quantum chemistry, they are less suited for defect calculations in semiconductors due to their basis set superposition error and difficulty in systematically approaching completeness. The plane-wave basis offers a controlled and systematically improvable approach, at the cost of requiring pseudopotentials to treat core electrons efficiently - a topic addressed in the next section.

2.4.2 Core-Valence Separations and Pseudopotentials

In plane-wave DFT calculations, it is computationally prohibitive to treat both valence and core electrons explicitly, especially for systems involving heavy atoms or large supercells. Core states oscillate rapidly near the nucleus, requiring an extremely large number of plane waves to be described accurately. However, in most materials, these core electrons are chemically inert and their contribution to bonding and defect physics is minimal. This motivates the use of pseudopotentials, which replace the strong all-electron Coulomb potential of the nucleus with a smoother effective potential that acts only on valence electrons.

The key requirement for a pseudopotential is that it reproduces the correct scattering properties of the all-electron atom - particularly the phase shifts of valence electrons outside a chosen core radius. A good pseudopotential allows the valence pseudo-wavefunction to match the all-electron wavefunction beyond this core region and ensures transferability across chemical environments.

In this work, all calculations were performed using norm-conserving pseudopotentials (NCPPs), specifically the Optimized Norm-Conserving Vanderbilt (ONCV) type from the SG15 library [82, 83]. These pseudopotentials were designed for high transferability and efficiency, with smooth nonlocal projectors that facilitate convergence even in demanding environments such as semiconductor defects and surface reconstructions. ONCV pseudopotentials strictly conserve the norm of the pseudo-wavefunction within the core region, ensuring that charge densities, forces, and total energies remain accurate across varying bonding environments.

While ultrasoft pseudopotentials (USPPs) and the projector augmented-wave (PAW) method are commonly used in plane-wave DFT codes like VASP [84, 85], they were not used in this thesis. USPPs relax the norm-conservation constraint to enable smaller basis sets, but require augmentation charges and more complex charge density corrections. PAW reconstructs the all-electron wavefunction from a pseudo representation via atom-centered projectors, enabling high accuracy for all-electron properties. These methods are especially useful for systems involving transition metals and heavy elements, but for the main group elements (Si, C, N, Al etc.) relevant to this work, ONCV norm-conserving pseudopotentials provided an excellent balance between efficiency and physical accuracy.

In conclusion, the choice of pseudopotential - particularly the use of high-quality norm-conserving pseudopotentials - plays a central role in ensuring the reliability of large scale plane-wave defect calculations. The pseudopotentials used throughout this thesis enabled accurate predictions of structural, electronic, and optical properties in both bulk and near-

surface environments.

2.4.3 Brillouin Zone Sampling

Accurate integration over the Brillouin zone is essential in plane-wave DFT calculations to obtain converged total energies, forces, and electronic properties. In principle, the total energy of a periodic system is computed as an integral over the first Brillouin zone of the crystal; in practice, this integral is replaced by a finite sum over discrete k-points, typically generated using Monkhorst-Pack or Γ -centered grids.

For bulk supercells, especially those containing relatively few atoms per unit cell (*e.g.* 2-8 atoms), dense Monkhorst-Pack grids are often necessary to resolve band dispersion and ensure convergence of total energies and stress tensors. However, in the context of this thesis, the majority of calculations involve large supercells (216-1000 atoms), where the Brillouin zone is correspondingly small. In this limit, the electronic structure becomes quasi-local in reciprocal space, and a Γ -point only calculation is typically sufficient. Moreover, for slab models that explicitly break translational symmetry along the surface normal, Γ -point sampling not only remains valid but also avoids artificial band folding and k-point dispersion artifacts.

2.4.4 Supercells, Slab Models, and Surface Terminations

The study of point defects and surface-induced phenomena in semiconductors requires the use of finite supercells to simulate localized perturbations within an otherwise periodic crystal. This approach allows for systematic control over defect-defect interactions and surface effects, while maintaining compatibility with plane-wave periodic boundary conditions. In this thesis, both bulk supercells and slab geometries were employed, depending on whether the goal was to probe isolated donor-acceptor behavior in the bulk or understand how surfaces influence electronic and optical properties of near-surface defects.

For bulk defect calculations, we used cubic supercells of diamond and 3C-SiC containing 216, 512, and up to 1000 atoms. For 4H-SiC, we used hexagonal, 576 atom supercells. These cells were constructed by repeating the primitive cell along the lattice vectors defining the primitive cell, and were kept large enough to ensure that the spurious electrostatic and elastic interactions between periodic images of defects were minimal.

To study surface effects in SiC, we constructed slab models with up to 11 bilayers of Si-C along the (001) or (0001) orientations of 3C- or 4H-SiC. The bottom two bilayers of each slab were fixed to mimic bulk-like conditions, while the remaining layers were fully relaxed. A vacuum spacing of 20 Å was introduced along the direction perpendicular to the surface to minimize interactions between repeated images of slabs. We validated that the electrostatic potential in the middle of the vacuum region is flattened, ensuring isolation.

A key consideration in slab modeling is the choice of surface terminations, which affect the local electrostatic environment and the presence of mid-gap states. In this thesis, we examined a variety of surface terminations, including the (2x1) reconstruction of the Si-rich surface of 3C-SiC terminated with H, O, F atoms and OH groups, as well as the (1x1) reconstruction of the Si-rich surface of 4H-SiC terminated with OH groups. A compact summary of all the different surface terminations and slab models used throughout this thesis is given in Figure 2.2. Hydrogen passivation suppresses surface states and is commonly used to mimic ideal, electronically inert surfaces. In contrast, hydroxyl termination introduces occupied surface states near the valence band, enabling the formation of surface-defect pairs (SDPs), in which an electron is excited from a surface state to nearby defect orbital, forming a spatially separated exciton. These SDPs exhibit intrinsic electric dipole moments aligned perpendicular to the surface, and their dipole strength is sensitive to defect depth.

A final consideration in using slab models is the dipole correction [5]. This correction is necessary for any asymmetric slab to remove artificial electric fields induced by nonzero net dipole moments along the surface normal. These corrections are essential for correctly

predicting electrostatic alignment, especially when simulating surface defects.

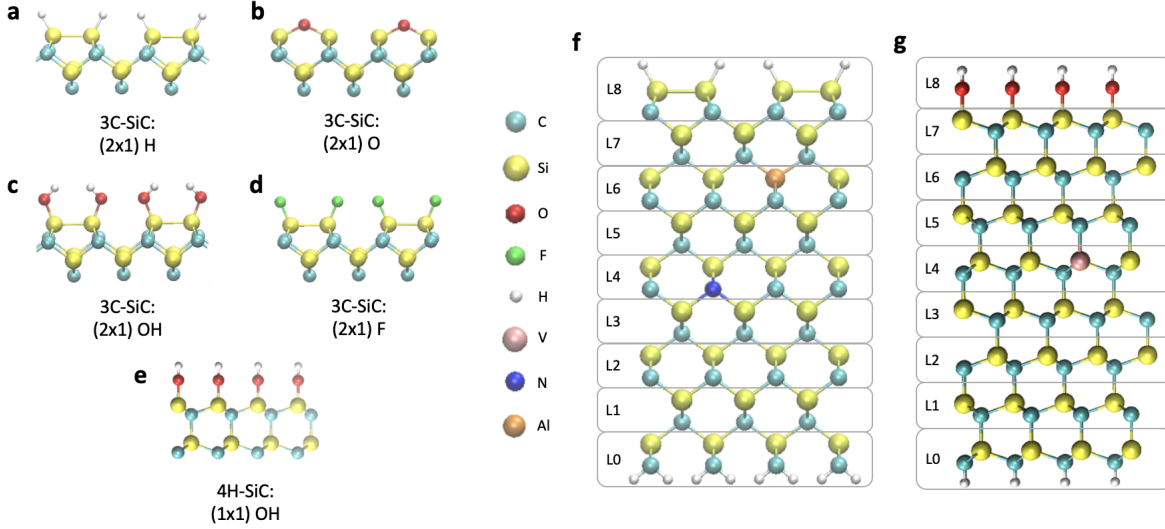


Figure 2.2: Atomistic structures of the Si-rich (001) surfaces of 3C-SiC with a (2x1) surface reconstruction terminated with (a) H atoms, (b) O atoms, (c) OH groups, and (d) F atoms, as well as the (e) Si-rich (0001) surface of 4H-SiC with a (1x1) reconstruction terminated with OH groups. (f) The side view of 3C-SiC slab with the (2x1) H-termination, where the bottom C-rich surface is passivated with H atoms. (g) The side of view of 4H-SiC slab with the (1x1) OH-termination. Both the slabs consist of 9 Si-C bilayers and are shown to include other defects within the slab.

2.4.5 Finite Size Corrections and Extrapolation Techniques

Finite size effects are a critical consideration in first-principles simulations of point defects, particularly when using charged supercells or thin slab models. Because periodic boundary conditions are applied to inherently non-periodic objects - such as isolated defects or surfaces - spurious interactions can and do arise between repeated images, leading to errors in defect energetics and transition levels. In this thesis, we employed a combination of scaling based extrapolation procedures and electrostatic correction schemes to mitigate these effects and ensure that all reported quantities reflect the dilute and physically meaningful limits.

For bulk defect calculations, we considered supercells of various sizes - typically 216, 512

and 1000 atoms for cubic supercells - to quantify and correct the scaling behavior of computed formation energies and charge transition levels (CTLs). Finite size errors in these quantities primarily originate from long-range electrostatic interaction between the periodic images of charged defects and from the compensating homogeneous background charge needed to maintain neutrality. These errors decay asymptotically as $1/L$ or $1/L^3$, where L is the linear dimension of the supercell. A majority of finite size correction schemes in bulk materials follow the work of Freysoldt, Neugebauer and van de Walle [86].

To extract physically meaningful quantities, we performed explicit extrapolation to the dilute limit by fitting CTLs across different supercell sizes. In hybrid functional calculations, which are computationally expensive, we avoided repeated calculations at multiple sizes by reusing the scaling behavior obtained from the PBE functional and applying an energy alignment shift from a single HSE or DDH calculation. This two step approach preserves the accuracy of the hybrid level energetics while leveraging the computational efficiency of PBE to capture finite size trends.

In slab models, finite size effects manifest differently: instead of three dimensional image interactions, the dominant errors arise from quantum confinement along the slab normal and from incomplete dielectric screening of charged or dipolar states near the surface [6, 7]. To correct these effects, we computed the CTLs for several thicknesses, with 7, 9 and 11 bilayers, and extrapolated them as a function of $1/N_L$, where N_L is the number of Si-C bilayers in the slab. This allowed us to approach the infinite-thickness limit in a controlled way, reducing the artificial lowering or raising of the defect levels induced by thin-slab confinement.

Although zero-phonon lines (ZPLs) are also expected to exhibit some finite size effects - due to changes in electronic level alignment, dielectric environment etc. - we did not perform explicit extrapolation of ZPLs with supercell size or slab thickness. Instead, we verified that calculated ZPL shifts remained within physically reasonable ranges when comparing ZPLs from successive DAP shells and put more emphasis on understanding trends rather than

having absolute accuracy.

In all cases, potential alignment corrections were also applied, particularly when computing CTLs in charged states. By aligning the average electrostatic potential in a region far from the defect, we ensured a consistent reference level across all simulations. This step is essential when dealing with slabs, where surface dipoles and localized defect charge can otherwise obscure the intrinsic defect level positions [87].

2.5 Calculation of Defect Properties

This section outlines the methods used to calculate both the ground and excited state properties of point defects, with a focus on quantities such as formation energies, charge transition levels (CTLs), zero-phonon lines (ZPLs), radiative lifetimes, and dipole moments. These properties are central to assessing defect stability, charge behavior and optical activity in both bulk and near-surface environments. The following subsections describe how we compute each of these properties: modeling excited-state potential energy surfaces and luminescence spectra using the configurational coordinate approach, estimating radiative recombination rates and extracting electric dipole moments via Wannier function based polarization analysis.

2.5.1 Formation Energies and Charge Transition Levels

The thermodynamic stability and electronic behavior of point defects are governed by their formation energies and charge transition levels (CTLs). These quantities determine whether a defect will form under given synthesis conditions, how it will interact with carriers, and whether it can serve as an optically active or electrically compensated carrier.

The formation energy $E_f[X^q]$ of a defect X in charge state q is defined relative to a reference bulk supercell and a set of chemical potential values. It is given by:

$$E_f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}}^q \quad (2.30)$$

where $E_{\text{tot}}[X^q]$ and $E_{\text{tot}}[\text{bulk}]$ are the total energy of the supercell containing the defect X in charge state q and that of the reference bulk supercell. n_i is the number of atoms of species i added ($n_i > 0$) or removed ($n_i < 0$) from the host, and μ_i are the chemical potentials associated with those atoms. E_F is the Fermi level referenced to the valence band maximum (VBM), and E_{corr}^q is the finite-size correction for charged supercells, as discussed in Section 2.4.5. Depending on whether this quantity is computed in the bulk [86] vs. near the surface within a slab model [87], the most commonly used correction schemes differ slightly.

The chemical potential μ_i is constrained by the thermodynamic stability of the host compound. For instance, in SiC, the chemical potentials must satisfy:

$$\mu_{\text{Si}} + \mu_{\text{C}} = \Delta H_f(\text{SiC}) \quad (2.31)$$

where $\Delta H_f(\text{SiC})$ is the enthalpy of formation of SiC. Under Si-rich conditions, $\mu_{\text{Si}} = \mu_{\text{Si}}^{\text{bulk}}$, and μ_{C} is derived accordingly. The formation energy of a defect thus depends not only on its intrinsic electronic structure but also on the external thermodynamic conditions during synthesis or annealing.

A defect's preferred charge state depends on the Fermi level E_F . The charge transition level $\epsilon(q/q')$ is the Fermi energy at which the formation energies of two charge states q and q' become equal [88]:

$$\epsilon(q/q') = \frac{E_f[X^q; E_F = 0] - E_f[X^{q'}; E_F = 0]}{q' - q} \quad (2.32)$$

where $E_f[X^q; E_F = 0]$ is the formation energy of the defect X at charge state q when the Fermi level is at the VBM ($E_F = 0$).

CTLs are intrinsic properties of the defect and do not depend on chemical potentials,

unlike the absolute formation energy. In wide-bandgap semiconductors, the position of CTLs within the bandgap informs whether a defect will act as a shallow donor, shallow acceptor or a deep charge trap. For instance, in Figure 2.3 we show the formation energy of the substitutional N defect (commonly known as the P1 center) in diamond. Note that the slope indicates the charge state of the corresponding defect. Only one CTL is predicted: $\epsilon(+/0) = E_{\text{CBM}} - 1.47$ eV, and therefore, the P1 center is predicted to be a deep donor with only two stable charge states in this example. However, keep in mind that the bandgap of diamond is severely underestimated with the PBE functional ($E_g = 4.2$ eV with PBE, as opposed to $E_g = 5.47$ eV experimentally). If this plot were further extended to the true bandgap, CTLs $\epsilon(0/-)$ and even $\epsilon(-/2-)$ could fall inside the bandgap and the charge states $q = -1$ and $q = -2$ could be interpreted as stable charge states. This example illustrates perfectly the potential pitfalls of using a functional that systematically underestimates bandgaps (such as PBE) and the erroneous / incomplete results such a choice can lead to.

2.5.2 *Configurational Coordinate Diagrams and Photoluminescence*

The optical emission properties of point defects in semiconductors are governed by transitions between vibrationally broadened electronic states. In the absence of an external photon or phonon reservoir, these transitions are governed by the Franck-Condon (FC) principle [89], which states that electronic transitions occur on timescales much faster than nuclear motion, resulting in vertical transitions between fixed ionic configurations. This framework is captured quantitatively by the configurational coordinate (CC) diagram [2, 90–93], a one dimensional model that relates the equilibrium geometries of the ground and excited states through a mass-weighted configurational coordinate Q :

$$Q^2 = \sum_{\alpha,i} M_{\alpha} (R_{\alpha,i}^{(e)} - R_{\alpha,i}^{(g)})^2 \quad (2.33)$$

where M_{α} is the mass of atom α , and $R_{\alpha,i}^{(g)}$, $R_{\alpha,i}^{(e)}$ are atomic positions in the ground and

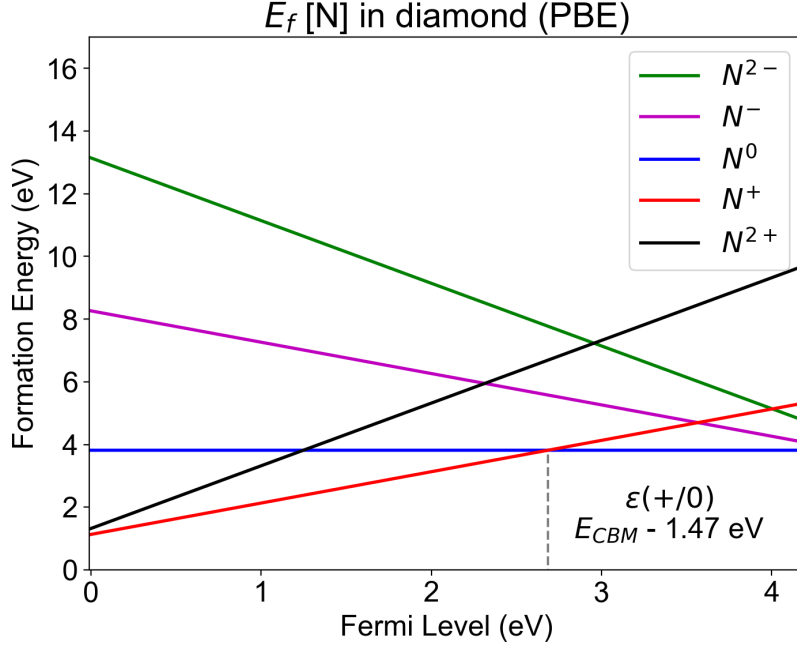


Figure 2.3: The formation energy diagram of the substitutional nitrogen defect in diamond (commonly known as the P1 center) as a function of the Fermi level, computed with the PBE functional.

excited states along Cartesian component $i \in \{x, y, z\}$. The potential energy surfaces (PES) are approximated as harmonic, with the excited state PES shifted by ΔQ :

$$E_g(Q) = \frac{1}{2}\Omega_g^2 Q^2, \quad E_e(Q) = E_{\text{ZPL}} + \frac{1}{2}\Omega_e^2 (Q - \Delta Q)^2 \quad (2.34)$$

where Ω_g and Ω_e are the effective one dimensional phonon frequencies in the ground and excited states. The equilibrium geometry of the ground state corresponds to $Q = 0$ and that of the excited state corresponds to $Q = \Delta Q$. The zero-phonon line (ZPL) energy is defined as the vertical energy difference between the relaxed geometries of the ground and excited states:

$$E_{\text{ZPL}} = E_{\text{tot}}^{(e)} - E_{\text{tot}}^{(g)} \quad (2.35)$$

ΔSCF is a commonly used method to compute excited state properties in molecules and

periodic crystalline systems [94], and in this thesis we also use this method. The application of this method has been shown to accurately predict ZPLs point defects with the right the right functional [89]. More advanced approaches to compute excited state properties exist, such as time-dependent density functional theory (TDDFT) or the [2, 95, 96] or the GW approximation [97] which is usually used in conjunction with the Bethe-Salpeter equation [98].

The Debye-Waller factor (DWF) quantifies the relative intensity of the ZPL in the photoluminescence (PL) spectra:

$$\text{DWF} = \frac{I_{\text{ZPL}}}{I_{\text{total}}} = e^{-\sum_k S_k} \quad (2.36)$$

where each term S_k is a partial Huang-Rhys (HR) factor associated with phonon mode k :

$$S_k = \frac{\omega_k \Delta Q_k^2}{2\hbar} \quad (2.37)$$

where ω_k is the frequency of the phonon mode k and each ΔQ_k is the mass-weighted displacement of the system projected onto phonon mode k :

$$\Delta Q_k = \sum_{\alpha,i} \sqrt{M_\alpha} (R_{\alpha,i}^{(e)} - R_{\alpha,i}^{(g)}) e_{k;\alpha,i} \quad (2.38)$$

with $e_{k;\alpha,i}$ being the normalized phonon eigenvector. The total HR factor $S = \sum_k S_k$ gives an estimate of the average number of phonons emitted per optical transition, and thus governs the spectral width of the PL sideband.

In the one dimensional (1D) model, where all phonon coupling is projected onto a single effective mode of frequency Ω , the HR factor simplifies to:

$$S = \frac{\Omega_{\{g,e\}} \Delta Q^2}{2\hbar} \quad (2.39)$$

where ΔQ is defined in Equation 2.33 and where $\Omega_{\{g,e\}}$ is given by:

$$\Omega_{\{g,e\}} = \frac{\sum_k \omega_{\{g,e\};k}^2 \Delta Q_k^2}{\sum_k \Delta Q_k^2} \quad (2.40)$$

Now that we have established what CC diagrams are and what they are used for, we focus on the PL spectrum of point defects. The PL spectrum of a defect originates from spontaneous emission between electronic excited and ground states, accompanied by vibrational relaxation. Within the FC approximation, we treat the electronic transition as instantaneous, such that the nuclei do not move during the electronic process. Thus, the intensity of the emitted photon at a given energy is determined by the overlap between vibrational wavefunctions of the initial (excited) and final (ground) states. This leads to a vibrationally broadened emission spectrum consisting of a ZPL and a phonon side-band (PSB). An illustration of the configurational coordinate diagram and the resulting PL spectrum including the ZPL and the PSB are given in Figure 2.4.

The total emission intensity as a function of photon energy $\hbar\omega$, at a given temperature T is expressed as:

$$I(\hbar\omega, T) = \frac{n_r \omega^3 |\mu_{eg}|^2}{3\pi\epsilon_0 c^3 \hbar} \sum_{i,j} P_j(T) |\langle \Theta_j^{(e)} | \Theta_i^{(g)} \rangle|^2 \delta(E_{\text{ZPL}} + E_j^{(e)} - E_i^{(g)} - \hbar\omega) \quad (2.41)$$

Each term is explained in detail below:

- n_r is the wavelength-dependent refractive index of the host material at photon energy $\hbar\omega$
- μ_{eg} is the optical transition dipole matrix element between the electronic excited state and the ground state $\mu_{eg} = \langle \psi_e | \vec{r} | \psi_g \rangle$, which governs the strength of the electronic transition.
- $P_j(T)$ is the thermal occupation probability of the vibrational level j in the excited

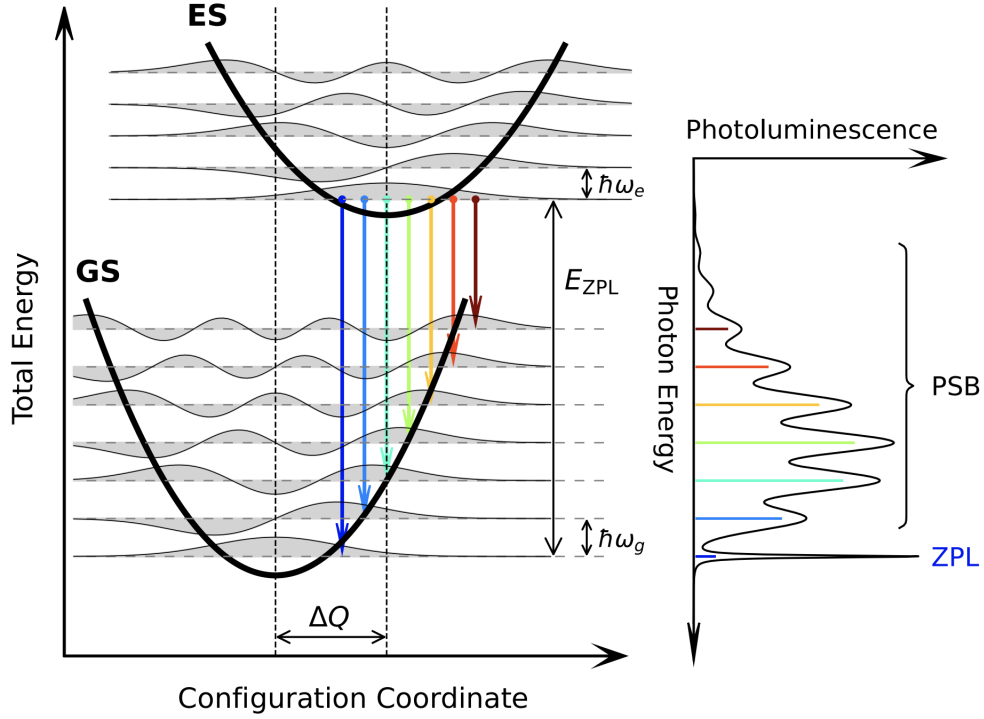


Figure 2.4: Schematic illustrating the configurational coordinate (CC) diagram and the resulting optical processes leading to photoluminescence (PL) spectra. Ground state (GS) and excited state (ES) potential energy surfaces are approximated by harmonic functions with frequency ω_g and ω_e respectively. Vibrational energy levels and wavefunctions are shown as horizontal dashed lines and gray areas respectively. ΔQ is the mass-weighted displacement between the local minimum of the GS and the ES energy curves. Colored arrows represent optical transitions at 0 K. The zero-phonon line (ZPL) originates from the transition between the 0th vibrational level of the ES to the 0th vibrational level of the GS. All other transitions contribute to the phonon sideband (PSB). Figure and caption reproduced from [2].

electronic state, given by the Boltzmann distribution:

$$P_j(T) = \frac{e^{-E_j^{(e)}/k_B T}}{\sum_j e^{-E_j^{(e)}/k_B T}} \quad (2.42)$$

- $\Theta_j^{(e)}$, $\Theta_i^{(g)}$ are the vibrational eigenstates of the excited and ground state potential energy surfaces respectively. These are solutions to the quantum harmonic oscillator

problem centered at their respective equilibrium configurations.

- $\langle \Theta_j^{(e)} | \Theta_i^{(g)} \rangle$ is the Franck-Condon overlap integral, which gives the probability amplitude for a transition between vibrational state j in the excited state and vibrational state i in the ground state. The square of this overlap integral gives the probability of that vibrational transition.
- $\delta(\cdot)$ is the Dirac delta function enforcing energy conservation between the photon, the ZPL, and the vibrational energies. In practice, this is broadened into a Gaussian or Lorentzian of width σ to simulate linewidth.

The vibrational energies of each level are given by:

$$E_i^{(g)} = \sum_k (n_k^{(g)} + \frac{1}{2}) \hbar \omega_k, \quad E_j^{(e)} = \sum_k (n_k^{(e)} + \frac{1}{2}) \hbar \omega_k \quad (2.43)$$

where $n_k^{(g)}$ and $n_k^{(e)}$ are the occupation numbers of mode k in the ground and excited state respectively.

To compute the spectrum explicitly, we assume that both the ground and excited state potential energy surfaces are harmonic, and that vibrational wavefunctions can be separated mode-by-mode. In principle, the total vibrational wavefunctions $\Theta_i^{(g)}$ and $\Theta_j^{(e)}$ are multidimensional functions defined over all normal modes, and their full Franck-Condon overlap is given by a product of mode resolved overlaps:

$$\langle \Theta_j^{(e)} | \Theta_i^{(g)} \rangle = \prod_k \langle \chi_{m_k}^{(e,k)} | \chi_{n_k}^{(g,k)} \rangle \quad (2.44)$$

where $\chi_{n_k}^{(g,k)}$ and $\chi_{m_k}^{(e,k)}$ are the 1D harmonic oscillator eigenfunctions for mode k in the ground and excited states, and n_k, m_k are the vibrational occupation numbers.

In many systems, including those studied in this thesis, only a small subset of phonon modes couple appreciably to the electronic transition. When the coupling is dominated by a single effective mode, the multidimensional overlap reduced to a single integral:

$$\langle \Theta_j^{(e)} | \Theta_i^{(g)} \rangle \approx \langle \chi_m^{(e)} | \chi_n^{(g)} \rangle \quad (2.45)$$

This simplification forms the basis of the 1D configurational coordinate model, where the vibrational wavefunctions are described by displaced harmonic oscillators. These wavefunctions are known analytically in terms of Hermite polynomials, and their overlaps can be written using closed-form expressions involving generalized Laguerre polynomials.

Specifically, the squared overlap (*i.e.* the Franck-Condon factor) between the m -th vibrational level in the excited state and the n -th level in the ground state is given by:

$$\langle \chi_m^{(e)} | \chi_n^{(g)} \rangle = \sqrt{\frac{m!}{n!}} S^{(n-m)/2} e^{-S/2} L_m^{(n-m)}(S) \quad \text{for } n \geq m \quad (2.46)$$

where S is the HR factor defined previously in Equation 2.39 and $L_m^{(n-m)}$ is a generalized Laguerre polynomial.

The PL spectrum constructed this way contains a prominent peak at $\hbar\omega = E_{\text{ZPL}}$, corresponding to a transition between the lowest vibrational states of the PESs, and a broader distribution of peaks at lower photon energies spaced by integer multiples of the effective 1D phonon energy $\hbar\Omega_g$ of the ground state.

Each of these vibrational transitions is weighted by the Franck-Condon factor and broadened for visual comparison to experiment or for plotting in simulated spectra. The total intensity of the ZPL corresponds to the $j = 0 \rightarrow i = 0$ transition, and the phonon sideband includes all other contributions.

While the configurational coordinate framework provides an intuitive and computationally tractable approach to modeling PL spectra, it is important to recognize its underlying assumptions and potential limitations. Chief among these is the reduction of the multidimensional vibrational problem to a single effective mode, which implicitly assumes that all phonon coupling can be projected onto one dominant structural distortion pathway. This approximation tends to work best when the HR factor S is moderately large, such that the

phonon sideband dominates and the system explores a broad range of nuclear configurations during the electronic transition. However, in cases where $S \ll 1$, the emission is sharply concentrated in the ZPL, and the harmonic approximation can fail to capture subtle asymmetries, mode mixing, or anharmonic effects. In such low- S systems, a full multidimensional treatment of phonon modes - or at least inclusion of multiple strongly coupled modes - may be required for quantitative accuracy. In this thesis, we still use the 1D configurational coordinate approach despite these shortcomings, acknowledging the fact that a more quantitatively rigorous treatment is necessary for a more complete picture. For our purposes of understanding which systems have a high or low amount of electron-phonon coupling, we believe that the 1D configurational coordinate approach still offers a powerful tool for capturing the essential physics of optical transitions in defects, and provides valuable insight into the structure-property relationships governing optical emission.

2.5.3 *Photoionization and Stimulated Emission Cross Sections*

In addition to spontaneous photoluminescence, defect states may interact with light through photoionization and stimulated emission processes. These transitions are central to understanding optical excitation mechanisms, photon absorption probabilities, and the coherent control of defect charge or spin states using resonant fields.

As derived earlier in Equation 2.41, the emission spectrum of a defect within the Franck-Condon approximation can be written as a sum over vibrational transitions between the excited and ground state potential energy surfaces. This full spectrum, normalized to remove the dependence on absolute dipole strength is expressed as:

$$L(\hbar\omega, T) = C\omega^3 A(\hbar\omega, T) \quad (2.47)$$

where $L(\hbar\omega, T)$ is the emission intensity at photon energy $\hbar\omega$ and is the normalized version of Equation 2.41. C is a constant term composed of other host related or known natural

constants and $A(\hbar\omega, T)$ is the electron-phonon spectral function given by:

$$A(\hbar\omega, T) = \sum_{i,j} P_j(T) |\langle \Theta_j^{(e)} | \Theta_i^{(g)} \rangle|^2 \delta(E_{\text{ZPL}} + E_j^{(e)} - E_i^{(g)} - \hbar\omega) \quad (2.48)$$

This electron-phonon spectral function $A(\hbar\omega, T)$ appears universally across all dipole-mediated light-matter interactions involving vibronic transitions. Once calculated via Franck-Condon overlaps, it can be reused to compute other observables like stimulated emission and photoionization cross sections.

The stimulated emission cross section quantifies the probability for an excited defect to emit a photon energy $\hbar\omega$ in the presence of an incident photon field. It shares the same transition dipole and spectral shape as the PL process, but includes the dipole matrix element explicitly.

$$\sigma_s(\hbar\omega, T) = \frac{4\pi^2\alpha}{n_r} \hbar\omega |\vec{\mu}_{eg}|^2 A(\hbar\omega, T) \quad (2.49)$$

where α is the fine structure constant, n_r is the refractive index of the host material, $\vec{\mu}_{eg} = \langle \psi_g | \vec{r} | \psi_e \rangle$ is the optical transition dipole moment and $A(\hbar\omega, T)$ is the electron-phonon spectral function defined in Equation 2.48. This form highlights that the shape of the stimulated emission cross section exactly mirrors the normalized PL shape, but its magnitude is scaled by the dipole strength and the photon energy. Thus, once $A(\hbar\omega, T)$ is known, the directional or polarization-resolved stimulated emission can be computed via the angular dependence of μ_{eg} .

In contrast to stimulated emission, photoionization describes the excitation of an electron from a lower-lying filled state (typically the valence band or a surface-localized state) into an unoccupied defect level. This is relevant for acceptor-like defects, neutral-to-negative charge transitions, or surface-defect pairs (SDPs).

The photoionization cross section for promoting an electron from a valence band state ψ_i^{VB} to an empty defect state ψ_d is given by:

$$\sigma_{ion}(\hbar\omega, T) = \frac{4\pi^2\alpha}{n_r}\hbar\omega \sum_i |\vec{\mu}_{id}|^2 A_i(\hbar\omega - E_i, T) \quad (2.50)$$

where $\vec{\mu}_{id} = \langle\psi_d|\vec{r}|\psi_i^{\text{VB}}\rangle$ is the dipole matrix element between the valence state and the defect state, and $A_i(\hbar\omega, T)$ is the electron-phonon spectral function describing transitions between the corresponding vibrational manifolds.

This formulation follows directly from the same electron-phonon framework used for PL and stimulated emission cross sections. In the 1D configurational coordinate model, it's common to assume that the shape of $A_i(\hbar\omega, T)$ is similar to that of $A(\hbar\omega, T)$, with the ZPL replaced by the optical ionization energy.

We note that an alternative definition of photoionization, commonly used for donor-like defects, involves ejecting an electron from the defect into the conduction band. That process is also governed by the same formalism, but involves different initial/final states and may be interpreted as photoemission rather than optical absorption. Both processes are valid under Fermi's Golden Rule and are conceptually linked to each other.

2.5.4 Radiative Recombination

Radiative recombination refers to the spontaneous decay of an excited electronic state via photon emission. For point defects in semiconductors, the rate of this process directly determines the radiative lifetime, which plays a critical role in photon emission efficiency, optical readout protocols, and device performance.

In principle, the strength of such transitions is governed by the optical dipole matrix element $\vec{\mu}_{eg} = \langle\psi_g|\vec{r}|\psi_e\rangle$, which enters into the expression for the spontaneous emission rate derived from Fermi's Golden Rule. However, in periodic systems, the position operator $\vec{r}$ is ill-defined due to the translation invariance of Bloch wavefunctions. That is, $\vec{r}$ is not a bounded or Hermitian operator under periodic boundary conditions, which complicated direct evaluation of matrix elements of the form $\langle\psi|\vec{r}|\psi\rangle$ when ψ is a Kohn-Sham orbital

delocalized across the supercell.

To circumvent this issue, it is common practice in periodic DFT to compute transition dipoles using the momentum operator formalism, which relates the dipole matrix element to the gradient of the wavefunction:

$$\vec{\mu}_{eg} = \langle \psi_g | e\vec{r} | \psi_e \rangle = \frac{e\hbar^2}{(\epsilon_f - \epsilon_i)m} \langle \phi_f | \nabla | \phi_i \rangle \quad (2.51)$$

where ϕ_i and ϕ_f are the initial and final Kohn-Sham orbitals involved in the optical transition, and ϵ_i , ϵ_f their corresponding eigenvalues. This expression is valid under the dipole approximation and assumes that the Kohn-Sham orbitals are reasonable proxy for the true many-body electronic states.

Using this formulation, the spontaneous emission rate (inverse radiative lifetime) is given by:

$$\Gamma_{\text{rad}} = \frac{1}{\tau_{\text{rad}}} = \frac{2n_r\omega^3}{3\epsilon_0\hbar c^3} |\vec{\mu}_{eg}|^2 \quad (2.52)$$

with $\hbar\omega = E_{\text{ZPL}}$ is the photon energy and n_r is the refractive index of the host material.

This expression reveals the inverse cubic scaling of lifetime with photon energy and the inverse quadratic scaling with dipole strength. Transitions with small dipole moments (*e.g.* due to weak wavefunction overlap or symmetry suppression) exhibit long lifetimes, while transitions with large energy gaps and strong orbital overlap are more radiatively active. In this thesis, we evaluate all optical transition dipole moments according to Equation 2.51 using the WEST code [8,9].

2.5.5 *Electric Dipole Moments from Wannier Functions*

A central goal in evaluating the functionality of donor-acceptor pairs (DAPs) and surface-defect pairs (SDPs) is to understand their electric dipole moment. In extended periodic systems, this task is complicated by the fact that the position operator $\vec{r}$ is defined due

to the boundary conditions imposed by translational symmetry. As a result, traditional definitions of polarization and dipole moment - based on real-space integration of charge densities - cannot be directly applied in crystalline solids.

To resolve this, we employ the modern theory of polarization [99, 100], which interprets macroscopic polarization in a crystal as a geometric phase (Berry phase) associated with the occupied electronic states. This formalism provides a rigorous way to compute polarization differences between two electronic states of the system, even when the absolute value of polarization is itself multi-valued due to the presence of polarization "branches" on the lattice separated from each other by $e\vec{R}_i/\Omega$, where Ω is the volume of the supercell and $\vec{R}_i$ is the lattice vector along direction i .

In the context of our work, the electric dipole moment $\vec{\mu}$ of a defect is computed as a difference in polarization between two states - typically the excited (initial) and ground (final) configurations - on the same polarization branch:

$$\vec{\mu} = \Omega \Delta \vec{P} = \Omega [\vec{P}_{es} - \vec{P}_{gs}] \quad (2.53)$$

where $\vec{P}_{gs}$ and $\vec{P}_{es}$ are the total polarizations of the ground and excited state configurations respectively, and Ω is the volume of the supercell. In practice, this is evaluated as:

$$\vec{\mu} = \Omega \Delta \vec{P} = \left(\sum_i Z_i \vec{R}_i - \sum_n^{occ} e \bar{\mathbf{r}}_n \right)^{es} - \left(\sum_i Z_i \vec{R}_i - \sum_n^{occ} e \bar{\mathbf{r}}_n \right)^{gs} \quad (2.54)$$

where Z_i and $\vec{R}_i$ are the nuclear charges and positions, and $\bar{\mathbf{r}}_n$ are the centers of maximally localized Wannier functions (MLWFs) constructed from the occupied electronic states.

Wannier functions $w_n(\vec{r})$ are spatially localized representations of the Bloch orbitals in a periodic solid, constructed via a unitary transformation. A Wannier function $w_n(\vec{r} - \vec{R})$ in supercell $\vec{R}$ associated with band n can be written as:

$$\begin{aligned}
w_n(\vec{r} - \vec{R}) &= \frac{\Omega}{(2\pi)^3} \int d^3\vec{k} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) \\
&= \frac{\Omega}{(2\pi)^3} \int d^3\vec{k} e^{i\vec{k}\cdot(\vec{r}-\vec{R})} u_{n\vec{k}}(\vec{r})
\end{aligned} \tag{2.55}$$

where $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})$ are the Bloch functions written with the cell-periodic part.

This transformation introduces a gauge freedom in the phase and mixing of the Bloch states, which can be fixed by minimizing the total quadratic spread of the resulting Wannier functions. The maximally localized Wannier functions (MLWFs) are those that minimize the functional:

$$\Omega_{\text{spread}} = \sum_n [\langle w_n | \vec{r}^2 | w_n \rangle - \langle w_n | \vec{r} | w_n \rangle^2] \tag{2.56}$$

which results in a unique and physically meaningful set of orbital centers $\bar{\mathbf{r}}_n$ given by:

$$\bar{\mathbf{r}}_n = \langle w_n | \vec{r} | w_n \rangle \tag{2.57}$$

The resulting orbital centers $\bar{\mathbf{r}}_n$ serve as a proxy for the electronic component of the total polarization since we treat these orbitals centers as where electrons are residing "on average". It is worth noting that the concept of a well-localized orbital center, embodied by a Wannier function, implicitly invokes a trade-off governed by the Heisenberg uncertainty principle. Any attempt to simultaneously assign both a position and momentum to an orbital is fundamentally limited by $\Delta x \Delta p \geq \hbar/2$. The process of constructing MLWFs minimizes the spatial spread of the orbital, maximizing our knowledge of its position, but at the cost of delocalizing its momentum content. In this way, the mathematical formalism underlying Wannier localization mirrors the physical constraints of quantum mechanics: the more tightly an orbital is confined in real space, the less certain we are of its crystal momentum, and vice versa.

In our calculations, the ground and excited states of DAPs and SDPs were computed using the Δ SCF method (also known as constrained DFT). MLWFs were constructed from the

occupied states using the Wannier90 [101] package. The total dipole moment was extracted from the polarization difference, using the above expressions, with care taken to remain on the same polarization branch in both configurations.

CHAPTER 3

DONOR-ACCEPTOR PAIRS IN BULK DIAMOND AND SILICON CARBIDE

Adapted from A. Bilgin, I. N. Hammock, J. Estes, Y. Jin, H. Bernien, A. A. High & G. Galli. Donor-Acceptor Pairs in Wide-Bandgap Semiconductors for Quantum Technology Applications. npj Comput. Mater. 10, 7 (2024)

3.1 Introduction

A central challenge in quantum engineering is identifying systems that support long-range, coherent interactions while remaining optically accessible and compatible with scalable device integration [15,102,103]. Solid-state platforms such as diamond and silicon carbide (SiC) have emerged as promising hosts for quantum technologies, owing to their wide bandgaps, high-quality crystal growth, and the ability to host point defects with coherent spin and optical transitions [15,32,34,45,61,104]. Defect centers such as the nitrogen-vacancy (NV) center in diamond and divacancies in SiC have been used to demonstrate single-qubit control, quantum memories, and spin-photon entanglement [32,33,44–46,105]. However, these systems remain limited in the range and tunability of interactions between qubits.

Most solid-state qubit platforms rely either on short-range spin-spin interactions [32] (which are limited to only a few nm) or on long-distance photonic links that require probabilistic entanglement schemes [44–46]. These extremes of the spatial interaction scale - atomic proximity and meter-scale optical channels - leave a critical gap in the $10^{-8} - 10^{-6}$ m range where deterministic interactions could enable fast, on-chip interactions that lead to local quantum gates across engineered arrays. Addressing this intermediate length scale requires new approaches for coupling quantum emitters.

One promising candidate is the donor-acceptor pair (DAP) system: a pair of oppositely

charged defects in a semiconductor host, separated by a fixed distance. Optical excitation causes the creation of an electron bound to the donor, and a hole bound to the acceptor site. The electron and hole can radiatively recombine to emit a photon, leaving behind a charged donor and acceptor. The resulting configuration supports an optically controllable electric dipole moment, a feature that can facilitate long-range dipole-dipole interactions and thus bridge the intermediate length scale problem of quantum emitters.

While DAPs have been widely studied in the past for their roles in photoluminescence and charge transport in semiconductors [58–61, 106], their relevance to quantum information science has only recently been recognized [65, 107]. Emerging proposals suggest that these defects can serve as qubit building blocks with reconfigurable interactions, leveraging their dipole moments in a way analogous to Rydberg atoms in cold-atom systems. In particular, dipolar coupling between DAPs scales as $1/R^3$, enabling interaction energies in the ~ 100 MHz range from tens of nm away, well within the fabrication capabilities of current nanofabrication tools and significantly exceeding typical spin-spin coupling strengths at the same distance.

In this chapter, we investigate DAPs in two archetypal wide bandgap semiconductors: diamond and SiC. Both materials are known for their excellent spin coherent properties, mature growth techniques, and wide bandgaps, which help isolate defect levels and suppress phonon mediated decoherence [108–111]. We focus on substitutional donors and acceptors placed on nearest-neighbor to mid-range lattice shells (up to the tenth shell number) and evaluate their electronic, optical, and dipolar properties using first-principles density functional theory. We characterize their zero-phonon line (ZPL) energies, electric dipole moment magnitudes and the resulting dipolar interaction strengths as well as their radiative lifetimes, phonon coupling properties and expected PL spectra.

The goal is to assess which DAP configurations exhibit favorable properties for quantum applications, and to understand the tradeoffs between host material, defect species,

dipole strength and spectral stability. Particular attention is paid to how these quantities vary across different lattice separations and orientations, and how well simple models (*e.g.* effective mass binding energies estimates) compare with first-principles predictions. By combining these insights, we aim to evaluate whether DAPs in bulk diamond and SiC offer a viable route to optically controllable, long-range and scalable interactions between quantum states in the solid-state.

3.2 Computational Methods

The electronic structure calculations presented in this chapter are based on density functional theory (DFT), as outlined in Chapter 2. Here, we provide a focused description of the specific methodological choices used in modeling donor-acceptor pairs (DAPs) in diamond and 3C-SiC, with emphasis on how these choices relate to the physical quantities of interest.

All calculations were performed using the Quantum ESPRESSO [79–81] package with plane-wave basis sets and SG15 ONCV pseudopotentials [82, 83]. A kinetic energy cutoff of 90 Ry was used in all calculations to ensure convergence of total energies and forces. For all structural relaxations, forces were minimized to below 1 meV/Å. Structural relaxations were done using both the PBE and the HSE functionals, leading to different converged lattice constants for PBE and HSE. Those lattice parameters obtained with PBE (HSE) were $a_0 = 3.568$ (3.543) Å for diamond and $a_0 = 4.381$ (4.362) Å for 3C-SiC respectively, compared with the experimental values of 3.567 Å for diamond and 4.360 Å for 3C-SiC.

All electronic structure related quantities, such as charge transition levels (CTLs) and zero-phonon lines (ZPLs) and the photoluminescence (PL) spectra were computed with supercells constructed and geometrically relaxed with the above parameters, both the PBE and the HSE functionals. Exceptions to this are radiative lifetimes, which were computed only using the PBE functional, as the implementation of Equation 2.51 with hybrid functionals was not available on WEST. The electric dipole moments of DAPs were also computed using

only the PBE functional, as this quantity is less a function of electronic structure and is more strongly determined by local geometry.

We employed primitive cubic supercells containing 512 atoms (*i.e.* 4x4x4 primitive unit cells) for all bulk DAP calculations. This cell size was selected based on convergence tests, ensuring that defect-defect image interactions are minimized and that CTLs are converged to within ~ 0.05 eV. All Brillouin zone sampling was done using the Γ -point only, as the large size of the supercell ensures adequate sampling of reciprocal space.

Defects were modeled as substitutional impurities. We focused on Group III and V impurities, specifically *B*, *N* and *P* atoms replacing carbon atoms in diamond; and *B*, *N* atoms replacing a carbon and *Al* replacing a silicon in SiC. We examined the ground and excited state geometry of each of these defects and computed their CTLs. For each DAP configuration, we generated catalog of atomic separations based on shell numbers (denoted $m_1, m_2, \dots$) Donors and acceptors were inserted into these shell positions, and the atomic structure was relaxed for both ground and excited states. The DAPs considered in this study span neighbor shells up to m_{10} , corresponding to a separation of 5.64 (6.93) Å in diamond (3C-SiC). This distance is slightly below $L/2 \approx 7.14$ (8.76) Å in diamond (3C-SiC) where L is the sidelength of the 512 atom cubic supercell. This upper bound ensures that the pairwise DAP distance within the same supercell remains smaller than any of the possible pairwise distances between images under periodic boundary conditions, thereby guaranteeing that the computed interaction and dipole moment correspond to an intra-supercell pair, and not to interactions with periodic images.

Excited states were treated using the constrained DFT (Δ SCF) approach, in which an electron is removed from the highest occupied molecular orbital (HOMO) and placed into the lowest unoccupied molecular orbital (LUMO), which in this case corresponds to creating a hole at the acceptor site by promoting the electron to the donor site. The ZPL energy was computed as the total energy difference between the relaxed excited and ground states. To

interpret the trends in ZPL energy as a function of donor-acceptor separation we compute Coulombic correction energy $J(R_m)$ mentioned in Section 1.1.1 according to Equation 1.5. This quantity accounts for the dominant redshift from expected ZPL values observed for small shell numbers where electron and hole wavefunctions overlap appreciably. By determining the ZPL energies and explicitly computing the Coulombic correction energies $J(R_m)$, we tested the DAP model Equation 1.9.

Additionally, different configurations of DAPs (with different donor-acceptor pairings) were used to compute the PL spectra with the 1D CC diagram (see Section 2.5.2), constructed from the ground and excited state relaxed geometries. The mass-weighted displacement ΔQ and effective phonon frequencies $\omega_{\{g,e\}}$ were used to compute the vibrational overlap integrals $\langle \chi_n^{(e)} | \chi_m^{(g)} \rangle$, from which we built the full PL spectrum. This allowed us to extract phonon sidebands and Debye-Waller factors related to different donor-acceptor pairings. These features are crucial for determining whether a given DAP exhibits narrow optical emission and is suitable for dipole-mediated coupling.

For estimating electric dipole moments, we employed the modern theory of polarization [99, 100] using maximally localized Wannier functions (MLWFs) constructed via Wannier90 [101]. Polarization differences between the ground and excited states, computed on the same branch of the polarization lattice, yield the total electric dipole moment of the DAPs. To validate this method, we constructed an independent check using Stark shift analysis: an external electric field was applied along a crystallographic axis, and the resulting ZPL shift was measured. The instantaneous slope at zero field yields the dipole moment, which agrees quantitatively with the MLWF-derived value within 5%.

All formation energies, CTLs were corrected for finite size effects using image-charged corrections [86] and extrapolation schemes where needed. For values obtained with hybrid functionals, we computed a scaling slope from the PBE data and used it to extrapolate the hybrid result to the dilute limit.

3.3 Results and Discussion

3.3.1 Structural Properties of Substitutional Defects

The formation of DAPs in diamond and silicon carbide is accompanied by local symmetry breaking and atomic relaxations, particularly when the charge state of the constituent defect changes during optical excitation. These structural distortions are central to understanding the resulting dipole moments, vibrational properties, and the overall response of the pair to applied fields. In this section, we analyze the relaxed geometries of individual donors and acceptors in their relevant charge states and seek to understand how their local geometry relates to other electronic properties discussed later on.

We begin by characterizing isolated defects in their relevant charge states. A compact summary of the local structure and bond lengths for all the impurities is given in Table 3.1. In Table 3.1, the bond lengths are given in units of the equilibrium C-C (Si-C) bond length of 1.55 (1.90) Å in diamond (SiC). For acceptors such as B_C in diamond (also in SiC) and Al_{Si} in silicon carbide, the neutral charge state typically exhibits C_{3v} symmetry, while the negative charge state recovers the T_d symmetry, with all nearest neighbor bonds equal. In the case of B_C in diamond, the neutral configuration shows three bond length of 1.58 Å, and one elongated bond at 1.61 Å, whereas the negatively charged state has four bonds of 1.58 Å each. A similar pattern of switching between T_d and C_{3v} symmetries upon changing the charge state is observed for Al_{Si} and B_C in SiC with slight variations to bond lengths.

In contrast, the nitrogen donor N_C exhibits markedly different behavior across hosts. In diamond, N_C undergoes a dramatic geometry change when transitioning from the positive to the neutral charge state. The positively charged state retains the T_d symmetry with bond lengths of 1.57 Å, while in the neutral state, one bond elongates to 2.06 Å, corresponding to a 33% distortion compared to the equilibrium C-C bond length of 1.55 Å. This is a substantial Jahn-Teller effect and a strong indicator of localization. This distortion foreshadows the

Table 3.1: A summary of symmetries and ground state geometries of substitutional defects in diamond and 3C-SiC are given based on their respective charge states. Bond lengths are given in units of the calculated diamond equilibrium C-C bond length of 1.55 Å for defects in diamond. For defects in 3C-SiC, the respective equilibrium Si-C bond length of 1.90 Å is used. The numbers in brackets indicate the number of bonds of the given length stemming from each central atom.

Host	Defect	q	Symmetry	Bond length
Diamond	B_C	0	C_{3v}	1.02(3), 1.04(1)
		-1	T_d	1.02(4)
	N_C	0	C_{3v}	0.95(3), 1.33(1)
		1	T_d	1.01(4)
	P_C	0	T_d	1.10(4)
		1	T_d	1.10(4)
3C-SiC	B_C	0	C_{3v}	1.02(3), 1.08(1)
		-1	T_d	1.01(4)
	N_C	0	T_d	1.01(4)
		1	T_d	1.01(4)
	Al_{Si}	0	C_{3v}	1.04(3), 1.07(1)
		-1	T_d	1.05(4)

strong vibrational coupling and high Huang-Rhys (HR) factor observed for N_C -containing DAPs as will be discussed in Section 3.3.6.

On the other hand, phosphorus P_C and N_C in SiC remain structurally rigid across charge states. For both cases, all four nearest neighbor bonds are essentially unchanged between charge configurations, indicating their shallow character and weak coupling to the lattice. Specifically, P_C retains T_d symmetry in both charge states with four identical bonds of 1.70 Å, while N_C in SiC remains at 1.92 Å regardless of its charge state. Considering the distortion compared to the equilibrium bond lengths, it is also straightforward to conclude that P_C , although still considered a shallow donor in diamond, is going to be a deeper donor

when compared with N_C in SiC, which shows very little distortion to the local equilibrium geometry.

The structural distortion of each isolated defect has direct implications for the geometry change between the ground and excited states of the DAP, which in turn determines key optical and dipolar properties. When a DAP transitions from the ground to the excited state, the local relaxation of the donor and acceptor sites induces a shift in equilibrium atomic positions. The total mass-weighted displacement ΔQ used in the CC model is computed from the combined geometry change across all atoms, and it is largely controlled by how much each defect locally distorts upon ionization. For this reason, defects such as N_C in diamond - which exhibit large single bond elongations - tend to contribute strongly to ΔQ when incorporated into a DAP.

This also affects the magnitude of the Huang-Rhys (HR) factor, which scales with ΔQ^2 , and consequently impacts the strength of the phonon sideband and the spectral sharpness of the defect's emission line. Hence, defects with highly asymmetric geometry changes tend to show stronger vibronic coupling and broader emission.

Furthermore, the directionality of the electric dipole moment generated by a DAP is sensitive to the specific nature of the distortion at each defect site. Because the electric dipole vector is determined not only by the net charge separation between donor and acceptor, but also by how the charge distribution shifts relative to the lattice, the orientation of the elongated bond can tilt the dipole away from the pure lattice vector connecting the two sites. When the elongated bond aligns with the DAP axis, the net dipole is reinforced in that direction; when it points in the opposite direction, the net dipole is suppressed. This behavior introduces configuration-dependent angular variation in the electric dipole, as discussed further in Section 3.3.4. Thus, even though the defect species and their separation largely determine the dipole magnitude in a point-charge picture, the local symmetry breaking and distortion patterns introduce important corrections that must be captured through

full atomic relaxation and real-space dipole analysis.

Table 3.2: Bandgaps of diamond, 3C- and 4H-SiC in eV computed using different exchange-correlation functionals, PBE [10], HSE [11], and DDH [12,13]. Experimental bandgaps values are also provided for comparison.

Host	PBE	HSE	DDH	Experimental
Diamond	4.17	5.37	5.42	5.48 [112]
3C-SiC	1.40	2.25	2.35	2.39 [113]
4H-SiC	2.25	3.23	3.26	3.23 [114]

3.3.2 Charge Transition Levels

The ability of a donor or acceptor to change their charge state within the bandgap is a key determinant of its optical addressability and electronic behavior. These charge transition levels (CTLs) define the Fermi-level positions at which a defect switches its most stable charge state, and they play a central role in determining the optical accessibility and emission energetics of DAPs. Accurate knowledge of the CTLs of defects is essential to ensure that (i) the neutral charge state (*i.e.* the excited state after optical excitation) is accessible upon optical excitation and (ii) the charged configuration is stable in the ground state. These conditions are prerequisites for the formation of a photoactive DAP with a well-defined optical transition and electric dipole moment. In this section, we report the computed CTLs for the isolated defects involved in DAP formation in both diamond and 3C-SiC, using both the PBE and HSE functionals. As a crucial reference point - both for this section and later comparisons - we first present the calculated bandgap values of diamond, 3C-SiC and 4H-SiC in Table 3.2. We then refer directly to the CTL data summarized in Table 1 of our previous work [3], also reprinted below for convenience in Table 3.3.

CTLs were computed as described in Chapter 2 using the expression:

$$\epsilon(q/q') = \frac{E_f[X^q; E_F = 0] - E_f[X^{q'}; E_F = 0]}{q' - q} \quad (3.1)$$

Table 3.3: Computed charge state transition levels (CTLs), referenced in eV to the valence (E_V) and conduction (E_C) band edges, for boron (B_C), nitrogen (N_C) and phosphorous (P_C) in diamond, and boron (B_C) and nitrogen (N_C) replacing carbon and aluminum replacing silicon (Al_{Si}) in 3C-SiC. We report results obtained with two density functionals, PBE [10] and HSE [11] as well as results of previous work.

Host	CTL	PBE (HSE)	Previous Work
Diamond	B_C (0/-)	$E_V + 0.35$ (0.35)	$E_V + [0.37-0.38]^a$
	N_C (+/0)	$E_C - 1.47$ (1.80)	$E_C - [1.7-1.9]^b$
	P_C (+/0)	$E_C - 0.45$ (0.47)	$E_C - [0.5-0.6]^c$
3C-SiC	B_C (0/-)	$E_V + 0.37$ (0.57)	$E_V + [0.6-0.73]^d$
	N_C (+/0)	$E_C - 0.16$ (0.16)	$E_C - [0.05-0.06]^e$
	Al_{Si} (0/-)	$E_V + 0.17$ (0.19)	$E_V + [0.24-0.26]^f$

^a Ref. [115, 116], ^b Ref. [15, 108, 116–119], ^c Ref. [120, 121]

^d Ref. [122, 123], ^e Ref. [123–125], ^f Ref. [122, 124, 125]

where $E_f[X^q; E_F = 0]$ is the formation energy of the defect X at charge state q evaluated at the valence band maximum (VBM), computed according to Equation 2.30. Potential alignment corrections and finite size extrapolation procedures were applied where relevant. Both the PBE and HSE functionals were employed, the former for efficient configurational sampling, and the latter for quantitatively accurate level positioning in wide bandgap hosts.

In diamond, we studied the following substitutional defects: boron (B_C) as an acceptor, nitrogen (N_C) and phosphorus (P_C) as donors. These span both shallow and deep behavior, offering insight into their electronic stability and lattice interaction.

- B_C shows a (0/-) transition at 0.35 eV above the valence band. This level lies relatively shallow in the gap and is consistent with B_C 's known role as a shallow acceptor in diamond. The transition corresponds to a delocalized hole with a rather large Bohr radius, as reflected by its small lattice distortion in Table 3.1.
- P_C shows a (+/0) transition at roughly 0.45 (0.47) eV below the conduction band as predicted by the PBE (HSE) functional, compared to the experimentally reported

values around 0.5-0.6 eV below the conduction band. Despite often being referred to as a "shallow" donor in experimental literature, and attempts to do n-doping in diamond with phosphorus, it remains too deep a donor level for thermal excitation of electrons into the conduction band at room temperature.

- N_C shows a $(+/0)$ transition at 1.47 (1.80) eV below the conduction band according to PBE (HSE). This defect introduces a deep donor level in the upper half of the bandgap. The HSE prediction puts the defect ~ 0.3 eV deeper, consistent with previous experimental characterizations. The large structural distortion the defect undergoes is indicative of a sharp localization of its associated electronic state, which the PBE functional underestimates significantly.

Similarly, we studied several substitutional defects in 3C-SiC. These include a boron acceptor B_C , and a nitrogen donor N_C , both replacing a carbon atom in the lattice, and an aluminum acceptor Al_{Si} , which replaces a Si atom instead.

- B_C shows a $(0/-)$ transition above 0.37 (0.57) eV above the valence band according to the PBE (HSE) functional. The ~ 0.2 eV increase in depth predicted by HSE reflects a slight correction due to increased localization. B_C remains an intermediate-depth acceptor in SiC and plays a secondary role in this work. Still, its position well within the ~ 2.3 -2.4 eV bandgap of 3C-SiC makes it a viable candidate in some DAP configurations, although its role is largely illustrative here.
- N_C has a $(+/0)$ transition 0.16 eV below the conduction band. Interestingly, the position of the donor level remains unchanged across both functionals. This is characteristic of a shallow defect, where the defect state has significant conduction or valence band character and is already well described by semi-local DFT. The small depth ensures strong electron availability and weak lattice perturbation, consistent with its modest geometry change upon a charge state transition.

- Al_{Si} gives a (0/-) transition at 0.17 (0.19) eV above the valence band with the PBE (HSE) functionals. Similar to N_C , Al_{Si} is located very close to its respective band edge. The minor HSE shift from PBE further confirms the delocalized nature of its hole state. The similarity between functionals here supports its role as a defect that only causes a minor lattice distortion.

Overall, PBE and HSE predictions differ most significantly for deep defects (notably N_C in diamond), while shallow defects like B_C in diamond or Al_{Si}/N_C in SiC show minimal discrepancy. The extent of the HSE shift correlates well with the degree of electronic localization and the magnitude of geometric distortion upon changing a charge state, in line with expectations from literature.

Crucially, in all cases, the relevant neutral and charged states of the donors and acceptors are stabilized well within the bandgap. This is a crucial result: it confirms that these donors and acceptors are stable both in the ground and excited state of DAP complexes that would be formed by pairing them. That is, upon optical excitation, charge transfer does not spontaneously relax into the conduction or valence band, ensuring the formation of a bound, dipolar excited state that can mediate interaction and emit photons in the optical range.

The agreement of HSE predictions with experimental ranges to within ~ 0.1 eV for all the defect types provides further validation of the underlying methodology and functional choice. These computed CTLs will serve as the foundation for all subsequent modeling in later sections.

3.3.3 Zero-Phonon Lines

The zero phonon line (ZPL) energy is a central quantity in evaluating the optical behavior of DAPs. It defines the energy of photon emission in the absence of phonon sidebands and is sensitive to both the electronic structure of the defect complex and its spatial configuration. In this work, ZPLs are computed using the constrained DFT (Δ SCF) approach, as outlined

in Section 2.5.2. The ZPL is evaluated as the total energy difference between the relaxed geometries of the excited and the ground states.

In order to evaluate ZPL energies as a function of increasing inter-defect distance R_m , indexed by the shell number, we placed donors and acceptors at increasingly large distances relative to each other. We re-write Equation 1.9 below, altered slightly to emphasize the linear fitting that is used:

$$\hbar\omega_m = E_g - (E_A + E_D) + \frac{k_e e^2}{\epsilon_r r_b} \frac{r_b}{R_m} + J(R_m) \quad (3.2)$$

Here, $\hbar\omega_m$ is the ZPL energy, E_g , E_D and E_A are the bandgap, and donor and acceptor binding energies respectively. k_e is the Coulomb constant and r_b is the equilibrium bond length between nearest neighbor atoms (1.55 Å for diamond, 1.90 Å for 3C-SiC). Finally $J(R_m)$ is the Coulomb correction energy mentioned in Section 1.1.1 that must be computed through an integral in order to test the linear fit. Note that the upon fitting the ZPL against $\frac{r_b}{R_m}$, the slope $\frac{k_e e^2}{\epsilon_r r_b}$ is determined only by host related constants ϵ_r and r_b . In other words, the slope is completely defect-agnostic, and can be used to test the goodness of fit for any DAP combination, regardless of the specific donor or acceptor species involved.

Another important factor to note here is that the ZPL values obtained from constrained DFT already include the effects captured by $J(R_m)$, and therefore, $J(R_m)$ needs to be subtracted from both sides of Equation 3.2 to fully linearize it and compare the DAP model equations with values obtained from constrained DFT. This is precisely what we did in Figure 3.2, and we present the summarized results in Table 3.4. We also include in Figure 3.1 the trends observed in the correction energy $J(R_m)$ as a function of distance. These integrals are calculated according to Equation 1.5 using Kohn-Sham orbitals corresponding to the hole and electron wavefunctions bound to acceptors and donors respectively. As expected, this correction term is significant especially for small pair separations [58, 61, 126], and quickly approaches zero as the pair separation is increased. We find that the magnitudes

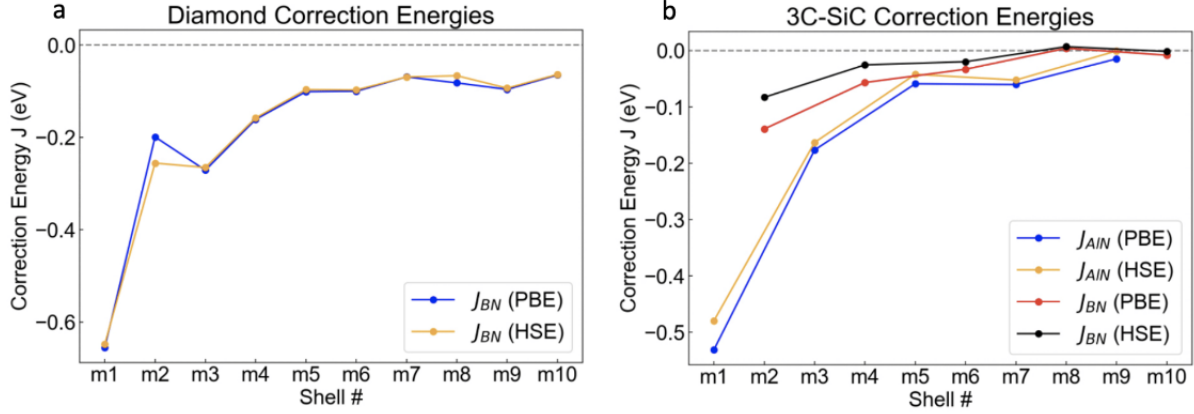


Figure 3.1: $J(R_m)$ correction energies are presented as a function of shell number in for (a) B-N DAPs diamond and (b) both for Al-N and B-N DAPs in 3C-SiC.

for correction energies in the first few shells are in the expected range according to previous calculations and observations [126, 127].

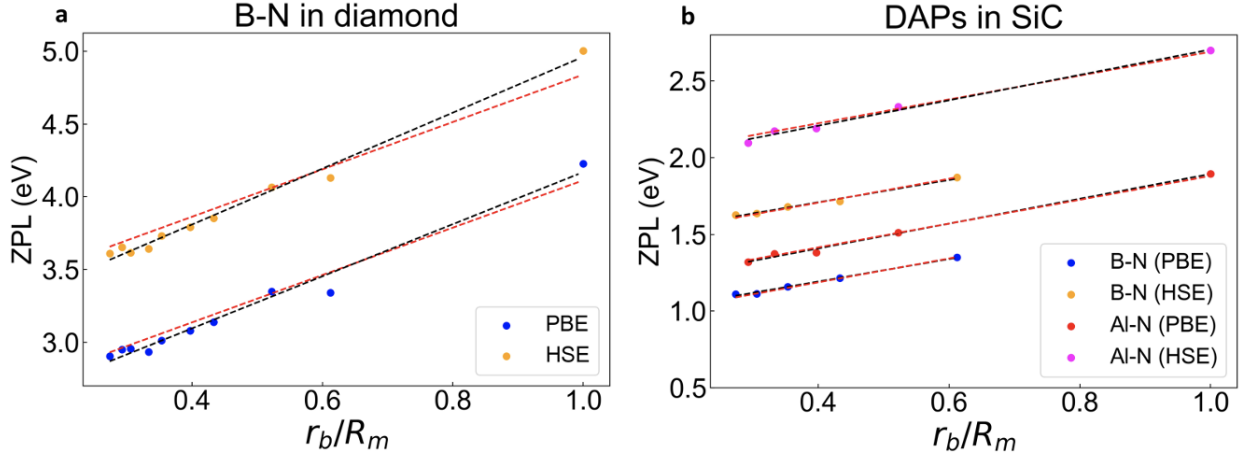


Figure 3.2: Computed zero-phonon lines (ZPL) energies using constrained DFT are compared with those obtained with the DAP model Equation 3.2 for both (a) diamond and (b) 3C-SiC. r_b is the equilibrium bond length between nearest neighbor atoms (1.55 Å for diamond, 1.90 Å for 3C-SiC) and R_m is the distance between the donor and acceptor for a given shell m . Red dashed lines represent Equation 3.2 and the black dashed lines are the results obtained from constrained DFT. Figure and caption reproduced from [3].

We observe systematic differences in ZPL predictions between functionals. As expected,

the HSE functional consistently yields higher ZPL values than PBE, with shifts ranging from 0.4 to 0.7 eV depending on the pair and shell. These shifts reflect the wider bandgap and improved defect level positioning obtained with HSE. However, the trends with distance are preserved across both functionals, and the two datasets are vertically offset rather than structurally distinct. This consistency allows us to use PBE to extract scaling trends efficiently, and anchor the absolute ZPL values with more computationally expensive HSE calculations.

The behavior of ZPL as a function of increased shell number is well reproduced by the DAP model. The DAP model predicts the theoretical value of the slope $\frac{k_e e^2}{\epsilon_r r_b}$ to be 1.64 (0.78) eV in diamond (3C-SiC) when $\epsilon_r = 5.7$ (9.72) and $r_b = 1.55$ (1.90) Å are used. The slopes obtained from computed ZPL values for both Al-N and B-N pairs in 3C-SiC are close to the ones predicted by the model. The PBE and HSE functionals yield similar results for B-N and Al-N pairs in 3C-SiC. The difference between model-predicted slope and the observed slope from DFT is considerably larger in diamond compared to DAPs in 3C-SiC. This difference stems from the approximations used for the wavefunctions in the DAP model (perturbed Hydrogen-like wavefunctions due to the effective mass approximation [59, 127]), which has different ranges of validity depending on the host and pair. Such an approximation performs poorly for defects that lie deeper in the bandgap, such as the N_C donor used here in diamond.

Table 3.4: A summary of the parameters obtained from Figure 3.2. The slope and y-intercept values for the linear fit are reported in units of eV for both the PBE and the HSE functionals. The sum of the binding energies is determined by subtracting the y-intercept from the bandgap E_g

	B-N (diamond)		B-N (3C-SiC)		Al-N (3C-SiC)	
	PBE	HSE	PBE	HSE	PBE	HSE
slope	1.79	1.92	0.73	0.73	0.81	0.83
y-int	2.38	3.04	0.90	1.42	1.08	1.88
$E_D + E_A$	1.82	2.33	0.50	0.84	0.32	0.38

From the y-intercept, we can also infer the sum of the binding energies of the donor and acceptor. In all cases, the predicted sums for the binding energies are within 0.1 eV of the calculated combinations of sums of binding energies from Table 3.3. Although we obtained all our results from first-principles, our comparisons with the DAP model show that this model is a useful tool to predict ZPL energies as a function of distance can be provide semi-quantitative results. Our calculated ZPL energies for the first few shells of Al-N pairs in 3C-SiC using the HSE functional are in the range 2.10-2.25 eV, in agreement with experimental values in the range 2.25-2.30 eV [128,129]. Similarly, our HSE predictions for the first few shells of B-N pairs in 3C-SiC fall within 1.6-1.8 eV, remarkably close to previous experimental observations in the range 1.75-1.95 eV [123].

From a quantum engineering perspective, the ability to tune ZPL energies over a wide spectral range simply by varying the DAP shell number is highly appealing. In both diamond and SiC, DAPs can be engineered to emit at a wide-range of energies depending on the donor and acceptor species, and their separation. The fact that a wide range of ZPL energies are available to DAPs distinguishes them from fixed-point defects such as NV- in diamond, whose ZPL is locked to 1.945 eV, and highlight the design flexibility enabled by DAP separation.

In summary, the ZPL scaling with shell number is well captured by the combined first-principles and DAP model approach, with $J(R_m)$ corrections enabling accurate trend isolation. Functional differences modulate the absolute values but do not alter the physical interpretation. The broad spectral range of emission energies, in agreement with experimental observations, establish ZPL control as a key asset of the DAP platform for quantum photonics applications.

3.3.4 *Electric Dipole Moments and Interaction Strength*

The key defining feature of DAPs is the emergence of a spatially separated electron-hole configuration in the excited state and a return to the ionized donor and acceptor picture in

the ground state. This produces a static electric dipole moment in the ground state configuration that can be switched off in the excited state via optical excitation. This property fundamentally distinguishes DAPs from other quantum emitters such as color centers, where dipole moments tend to be small, fixed by crystal symmetry, and often vanish due to inversion symmetry. In contrast, the dipole in DAPs is large, tunable via spatial separation, and oriented along the axis connecting the donor and acceptor. This opens a pathway for achieving dipole-dipole interactions at meaningful distances, providing a physical mechanism for implementing conditional gates and long-range qubit coupling in solid-state quantum networks.

We compute the dipole moments using the Modern Theory of Polarization [99, 100], as discussed in Section 2.5.5. Specifically, we evaluate the change in polarization between the ground and excited states using ionic coordinates and maximally localized Wannier functions (MLWF):

$$\vec{\mu} = \Omega(\vec{P}_{es} - \vec{P}_{gs}) \quad (3.3)$$

where Ω is the volume of the supercell and $\vec{P}_{gs}$, $\vec{P}_{es}$ are the total polarizations (electronic + ionic) in the ground and excited states. These polarizations are computed using MLWFs, ensuring the resulting is gauge invariant and physically meaningful within the periodic supercell framework.

For each DAP configuration, the donor and acceptor are placed on specific crystallographic shells labeled m_1 to m_{10} (from 1.6 Å to 5.6 Å) in diamond, and m_2 to m_{10} in SiC (3.1 Å to 6.9 Å). We start from m_2 in SiC because B-N DAPs cannot be nearest neighbors in SiC, since both B_C and N_C replace carbon atoms in the lattice. The computed dipole moments vary accordingly, and, in average, scale proportionally to R_m . The results are graphically summarized in Figure 3.3 and presented in full detail in Table 3.5.

To first order, the magnitude of the dipole should scale linearly with the spatial separation

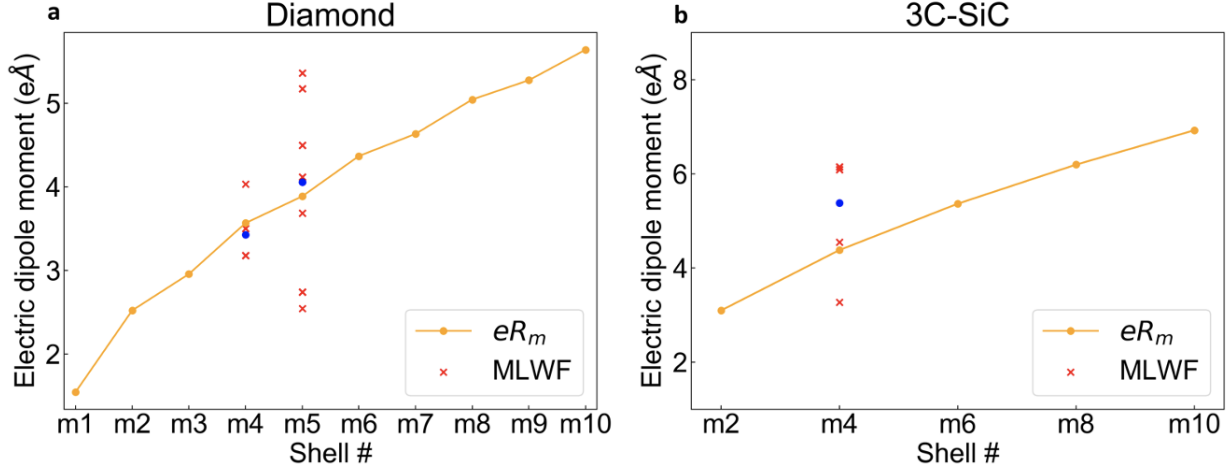


Figure 3.3: Electric dipole moments for B-N pairs (a) in diamond and (b) in 3C-SiC calculated using the approximate formula eR_m , where R_m is the donor-acceptor distance (orange dots) and Maximally localized Wannier Functions (MLWF, blue dots). The MLWF values have been obtained by averaging over the different configurations (red crosses) that the distorted bonds may attain in the crystal. The details on the relative orientations of each data point are given in Table 3.5. Figure and caption reproduced from [3].

between the donor and acceptor, *i.e.*

$$|\vec{\mu}| \approx eR_m \quad (3.4)$$

Indeed, we find that the average dipole magnitude for each shell closely tracks this expectation. However, there is notable configuration-dependent scatter within each shell due to the influence of local asymmetry and structural distortions. This variation is captured quantitatively in shells m_4 and m_5 in Figure 3.3(a), and in shell m_4 in Figure 3.3(b). Collectively they show both the mean dipole magnitude (blue dots) and the variation across all the possible geometries within their respective shells.

Although the average dipole moment in each shell follows the expected eR_m scaling, individual configurations within a given shell show considerable variation, within approximately one equilibrium bond length ($1.55 \text{ \AA}$ in diamond, $1.90 \text{ \AA}$ in SiC). This spread arises not from differences in donor-acceptor distance (which is fixed within a shell) but from the specific

DAP	Orientation	Dipole moment (eÅ)
B-N m4 (diamond)	[1, 0, 0]	3.179
B-N m4 (diamond)	[-1, 0, 0]	3.502
B-N m4 (diamond)	[0, 1, 0]	3.179
B-N m4 (diamond)	[0, -1, 0]	3.502
B-N m4 (diamond)	[0, 0, 1]	3.179
B-N m4 (diamond)	[0, 0, -1]	4.036
B-N m5 (diamond)	[0.25, 0.75, 0.75]	3.687
B-N m5 (diamond)	[0.25, -0.75, -0.75]	4.117
B-N m5 (diamond)	[-0.25, 0.75, -0.75]	2.547
B-N m5 (diamond)	[-0.25, -0.75, 0.75]	5.175
B-N m5 (diamond)	[0.75, 0.25, 0.75]	2.746
B-N m5 (diamond)	[-0.75, 0.25, -0.75]	4.499
B-N m5 (diamond)	[-0.75, -0.25, 0.75]	5.175
B-N m5 (diamond)	[0.75, -0.25, -0.75]	4.117
B-N m5 (diamond)	[0.75, 0.75, 0.25]	2.746
B-N m5 (diamond)	[0.75, 0.75, 0.25]	2.746
B-N m5 (diamond)	[-0.75, -0.75, 0.25]	5.364
B-N m5 (diamond)	[0.75, -0.75, -0.25]	4.499
B-N m5 (diamond)	[-0.75, 0.75, -0.25]	5.364
B-N m4 (SiC)	[1, 0, 0]	3.279
B-N m4 (SiC)	[-1, 0, 0]	4.546
B-N m4 (SiC)	[0, 1, 0]	6.093
B-N m4 (SiC)	[0, -1, 0]	6.153
B-N m4 (SiC)	[0, 0, 1]	6.093
B-N m4 (SiC)	[0, 0, -1]	6.153
B-N m6 (SiC)	[-0.5, -0.5, -1]	6.483
B-N m6 (SiC)	[-0.5, -1, -0.5]	6.455
B-N m6 (SiC)	[-1, -0.5, -0.5]	5.274
B-N m6 (SiC)	[-0.5, -1, 0.5]	4.739
B-N m8 (SiC)	[1, 1, 0]	7.521
B-N m8 (SiC)	[-1, -1, 0]	7.420
B-N m8 (SiC)	[-1, 0, -1]	7.420
B-N m8 (SiC)	[0, -1, 1]	6.687
B-N m8 (SiC)	[0, -1, -1]	6.687

Table 3.5: Electric dipole moment dependence on DAP orientations in the crystal. Orientations of the donor atom with respect to the acceptor atom in the supercell in units of the lattice constant a_0 , and the resulting dipole moments from MLWF calculations are given. For example, [1,0,0] orientation refers to the donor atom that is displaced by a_0 in the x-direction with respect to the acceptor. This table references the additional data (red crosses) from Figure 3.3.

orientations of the elongated bonds at the donor and acceptor sites, which distort the local charge distribution. These asymmetric distortions modify the spatial centers of donor and acceptor wavefunctions, shifting the effective centers of charge away from their lattice sites.

When the elongated bonds at the donor and acceptor sites face one another along the DAP axis, the associated charge distributions become more spatially compact, effectively resulting in a reduced dipole moment, often noticeably below eR_m . Conversely, when both distorted bonds point away from each other, the charge distribution extends further apart, amplifying the dipole beyond the point charge estimate, to noticeably above eR_m . Configurations in which the donor and acceptor relax asymmetrically, that is, not along the DAP axis but in ways perpendicular to it, tend to produce dipole magnitudes close to eR_m . These subtleties highlight the importance of considering not just the nominal defect positions but also their local structural environments when modeling dipolar interactions in DAP systems.

To independently validate the dipole moments obtained from Wannier-function-based polarization differences, we performed a series of Stark shift calculations using constrained DFT, shown in Figure 3.4. In these simulations, a uniform external electric field was applied along a fixed crystallographic direction, and the change in ZPL energy was computed as a function of electric field strength. The slope of the ZPL shift with respect to field yields an effective dipole moment according to $\Delta E_{\text{ZPL}} = \vec{\mu} \cdot \vec{E}$. The extracted dipole magnitudes from this method were found to closely match those obtained from the MLWF approach, providing strong confirmation of the consistency and physical interpretability of our dipole moment analysis. These Stark shift simulations also underscore the extreme field sensitivity of DAPs, with ZPL tuning rates in the THz range! This highlights the potential for using electric fields to selectively tune emission wavelengths and precise angular control with respect to DAP's dipole orientation.

The physical consequence of these dipole magnitudes is the possibility of achieving strong, tunable dipole-dipole interactions between DAPs. Using the standard electrostatic formula

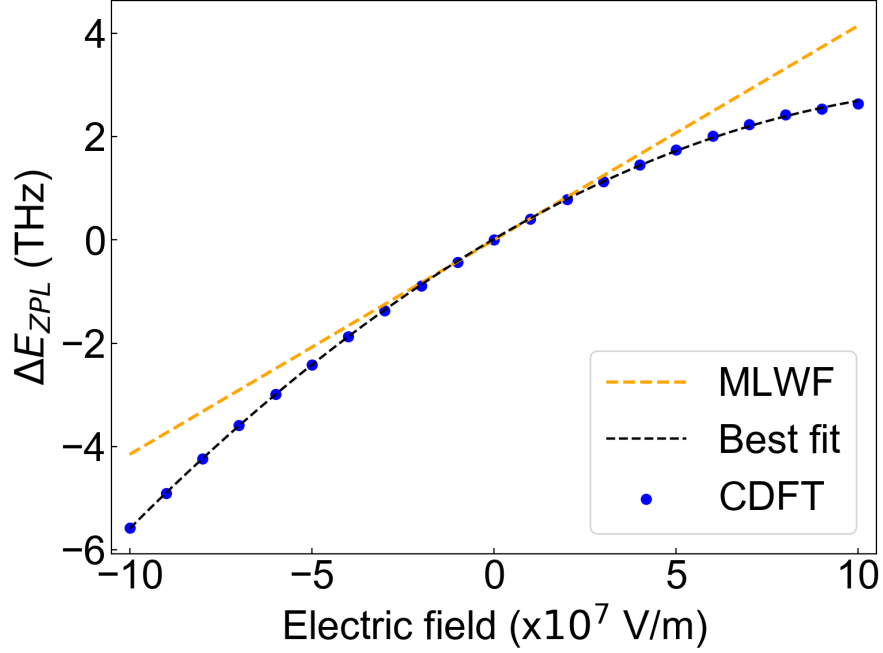


Figure 3.4: Stark shift of donor-acceptor pairs. Computed zero phonon line shift (ΔE_{ZPL}) for the m_5 shell of B-N DAPs in diamond under homogeneous applied electric field in the $[100]$ direction. The slope at zero field gives the electric dipole moment. The orange dashed line indicates the first-order energy shift to ZPL with the slope obtained from maximally localized Wannier functions (MLWF) calculations. The dark blue circles are results obtained from constrained DFT calculations with the PBE functional and the dashed line is a quadratic fit.

for dipole-dipole interaction and inserting the values obtained from MLWF-based dipole analysis, we compute the expected interaction energy between two dipoles with Equation 1.17 in Figure 3.5. Taking dielectric constants of $\epsilon_r = 5.7$ for diamond and $\epsilon_r = 9.72$ for SiC, and typical values of $\mu \approx 5\text{-}15 \text{ e}\text{\AA}$, we see that the interaction energy can be as large as 100 MHz when two DAPs are 100 nm apart. The interaction magnitude can still be quite large even when the DAPs are 200 nm apart, with estimates ranging from 1 to 10 MHz in strength, depending on the dipole magnitude. This interaction magnitude should be compared to the linewidths of resonant control lasers usually employed in these systems, which are usually no more than a few MHz. The dipole magnitudes computed here are more than capable to provide sufficient dipolar coupling between distant DAPs, separated 100 to 200 nm apart, provided that noise levels can be mitigated to sub-MHz levels. But given their large dipoles, and as shown in Figure 3.4, DAPs are very sensitive to electrical noise under the Stark shift, which can broaden their optical transitions. Such noise can be mitigated by integrating DAPs in PIN heterostructures, as experimentally demonstrated, for example, for divacancies in SiC [130]. Our proposed DAP platform is fully compatible with such structures - for instance, they can be included in functional material heterostructures such as PIN structures during growth or ion implantation - and given that the achievable dipolar interaction strength for DAPs exceeds MHz level noise, we expect that robust, coherent control for this system should be achievable.

The analysis presented here establishes DAPs as highly dipolar systems, with dipole magnitudes exceeding those of conventional point defects by orders of magnitude. These dipoles are both scalable with shell separation and directionally aligned with the DAP axis, making them exceptionally well-suited for controlled, long-range interactions. Using both polarization differences through MLWF, and Stark shift calculations, we confirmed that the ZPLs of these pairs respond sensitively to external electric fields, with tuning rates on the order of several THz. The large dipole moments of DAPs are the source of both

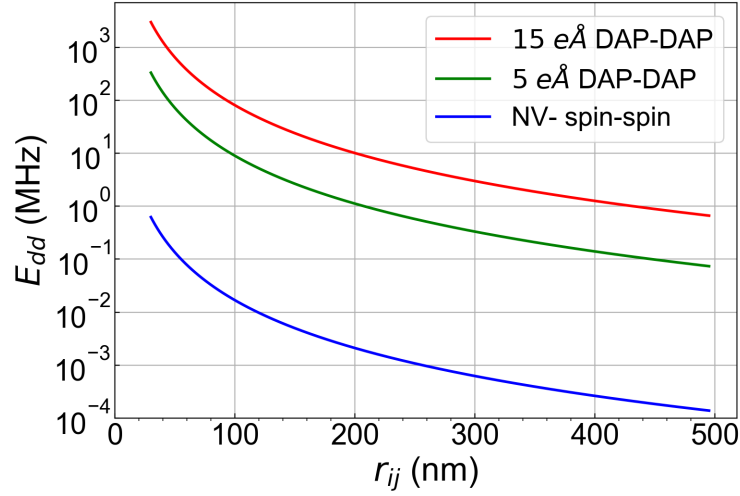


Figure 3.5: The dipole-dipole interaction strength of two DAPs assumed to have dipole moments of 15 eÅ (red, expected dipole moment from shell m_{45}) and 5 eÅ (green, expected dipole moment from shell m_6 in SiC), compared to spin-spin interactions of NV- centers in diamond (blue).

their unique strengths and some challenges. On one hand, they enable deterministic dipole-dipole interactions strong enough to support coupling over 100-200 nm distances, providing a physical basis for non-photon quantum gates, Rydberg blockades, and other collective control schemes. On the other hand, these same dipoles render DAPs highly sensitive to stray electric fields, leading to pronounced Stark shifts that can make spectral stability a challenge. These large dipoles and their sensitivity to their environment are a double-edged sword: while they complicate noise management, they also allow for precise spectral tuning and dipolar coupling in the first place. To mitigate uncontrolled fluctuations while retaining its tunability, we have proposed integrating DAPs into engineered PIN heterostructures, where noise levels can be stabilized to below MHz levels. Such a platform supports both field-mediated interaction control and scalable optical access, advancing DAPs toward viable, tunable building blocks for quantum photonic architectures.

3.3.5 Radiative Lifetimes

In any solid-state quantum emitter, the radiative lifetime determines the timescale on which a photon is emitted following electronic excitation. This lifetime not only constrains how quickly optical cycling can occur, but also defines the operational window for spin-photon entanglement protocols, photon indistinguishability, and coupling to optical cavities. For DAPs, the excited features a spatially separated electron and hole bound to donor and acceptor defects respectively. The radiative recombination rate of this pair is governed both by the optical transition dipole moment and the ZPL energy, which together determine spontaneous emission probability. We compute this quantity according to Equation 2.52 after computing the transition dipole moment matrix element as implemented in the WEST code [8, 9]. It is important that this dipole matrix element is computed in the excited state, where the electron-hole pair exists, in order to capture the correct charge distribution associated with the DAP system.

There’s a wide range of radiative recombination lifetimes reported in the literature, depending on the host and defect atoms, ranging from 100s of ps [131] to 100s of μs [60, 61], and even few ms [132]. In addition, temperature and dopant concentration levels play an important role in determining lifetimes [133]. Thomas, Hopfield and Augustyniak [133] observe luminescence in GaP after flash excitation, and their model gives μs range results. However, they also observe less than 10^{-8} second lifetimes for certain closely separated pairs. Ziemelis and Parsons [60] attribute their observation of 70-100 μs lifetimes in Si to pairs separated by 7.7 to 20 Å. On the other hand, Schneider and Dischler observe 100s of ps of radiative decay times from DAPs in diamond [131].

Our computed radiative recombination lifetimes of DAPs in diamond are estimated to be in the ns range for the first ten shells in diamond, putting these results closer to the lifetimes obtained by Schneider and Dischler in their experiments, and appear to agree with the observation of less than 10^{-8} second lifetimes for closely-separated pairs. Our predictions

for lifetimes in 3C-SiC are longer, in the μs range, closer to the predictions of [133], in part because of the energy difference involved in the transition between charged states. For example, the B-N transitions in diamond are much more energetic than B-N or Al-N transitions in SiC, and approximately order of magnitude difference in lifetimes is explained through this energy difference alone. Another order of magnitude difference comes from the optical transition dipole moment. The squared norm of the optical transition dipole moment is roughly one order of magnitude smaller in 3C-SiC compared to diamond. Taken together, the differences in energy level positions and optical dipole moment give rise to sizable differences between the expected lifetimes of B-N pairs in diamond and 3C-SiC.

We also observe distance dependent scaling of the radiative lifetime for a given species of DAPs. In diamond, we find that the first shell m_1 has a radiative lifetime of 1.8 ns, going up to 15.1 ns for the tenth shell m_{10} . we see a similar pattern emerge for Al-N and B-N DAPs in 3C-SiC, with m_1 and m_2 lifetimes around $\sim 1.3 \mu\text{s}$ and going up to $\sim 5.4 \mu\text{s}$ for m_9 and m_{10} . This pattern of longer radiative lifetimes is expected. As the donor and acceptor distance R_m is increased, there's less spatial overlap between the wavefunctions of the electron and hole, which manifests itself as a weaker optical transition dipole moment. The longer radiative lifetimes found here for Al-N and B-N pairs in 3C-SiC point to how those pairs would be more desirable compared to B-N pairs in diamond, simply because of the increased flexibility that comes with longer lifetimes in conducting optical control schemes. Radiative lifetimes in the μs range can allow for sufficient manipulation of DAP states with lasers, whereas ns range lifetimes for B-N pairs in diamond would not be long enough for similar manipulation.

3.3.6 *Electron-Phonon Coupling and Photoluminescence Spectra*

The optical properties of DAPs are not fully determined by their ZPLs alone. A critical companion quantity is the electron-phonon coupling strength, which dictates how optical emission is distributed between the ZPL and phonon sidebands. This strength is quantified

through the Huang-Rhys (HR) factor [134], the mass-weighted displacement ΔQ , and the resulting Debye-Waller factor (DWF). These quantities provide insight into the sharpness and spectral resolution of DAP emission and are indispensable for evaluating the viability of DAPs as solid-state quantum emitters.

The HR factor and DWF are computed here using a one-dimensional configurational coordinate (1D-CC) model, described in detail in Section 2.5.2. This model treats the emission process as a transition between two displaced harmonic potential energy surfaces (PESs), representing the excited and ground electronic states. From the relaxed geometries, we compute the mass-weighted displacement ΔQ , effective phonon frequencies Ω_g, Ω_e in the ground and excited states, and derive the HF factors as:

$$S_{\{g,e\}} = \frac{\Omega_{\{g,e\}} \Delta Q^2}{2\hbar} \quad (3.5)$$

The DWF is given by $\text{DWF} = e^{-S}$, a metric that captures the fraction of optical emission retained in the ZPL.

In DAPs, the electron-phonon coupling strength is particularly sensitive to the charge-dependent structural relaxation of both donor and acceptor sites, as well as the identity and depth of the defect states involved. Through the 1D-CC model, we extract detailed information on mass-weighted displacements ΔQ , effective phonon frequencies $\Omega_{\{g,e\}}$, and HR factors for each DAP configuration. These quantities, reported in Tables 3.6 and 3.7 allow us to construct a predictive framework for PL spectra and evaluate which DAPs offer viable, spectrally resolved quantum emission.

As previously stated, the electron-phonon coupling strength in DAPs is strongly linked to the geometric distortion that occurs between the ground and excited states. Deep donors such as N_C in diamond, for example, exhibit a very large geometric distortion when in its neutral state, resulting in a 33% elongation of one of its bonds compared to the equilibrium bond length. Upon ionization ($N_C \rightarrow N_C^+$), the geometry reverts to the high-symmetry

tetrahedral configuration, resulting in a substantial geometry shift. A similar though slightly weaker effect is seen for B_C in both diamond and SiC. These large distortions translate to high values of ΔQ and thus high HR factors, often exceeding 20, as is the case for B-N pairs in diamond.

In contrast, shallow donors and acceptors, such as Al_{Si} and N_C in SiC maintain near-identical geometries across charge states. The donor N_C remains in T_d symmetry in both +1 and 0 charge states, with minimal changes in bond lengths. Al_{Si} similarly undergoes only subtle geometric relaxation when switching between 0 and -1 charge states. These cases produce small ΔQ values, modest HR factors (often below 2) and Debye-Waller factors greater than 5-10%, more than sufficient to yield optically resolvable, narrow ZPL emission.

The difference in PL spectra between DAPs consisting of shallow, intermediate, and deep donors and acceptors are shown in Figure 3.6. We give a case-by-case comparison of them below:

- **B-N DAPs in diamond:** This donor-acceptor pairing demonstrates the strongest electron-phonon coupling observed in this study. As shown in Figure 3.6a, the PL spectrum of B-N DAPs from the 8th shell (m_8) is broad and featureless, lacking any identifiable ZPL peak. The mass-weighted displacement ΔQ is predicted to be around 1.4 to 1.5 amu^{1/2}Å for all B-N DAPs across all shells and the resulting HR factor is around ~ 19 with the PBE functionals or even exceeding 20 with the HSE functional. Consequently, the Debye-Waller factor is almost zero. This behavior is driven primarily by the large lattice distortion of the N_C donor. The large lattice distortions caused by N_C accounts for a large majority of the ΔQ . This system exemplifies the undesirable regime of extreme phonon broadening, where shell-specific PL signatures cannot be resolved experimentally, even though the dipole moments and ZPLs themselves are well-behaved on paper. With this extreme amount of electron-phonon coupling, it is not possible to resolve the ZPL signal from the dominant phonon sideband.

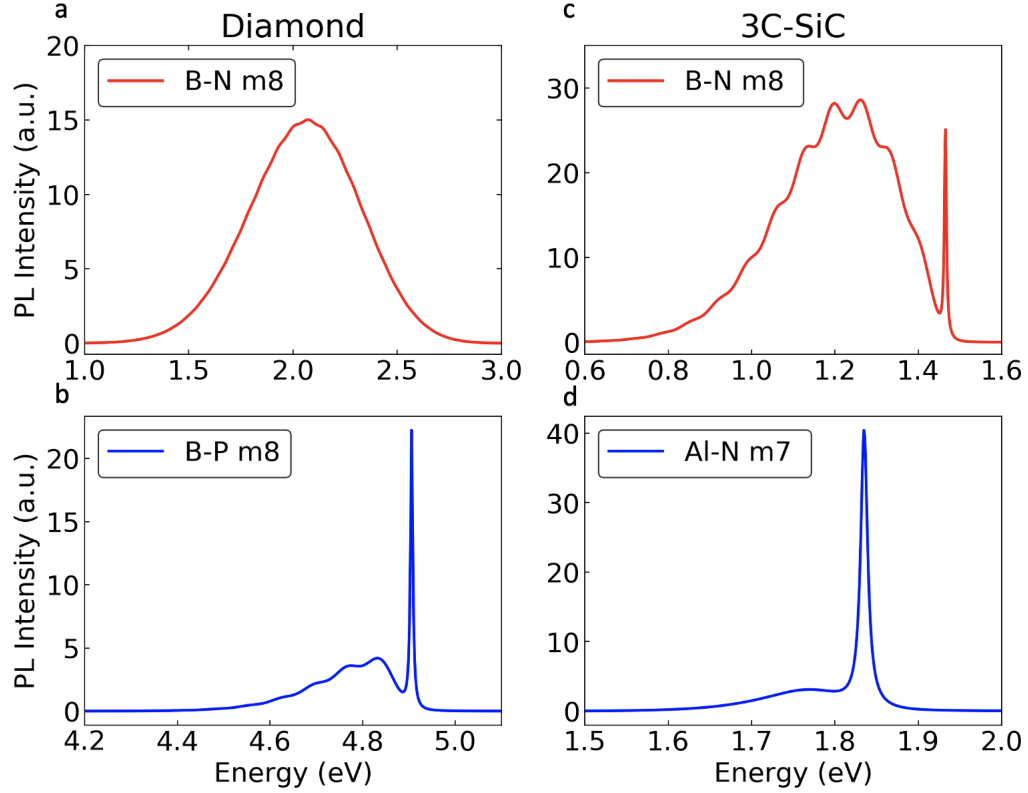


Figure 3.6: Photoluminescence (PL) spectra of donor-acceptor pairs obtained from one-dimensional configurational-coordinate diagram using the HSE functional for (a) B-N (m8) and (b) B-P (m8) pairs in diamond, and (c) B-N (m8) and (d) Al-N (m7) pairs in 3C-SiC. PL lineshapes were calculated at 5K using a Lorentzian broadening parameter $\gamma = 3$ meV for the zero-phonon line (ZPL) and a Gaussian broadening parameter $\sigma = 30$ meV for approximating the broadening of the spectral function $S(\hbar\omega)$ for phonon modes responsible for the phonon side-band (See Ref. [4]).

- B-P DAPs in diamond:** A more favorable system compared to B-N DAPs in diamond. B-P pairs in diamond show a small HR factor (~ 0.6 with PBE and ~ 1.5 - 1.8 with HSE), as shown in Figure 3.6b, with a visible ZPL flanked by modest phonon sidebands. The P_C donor remains structurally rigid across charge states, limited the geometry change upon a charge transition during optical excitations. The result is a small ΔQ value of 0.25 (0.47) $\text{amu}^{1/2}\text{\AA}$ as predicted by the PBE (HSE) functional, and a ZPL that is distinct and resolvable. The small HR factor ensures that a significant fraction of the optical emission is concentrated in the ZPL, with a DWF exceeding 10%. This makes B-P pairs in diamond promising candidates for resonant optical control at their ZPL energy, binned and modulated through their shell numbers, and offering access to different electric dipole moment magnitudes.
- B-N DAPs in 3C-SiC:** In SiC, the same B-N pair shows intermediate phonon coupling, as shown in Figure 3.6c. The PL lineshape is visibly broadened, but the ZPL remains discernible despite a pronounced phonon sideband. The HR factors in this system as consistently lower than in diamond (*e.g.* $S \sim 4$ - 5 compared to ~ 22 - 23 in diamond) Interestingly, the roles of B and N are reversed in SiC when compared to diamond. N_C is much shallower compared to B_C in SiC, and mostly retains its geometry upon changes in its charge state. B_C however, undergoes moderate geometry disruptions that give rise to a moderate ΔQ value of ~ 0.5 - 0.6 (~ 0.7 - 0.8) $\text{amu}^{1/2}\text{\AA}$ with the PBE (HSE) functional. The electron-phonon coupling remains in a marginally acceptable range for spectral addressing when looking at the PL spectrum originating from a single shell. However, when one considers the cumulative PL spectra originating from many shells simultaneously, it is possible that the pronounced phonon sidebands could make it challenging to experimentally resolve the ZPL peaks.
- Al-N DAPs in 3C-SiC:** This system stands out for its excellent spectral performance, as shown in Figure 3.6d. With HR factors safely below 1 (as predicted by both PBE

Table 3.6: Summary of parameters obtained from the effective 1D-CC model. ZPL energies and total mass-weighted distortion ΔQ are given for different DAP pairings in diamond and 3C-SiC. for both the PBE and HSE functionals.

DAP	ZPL (eV) PBE (HSE)	ΔQ (amu ^{1/2} Å) PBE (HSE)
B-N (SiC) m2	1.21 (1.60)	0.521 (0.796)
B-N (SiC) m4	1.16 (1.51)	0.627 (0.854)
B-N (SiC) m6	1.13 (1.48)	0.578 (0.767)
B-N (SiC) m8	1.12 (1.47)	0.597 (0.781)
B-N (SiC) m10	1.10 (1.45)	0.601 (0.780)
Al-N (SiC) m1	1.37 (1.90)	0.111 (0.112)
Al-N (SiC) m3	1.34 (1.86)	0.170 (0.206)
Al-N (SiC) m5	1.32 (1.85)	0.198 (0.239)
Al-N (SiC) m7	1.31 (1.84)	0.213 (0.274)
Al-N (SiC) m9	1.31 (1.82)	0.222 (0.314)
B-N (diamond) m2	3.14 (3.88)	1.431 (1.498)
B-N (diamond) m5	2.98 (3.69)	1.439 (1.501)
B-N (diamond) m8	2.87 (3.57)	1.428 (1.472)
B-P (diamond) m2	3.97 (5.10)	0.184 (0.239)
B-P (diamond) m5	3.90 (5.00)	0.231 (0.420)
B-P (diamond) m8	3.83 (4.91)	0.252 (0.470)

and HSE functionals) and a minimal mass-weighted displacement ΔQ value of ~ 0.1 - 0.3 amu^{1/2}Å, Al-N pairs in SiC exhibit sharp ZPLs that are easily resolvable. The small distortions that both Al_{Si} and N_C undergoes minimizes the ΔQ , leading to narrow optical transitions. This enables clean spectral resolution of different DAP shells - a necessary feature for multi-channel emission and shell-multiplexed quantum logic operations.

As presented in Tables 3.6 and 3.7, we systematically computed these quantities using both the PBE and HSE functionals. Across all systems studied, HSE predicts slightly larger lattice distortions (though the difference from PBE geometries remains less than ~ 1 - 2%), and steeper harmonic potentials with higher effective phonon frequencies $\Omega_{\{g,e\}}$. The combined effect of the two results in higher HR factors as predicted by the HSE functional. This trend

Table 3.7: Summary of parameters from the effective 1D-CC model. Effective phonon frequencies ($\Omega_{\{g,e\}}$), as well as the corresponding HR factors ($S_{\{g,e\}}$) are given in the ground and excited states for both the PBE and the HSE functionals.

DAP	$\hbar\Omega_g$ (meV) PBE (HSE)	$\hbar\Omega_e$ (meV) PBE (HSE)	S_g PBE (HSE)	S_e PBE (HSE)
B-N (SiC) m2	60.35 (61.90)	46.72 (48.74)	1.96 (4.69)	1.52 (3.69)
B-N (SiC) m4	60.03 (61.50)	47.64 (51.18)	2.82 (5.36)	2.24 (4.46)
B-N (SiC) m6	63.13 (67.45)	50.49 (55.54)	2.53 (4.75)	2.02 (3.91)
B-N (SiC) m8	63.83 (67.83)	51.65 (56.37)	2.72 (4.96)	2.20 (4.12)
B-N (SiC) m10	63.63 (67.67)	51.47 (56.61)	2.75 (4.92)	2.23 (4.12)
Al-N (SiC) m1	75.29 (77.54)	74.52 (76.62)	0.11 (0.12)	0.11 (0.12)
Al-N (SiC) m3	70.84 (71.31)	66.28 (61.73)	0.25 (0.36)	0.23 (0.31)
Al-N (SiC) m5	65.37 (66.12)	60.73 (57.53)	0.31 (0.45)	0.28 (0.39)
Al-N (SiC) m7	63.91 (66.40)	57.99 (53.80)	0.35 (0.60)	0.31 (0.48)
Al-N (SiC) m9	66.10 (67.78)	59.34 (52.07)	0.39 (0.80)	0.35 (0.61)
B-N (diamond) m2	69.09 (70.77)	77.72 (84.97)	16.91 (19.00)	19.03 (22.82)
B-N (diamond) m5	68.74 (70.89)	78.80 (85.67)	17.02 (19.10)	19.51 (23.09)
B-N (diamond) m8	68.75 (71.31)	80.06 (87.52)	16.77 (18.48)	19.53 (22.68)
B-P (diamond) m2	92.60 (86.43)	90.20 (81.33)	0.37 (0.59)	0.37 (0.56)
B-P (diamond) m5	83.45 (70.08)	78.86 (57.73)	0.53 (1.48)	0.50 (1.22)
B-P (diamond) m8	80.61 (69.49)	76.87 (56.23)	0.61 (1.84)	0.58 (1.49)

is directly attributable to the improved localization of defect orbitals and deeper CTLs within the HSE formalism. For example, for B-N DAPs in 3C-SiC at shell m_8 , the PBE-computed ΔQ is $0.597 \text{ amu}^{1/2}\text{\AA}$ with HR factor $S_g = 2.72$, while HSE yields $0.781 \text{ amu}^{1/2}\text{\AA}$ and $S_g = 4.96$. Such increases in HR factor directly correlate with enhanced phonon sideband intensity and broader PL spectra.

These functional dependencies persist across all defect types and hosts. Al-N pairs in SiC, for instance, exhibit HR factors $S_g \sim 0.1\text{-}0.4$ (PBE) versus $0.1\text{-}0.8$ (HSE). Likewise, B-P pairs in diamond show slightly increase HR factors with HSE compared to the PBE functional. The implication is that even modest differences in geometry and the shallow/deep character of a donor/acceptor can have a significant impact on the resulting electron-phonon coupling and the PL spectra, and settle the difference between a superb DAP candidate and a moderately acceptable one.

3.4 Summary and Takeaways

In this chapter, we carried out a detailed computational investigation of donor-acceptor pairs (DAPs) in two leading wide-bandgap semiconductors - diamond and 3C-SiC - using density functional theory with PBE and HSE functionals. By constructing substitutional donor and acceptor pairs (*e.g.* P-B, B-N, Al-Si) across multiple crystallographic shells up to m_{10} , we characterized the full spectrum of relevant defect properties, including charge transition levels (CTLs), zero-phonon line energies (ZPLs), electric dipole moments, radiative lifetimes, electron-phonon coupling and the resulting photoluminescence (PL) spectra. Our findings confirm that these DAPs support stable charge states in both ground and excited state configurations, with CTLs well within the bandgaps of both host materials. Functional comparison showed strong agreement in trends, with HSE generally predicting deeper levels and more localized states - especially important for deep defects like N_C .

We demonstrated that ZPL energies in both diamond and SiC follow a $1/R_m$ pattern

with increasing inter-defect distance one the Coulomb binding energy $J(R_m)$ is properly accounted for closely separated pairs. This correction enabled linear fits to ZPL vs. $1/R_m$, with residuals confirming the reliability of our distance dependent scaling model. Alongside the ZPL values, we computed the static electric dipole moments of DAPs. These dipoles are shown to be scaling approximately proportional to eR_m , reaching values (~ 15 eÅ) capable of maintaining 10-100 MHz dipolar interaction energy from a separation of ~ 100 nm, making them excellent candidates for implementing non-photon qubit coupling over intermediate distances in the solid-state.

We validated these dipole moments using both Wannier function based polarization differences and electric field induced Stark shifts of the ZPL. The excellent agreement between these methods confirmed not only the magnitude of the dipoles, but also their field sensitivity. While these strong dipoles provide a powerful mechanism for tuning and interacting with DAPs, they also introduce susceptibility to electric field noise. As proposed in our work, embedding DAPs in PIN heterostructures provides a pathway to stabilize the local electrostatic environment while retaining optical and electrical control, making the platform suitable for scalable and addressable emitter arrays.

Finally, our analysis of phonon coupling revealed that optical emission quality is highly sensitive to charge-dependent lattice relaxation at each defect site. Deep level donors or acceptors, such as N_C , exhibit large mass-weighted displacements and HR factors when participating in a donor-acceptor pairing, leading to broad phonon sidebands and severely suppressed ZPLs. In contrast, DAPs formed from shallow defects like Al_{Si} and N_C in 3C-SiC show minimal geometry change, low HR factors, and high Debye-Waller factors, resulting in narrowband emission with strong ZPL visibility. These sharp spectral features are preserved even in multi-shell arrays and can enable shell-specific photon emission or frequency-multiplexed quantum addressing. Altogether, this chapter shows that by selecting appropriate donor-acceptor combinations and controlling their spatial arrangement, DAPs

can serve as dipole-active, spectrally tunable quantum emitters with potential applications in optical networks, quantum gates, and scalable dipolar qubit architectures.

CHAPTER 4

DONOR-ACCEPTOR PAIRS AND SURFACE-DEFECT PAIRS NEAR SILICON CARBIDE SURFACES

Adapted from A. Bilgin, I. N. Hammock, A. A. High & G. Galli. Donor-acceptor Pairs Near Silicon Carbide Surfaces. ACS Nano (In Review) 2025

4.1 Introduction

As quantum technologies progress toward integration with scalable nanostructures, there is urgent need for solid-state quantum emitters that are not only optically addressable and long-lived but also capable of long-range, controllable interactions [14, 15, 19, 31]. Wide bandgap semiconductors such as diamond [48, 135, 136] and silicon carbide (SiC) [137–139] have emerged as prime hosts for such emitters due to their exceptional material quality, favorable defect physics, and compatibility with industrial semiconductor processing, especially for silicon carbide. In particular, we recently proposed donor-acceptor pairs (DAPs) as promising candidates for building dipole-coupled quantum emitter arrays, owing to their large, optically reconfigurable dipole moments and spectrally tunable emission [3].

Our work on DAPs in bulk diamond and SiC showed that they can support 10-100 MHz coupling strengths from ~ 100 nm away. We found that Al-N pairs in SiC were particularly strong candidates with strong, sharp emission into their zero-phonon lines (ZPLs) and minimal broadening due to electron-phonon coupling across many crystallographic shells. However, these findings also revealed two key shortcomings. First, the electric dipole moment exists in the ground state when the donor and acceptor atoms are effectively ionized (D^+ and A^-) and it vanishes in the excited state when the electron-hole pair is formed and the defects are neutral [127]. Although this provides an optically controllable dipole moment, the configuration is reversed in direction - it is opposite to what would be ideal for

implementing an optically switchable "on-off" dipolar interaction akin to Rydberg blockade protocols [140]. The "default" ground state possessing the dipole moment as opposed to the excited state creates unwanted complications by creating a situation where the interactions are "on" all the time, and turned "off" only in the excited state. Second, the dipole orientations in the bulk are randomly distributed due to thermal processes related to defect formation, limited control over the placement of donor and acceptor atoms during growth or implantation. This random distribution of dipole directions significantly complicates efforts to scale up DAPs into coherent, addressable quantum arrays, where alignment between emitters is essential for interaction uniformity and optical selectivity.

At the same time, realistic quantum device architectures will require defects to be placed near surfaces and interfaces, whether for coupling to photonic cavities, implementing local electrical control, or integrating with microwave lines and gate electrodes. Proximity to surfaces introduces both challenges and opportunities: charge trapping, surface termination and chemistry, altered dielectric screening, and band bending can perturb defect levels [141, 142], but these effects can also be harnessed to stabilize specific configurations, modulate emission spectra, and align dipole orientations. The key question, therefore, is whether favorable properties of bulk DAPs can be retained or improved near surfaces, or whether new defect architectures must be designed.

In this chapter, we address this question by examining both conventional Al-N DAPs near hydrogen- and hydroxyl-terminated SiC surfaces, as well as a new class of surface-bound dipolar emitters, which we refer to as surface-defect pairs (SDPs). These SDPs are formed by optical excitation between a substitutional defect and a surface-bound electronic state, producing a spatially extended exciton with a dipole naturally aligned perpendicular to the surface. Unlike conventional DAPs, these SDPs offer deterministic dipole orientation, no dipole reversal between ground and excited states. Additionally, they exhibit highly tunable optical properties, such as highly polarization-dependent stimulated emission and

photoionization response. Taken together, these properties render them promising building blocks for hybrid quantum-photonic platforms and dipole-aligned emitter arrays for many applications in quantum science and technology.

4.2 Computational Methods

The results presented in this chapter are based on first-principles density functional theory (DFT) calculations, building on the theoretical background introduced in Chapter 2 and employing methodological conventions similar to those detailed in 3. The focus of this work is on donor-acceptor pairs (DAPs) and surface-defect pairs (SDPs) located near reconstructed SiC surfaces with various terminations. Calculations are carried out using the Quantum ESPRESSO [79–81] software package for total energy, force, and geometry optimization calculations. Once again we use plane-wave basis sets and the SG15 ONCV pseudopotentials [82, 83]. However, this time we use a kinetic energy cutoff of 80 Ry. This is because in this chapter, we deal exclusively with SiC, and similar convergence criteria with this lower cutoff was attainable for SiC. In contrast, in Chapter 3, we worked with diamond and SiC simultaneously, and for properly comparing our results across both hosts, we used the higher cutoff of 90 Ry that was appropriate for diamond.

We carry out lattice geometry optimizations to determine the charge transition levels (CTLs) of N_C , Al_{Si} and V_{Si} defects using three different functionals, namely PBE [10], HSE [11], and DDH [12, 13]. The screening and mixing parameters used for HSE are 0.2 $\text{\AA}^{-1}$ and 25% respectively. For the DDH functional, we use a mixing parameter $\epsilon_\infty^{-1} = 0.153$. For determining other properties, we use lattice optimizations based on the PBE functional, but compute the electronic structure using HSE and DDH, and clarify which one is used depending on the context. All lattice optimizations use a force convergence threshold of 10 meV/ $\text{\AA}$, and we sample the Brillouin zone at the Γ point in all calculations. The calculations of properties in the excited state are done using the constrained DFT (Δ SCF) method.

We determine many properties of DAPs and SDPs with the same methods we used in Chapter 3. This includes the electric dipole moments of DAPs and SDPs, computed according to the Modern Theory of Polarization [99, 100] using maximally localized Wannier functions (MLWF) and the Wannier90 package [101]. We compute the ZPL values using both the HSE and DDH functionals, and clarify in the text which one is used. We determine the Debye-Waller factors (DWF) and the phonon sideband of the PL spectra using the one-dimensional model to obtain one effective phonon mode [2, 90–93]. We approximate the effective phonon frequencies in the ground and excited states by using a scaling factor based on the PBE results following the same method outlined in Ref [2]. This scaling factor is evaluated from the ratio of frequencies of the bulk system’s optical phonons computed at different levels of theory. In our calculations for the photoionization and stimulated emission cross sections, we determine the electron-phonon spectral function $A(\hbar\omega)$ based on this one-dimensional method. We compute the transition dipole matrix elements using the WEST code [8, 9]. For stimulated emission and photoionization calculations the matrix elements are computed in the excited state and ground state respectively.

In our slab calculations, we use 9-bilayer slabs to study three different surface reconstructions of two different polytypes of SiC. We consider the Si-rich (001) surface of 3C-SiC, and study its (2x1) reconstruction terminated with either H atoms or OH groups. We also study the Si-rich (0001) surface of 4H-SiC with a (1x1) reconstruction terminated with OH groups. We saturate the bottom C-rich surface with H atoms and add 20 Å of vacuum between the periodic images of the slabs. The bottom two bilayers of the slabs are kept frozen during lattice optimizations. In all of our calculations we use a dipole correction scheme [5] to offset the artificial dipole arising from the use of a non-symmetric slab. The (2x1) H-terminated and OH-terminated slabs of 3C-SiC contain 672 and 704 atoms respectively, whereas the slab with the (1x1) OH-terminated surface of 4H-SiC has 684 atoms. We show the atomistic models we use to build our slabs in Figure 2.2 in Chapter 2, but also reprint it below in

Figure 4.1 for convenience.

DAPs are modeled by placing substitutional defects on different sites lattice sites near the surface, exploring in-plane and depth-dependent separations. The shell indexing convention used throughout Chapter 3 is extended to slab geometries, with special care taken to avoid introducing spurious defect-defect interactions across periodic boundaries. The maximum DAP separation studied was approximately 6.5 Å, corresponding to the m_9 shell in SiC.

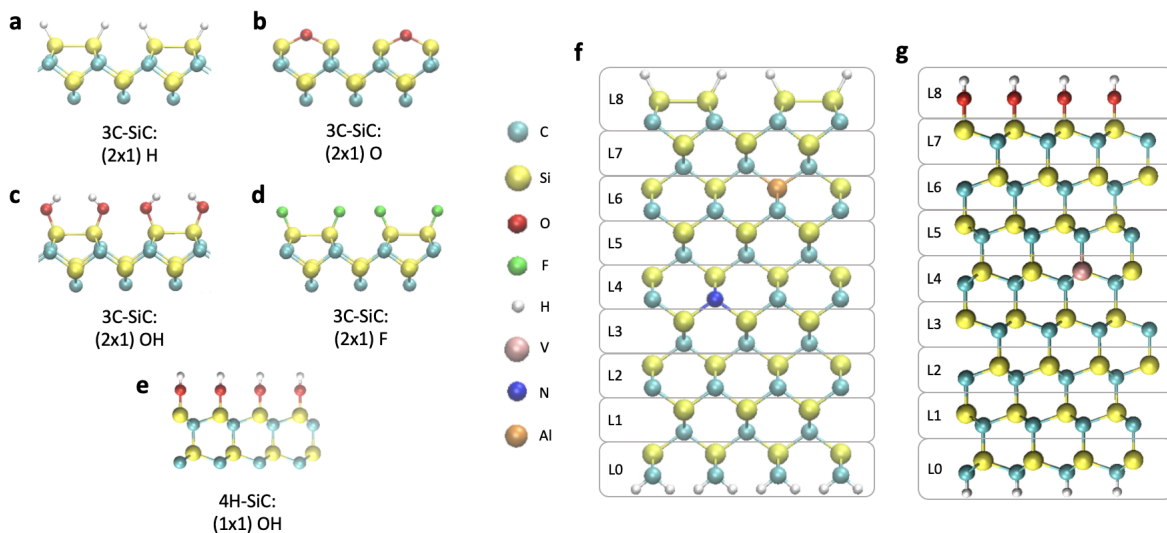


Figure 4.1: Atomistic structures of the Si-rich (001) surfaces of 3C-SiC with a (2x1) surface reconstruction terminated with (a) H atoms, (b) O atoms, (c) OH groups, and (d) F atoms, as well as the (e) Si-rich (0001) surface of 4H-SiC with a (1x1) reconstruction terminated with OH groups. (f) The side view of 3C-SiC slab with the (2x1) H-termination, where the bottom C-rich surface is passivated with H atoms. (g) The side of view of 4H-SiC slab with the (1x1) OH-termination. Both the slabs consist of 9 Si-C bilayers and are shown to include other defects within the slab.

4.3 Results and Discussion

4.3.1 Electronic Structure and Surface Electron Affinity of SiC Surfaces

Understanding the electronic structure of SiC surfaces is essential for evaluating the viability of near-surface donor-acceptor pairs (DAPs) and surface-defect pairs (SDPs) as quantum

emitters. Surface reconstructions and terminations can significantly impact key quantities such as the band bending, charge trapping, the presence of mid-gap states and the surface electron affinity. All of these quantities directly affect charge stability, excitonic localization, and the susceptibility of near-surface defects to ionization or unwanted recombination. Here, we examine five distinct slab configurations: the Si-rich (001) surface of 3C-SiC with a (2x1) reconstruction terminated by H-, F-, O- atoms and OH groups, and the Si-rich (0001) surface of 4H-SiC with a (1x1) reconstruction terminated by OH groups.

We start by characterizing the surface electron affinity, defined as the energy difference between the vacuum level and the conduction band maximum (CBM):

$$\chi = E_{\text{vac}} - E_{\text{CBM}} \quad (4.1)$$

A positive electron affinity is desired for most quantum applications, as it prevents the loss of excited electrons from the surface into the vacuum [142]. We determine the vacuum level by plotting the planar averages of the electrostatic potential within the supercell as a function of z , in the direction of the surface normal (slabs are separated with 20 Å vacuum in the z direction). This is shown in Figure 4.2.

After plotting the electrostatic potentials, we determine the vacuum level as the flat region adjacent to the surface of interest. Note that there are two inequivalent vacuum regions with differing energies, with a discontinuity at the edge of the supercell. This is due to the sawtooth potential applied as part of the dipole correction in slab calculations [5]. We also assume that the average electrostatic potential energy within the slab is the same as that of the bulk, and hence, by aligning the potential levels, we compute the surface electron affinities χ . In Table 4.1 we present our results for surface electron affinities obtained with the HSE functional for all the surfaces we study, and find positive electron affinities for all of them.

Second, we move to characterize the electronic structure of these surfaces. We identify

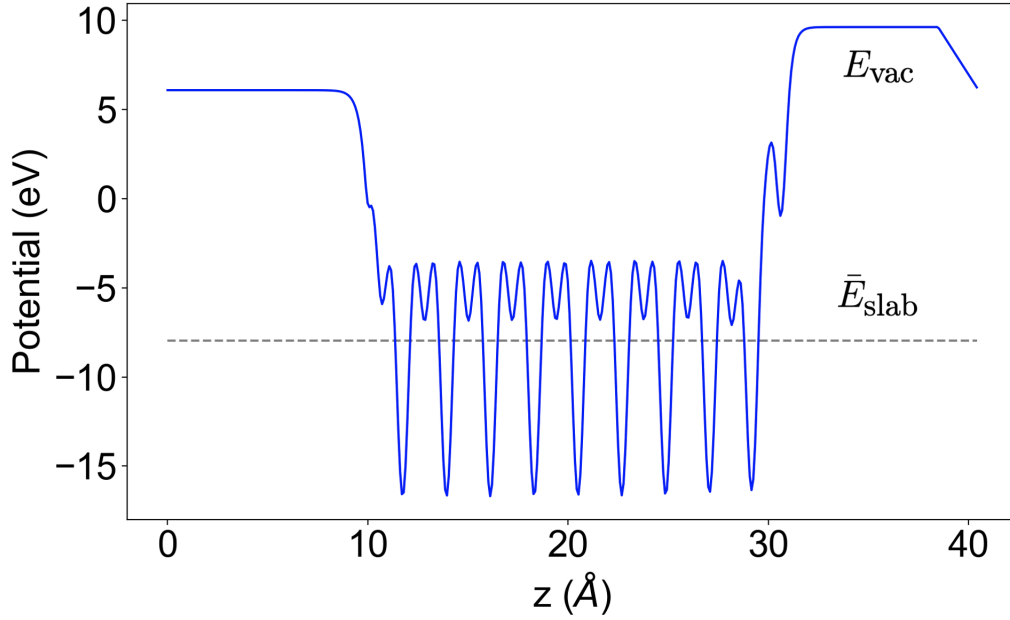


Figure 4.2: The planar average of the electrostatic potential for the (2x1) F-terminated slab of 3C-SiC plotted as a function of z . The slab is placed in the middle of the supercell, with approximately 10 Å of vacuum on each side. The average potential energy of the slab $\bar{E}_{\text{slab}}$ is marked by the gray dashed line and E_{vac} is labeled as the flat region to the right of the supercell. Note that there exists two inequivalent vacuum regions to the left (bottom) and to the right (top) of the slab, with a discontinuity at the edge of the supercell. This is a natural consequence of the use of a sawtooth potential as part of a dipole correction [5]. Since we are interested in the F-terminated (top) surface, we define E_{vac} as the electrostatic potential energy to the right of the slab, or equivalently, at the top surface.

Table 4.1: Computed surface electron affinity (χ) for the Si-rich (001) surfaces of 3C-SiC and (0001) surfaces of 4H-SiC with various surface terminations. All quantities are computed with the HSE functional.

Surface termination	χ (eV)
3C: (2x1)-H	4.0
3C: (2x1)-F	6.3
3C: (2x1)-O	3.0
3C: (2x1)-OH	4.8
4H: (1x1)-OH	3.8

whether there exists surface states in the bandgap by plotting the planar average of each individual Kohn-Sham orbital close to the valence and conduction bands:

$$|\phi|_{\text{avg.}}^2(z) = \iint_{\langle x,y \rangle} |\phi(x,y,z)|^2 dx dy \quad (4.2)$$

If this plane-averaged Kohn-Sham orbital $|\phi|_{\text{avg.}}^2(z)$ is strongly localized around the surface, we consider it a surface state. The cutoff threshold for this consideration is having more than 30% of the total planar-averaged orbital be concentrated within 3 Å of the top surface. In addition to this criteria, such states are rather easily identifiable by inspection upon plotting individual plane-averaged Kohn-Sham orbitals as a function of z . An example of this is given in Figure 4.3 for the (2x1) OH-terminated surface of 3C-SiC.

We use the same plane-averaged wavefunction analysis for all the surfaces we study, but we focus specifically on three surface terminations in the remainder of this chapter. These surfaces are the (2x1) reconstruction of the 3C-SiC surface with the H- and OH- terminations and the (1x1) reconstruction of the 4H-SiC surface, also with the OH- termination. We identify that the (2x1) H-terminated surface of 3C-SiC doesn't exhibit any surface states in the bandgap, as corroborated by previous studies as well [141,143]. However, as shown in Figure 4.3, the (2x1) OH-terminated surface of 3C-SiC exhibits occupied surface states in the bandgap immediately above the VBM. Moreover, we find that the (1x1) reconstruction of the OH-terminated 4H-SiC surface has electronic structure qualitatively similar to that of the (2x1) OH-terminated surface of 3C-SiC, with occupied surface states above the valence band. We summarize the electronic structure of these three surfaces in Figure 4.4 side by side.

The absence of surface states in H-terminated surfaces makes them well-suited for DAPs, where the excited-state electron and hole are tightly bound to donor and acceptor states and must not interact with extraneous surface levels. Because no gap states exist to interfere with the DAP transition, this surface type offers the cleanest platform for near-surface DAP

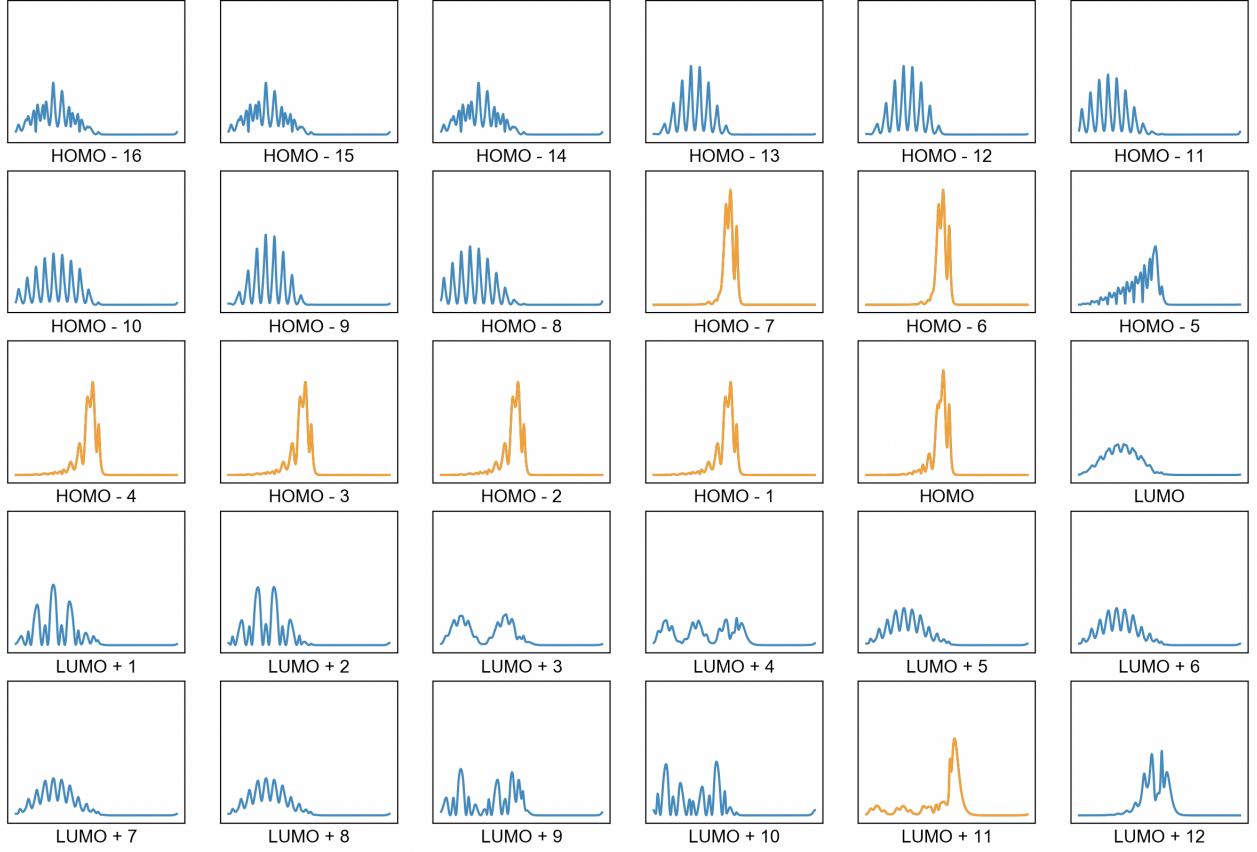


Figure 4.3: Plane-averaged Kohn-Sham orbitals $|\phi|_{\text{avg}}^2(z)$ are plotted as a function of z in the vicinity of the bandgap for the (2x1) OH-terminated surface of 3C-SiC. The wavefunctions are labeled by their ordering with respect to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Surface states are easily identifiable with their sharp concentration around the surface, and are shown in orange.

deployment, allowing placement just a few layers below the surface without spectral degradation. On the other hand, the presence of occupied surface states in OH-terminated slabs opens the door to hybrid excitonic structures, namely surface-defect pairs (SDPs). In SDPs, a hole is left behind in a surface-bound state after photoexcitation, while the excited electron resides in a nearby defect orbital that can accommodate it. This configuration gives rise to an intrinsic electric dipole aligned normal to the surface, offering unique advantages in field tunability, dipole alignment, and coupling uniformity. The intentional use of a surface state, normally seen as a liability, as an active quantum level is a paradigm shift in the design of

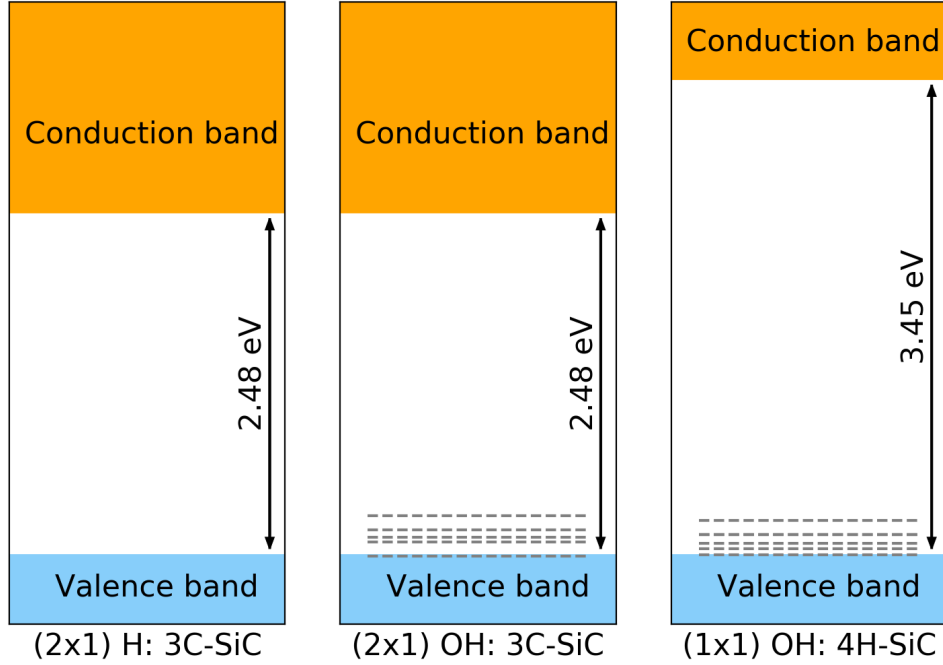


Figure 4.4: The electronic structure of the three different surface terminations studied in 3C- and 4H-SiC as computed by the HSE functional in a 9-bilayer SiC slab configuration. The surface states in the bandgap are shown with gray dashed lines. The (2x1) H-terminated surface of 3C-SiC doesn't introduce any surface states in the bandgap, whereas both the OH-terminated surfaces (in 3C- and 4H-SiC) exhibit occupied surface states above the valence band and are qualitatively similar. The bandgaps are slightly overestimated compared to the values computed in bulk shown in Table 3.2 due to the quantum confinement effect [6, 7]

defect-based qubits.

4.3.2 Donor-Acceptor Pairs near Hydrogen-Terminated SiC Surfaces

Defect-based quantum emitters embedded near semiconductor surfaces offer practical pathways towards scalable integration with nanophotonic platforms. However, the proximity of a defect to the surface can significantly influence its electronic structure, charge stability, and radiative properties. Here, we focus specifically on DAPs composed of Al_{Si} and N_C defects, identified in Chapter 3 as the most promising candidates for quantum applications due to

their sharp ZPL emission and minimal electron-phonon coupling. We embed these defects within our slabs, as shown in Figure 4.1, to investigate whether these defects can preserve their desirable bulk-like optical properties and electronic features while residing near the silicon carbide surface.

This section presents a detailed analysis of Al-N DAPs placed beneath H-terminated 3C-SiC surfaces, highlighting how their charge transition levels (CTLs), zero-phonon lines (ZPLs), electron-phonon coupling, and photoluminescence (PL) spectra evolve as a function of depth and separation.

We perform all our calculations on a 3C-SiC slab containing 9 Si-C bilayers with the (2x1) reconstruction terminated with H- atoms. The slabs are separated with 20 Å of vacuum, and dipole corrections [5] are applied along the surface normal to eliminate electric fields arising due to electronegativity differences between Si and C across periodic boundaries. We form DAPs by positioning N_C donors in the middle bilayer of the slab (L4 in Figure 4.1) and varying the position of Al_{Si} acceptors, thus varying the donor-acceptor pair distance (R_m) and the relative orientation with respect to the surface. In order to distinguish surface-related and quantum confinement-related effects, we employ two methods: We compute the same set of defect properties in a 512-atom bulk 3C-SiC supercell, and we extrapolate CTLs to the infinite slab limit by using 7-bilayer and 11-bilayer slabs and plotting the CTLs v. $1/N_L$, where N_L is the number of bilayers. The linear trend observed with the PBE functional is used to correct hybrid functional values, following the procedure described in Section 2.4.5.

A comparative summary of the CTLs for N_C donors and Al_{Si} acceptors, computed in both bulk and near the surface, is presented in Table 4.2. After extrapolating both bulk supercell and slab data to their respective infinite-size limits, we find that the CTLs in the slab geometries are only slightly shallower than their bulk counterparts. These differences are sufficiently small that, at typical operating temperatures, surface and bulk CTLs can be considered effectively equivalent. That said, in calculations using the 9-bilayer slab, we

Functional	$N_C(+/0)$ (Slab)	$N_C(+/0)$ (Bulk)	$Al_{Si}(0/-)$ (Slab)	$Al_{Si}(0/-)$ (Bulk)	Bandgap (Slab)
PBE	0.04	0.11	0.09	0.11	1.31
HSE	0.12	0.15	0.13	0.16	2.17
DDH	0.25	0.27	0.29	0.33	2.25
Expt.	-	0.05-0.07 ^a	-	0.24-0.26 ^b	-

^a Ref. [123–125] ^b Ref. [122, 124, 125]

Table 4.2: Charge transition levels (CTL) of N_C and Al_{Si} in bulk 3C-SiC and near the (2x1) Hydrogen terminated Si-rich surface of 3C-SiC (slab), computed with three different functionals (PBE, [10] HSE [11] and DDH [12, 13]), extrapolated to the dilute limit and infinite slab thickness, respectively. The bandgap values are also extrapolated and the slab and bulk extrapolations yield the same number within 0.1 eV. CTLs for N_C and Al_{Si} are given relative to the conduction band minimum and valence band maximum respectively. Experimental values (Expt.) measured for 3C-SiC at room temperature are also reported. All values are in eV. The bandgap computed in a 9-layered slab is ~ 0.1 eV larger than the extrapolated value for all functionals. The CTLs computed in a 9-layered slab are ~ 0.13 eV higher (*i.e.* defects are deeper) than extrapolated values for both defects

observe a modest increase of approximately 0.16-0.18 eV in the bandgap and a corresponding shift of about 0.13 eV in the CTLs. We attribute these shifts to quantum confinement effects, which become increasingly pronounced at reduced dimensionality [6, 7]. Despite this, we continue to use the 9-bilayer slab setup for our DAP calculations, as it offers a practical balance between computational cost and accuracy, with the understanding that minor finite size corrections are present when comparing to bulk-like behavior.

As expected, the PBE functional substantially underestimates the electronic bandgap of bulk 3C-SiC, yielding a value of 1.40 eV compared to the experimental bandgap of 2.36 eV [114]. In contrast, hybrid functional provide far more accurate results: HSE predicts a gap of 2.27 eV, while DDH gives a closely matching value of 2.35 eV. When comparing defect levels, both functionals identify Al_{Si} and N_C shallow defects, but the precise CTLs differ. Specifically, HSE places the (+/0) CTL of N_C , which has this level ~ 50 -70 meV below the CBM [123–125], about 0.15 eV below the CBM in the bulk, whereas DDH yields a slightly deeper level at 0.27 eV. In the 9-bilayer slab, these values shift slightly to 0.12 eV (HSE) and

0.25 eV (DDH).

Similarly for Al_{Si} , the (0/-) CTL in the bulk is located 0.16 eV above the VBM using HSE, and 0.33 eV using DDH. In slab calculations, the corresponding levels are 0.13 eV (HSE) and 0.29 eV (DDH). These align reasonably well with experimental measurements that place this transition at approximately 250 meV above the VBM [122, 124, 125].

Although neither hybrid functional achieves perfect agreement with all experimental CTL values, the HSE functional achieves a slightly closer values overall. Still, it is important to recognize that the ~ 0.1 eV discrepancy between the HSE and DDH results is comparable in magnitude to the zero-point renormalization of SiC’s bandgap [109, 144]. As such, it is difficult to unambiguously determine whether either functional is definitely superior in this context.

We now continue with evaluating the ZPLs and PL spectra of Al-N DAPs located beneath the (2x1) H-terminated SiC surface. ZPL energies are obtained using the HSE functional, while the Debye-Waller factors and PL lineshapes are computed via the 1D-CC model [2, 90–93]. While using this model, we scale the phonon frequencies in both the ground and excited states relative to PBE-level calculations, using a multiplicative scaling factor determined by the ratio of optical phonon modes between PBE and HSE calculations for bulk systems, which only amount to $\sim 5\%$ difference [2].

Using this method for a 9-bilayer slab, we observe that surface proximal ZPLs are blueshifted by approximately 0.2 to 0.3 eV relative to their bulk analogues. However, since the difference in computed Franck-Condon shifts between bulk and slab systems is only about 10-15 meV, and extrapolated values shown in Table 4.2 closely match bulk behavior, we attribute this ZPL increase primarily to finite size effects inherent in the slab geometry. Therefore, we conclude that surface and bulk ZPLs do not show any notable changes, especially at finite temperature.

Analyzing the dependence on shell separation, we find that ZPL values decrease mono-

tonically with increasing donor-acceptor distance R_m , as expected due to reduced Coulomb binding [58–62]. Across all configurations, DAPs near the surface show enhanced mass-weighted displacements ΔQ compared to their bulk counterparts. This leads to stronger Huang-Rhys (HR) coupling [134] and a consequent reduction in the Debye-Waller factor. Additionally, we find that orientation with respect to the surface affect ΔQ : DAPs at the same distance R_m but with different angular arrangements, may exhibit different displacement magnitudes. In particular, the increase in ΔQ is most pronounced when the Al_{Si} acceptor is positioned in the topmost layers of the slab (L6 or L7, see Figure 4.1). Conversely, placing the acceptor deeper (L3-L5) yields smaller displacements. The primary contribution to these distortions originates from Si atoms near the surface, indicating that the acceptor perturbs the local lattice environment most significantly in this region. Quantitatively, the near surface Al-N DAPs exhibit ΔQ values in the range of 0.32-0.88 amu^{1/2}Å, compared to bulk values of just 0.1-0.25 amu^{1/2}Å. Corresponding HR factors span from 0.35 to 1.9 near the surface, a notable increase from bulk values of 0.1 to 0.4. While this represents a three to fourfold increase, these values remain relatively moderate; for instance, the NV- center in diamond has an HR factor of approximately 3.6 [4]. Thus, even at elevated electron-phonon coupling strength, the optical quality of Al-N DAPs near the surface is preserved.

We show the cumulative PL emission from shells m_1 through m_{10} in Figure 4.5, alongside a comparison of the m_7 shell between bulk and slab environments. Although phonon sidebands are more prominent near the surface due to larger ΔQ , the ZPL peaks remain clearly defined. Additionally, we observe a broadband shoulder at lower photon energies originating from the sum of all emissions into phonon sidebands, a phenomenon widely observed with DAPs in semiconductors [58,59]. Experimentally, such broadband features become especially pronounced for shell numbers beyond m_{30} or m_{40} [58–62], whereas our calculations already show their onset at shell m_9 . The side-by-side PL spectra for shell m_7 reveal a modest reduction in ZPL intensity and a corresponding increase in phonon sideband weight for the

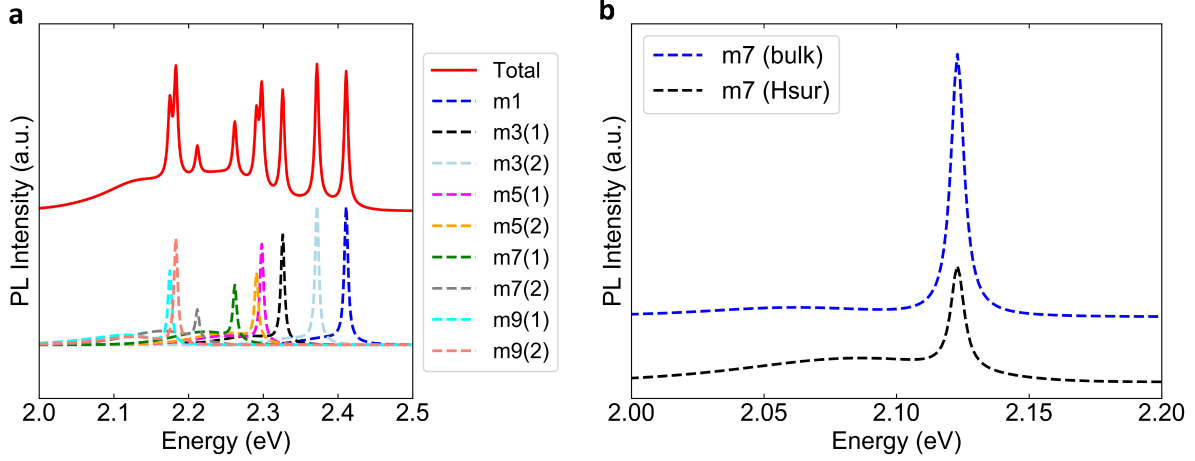


Figure 4.5: (a) The cumulative photoluminescence (PL) spectra (red line) of the first 9 shells (m1-m9) of Al-N DAPs near a (2x1) H-terminated Si-rich surface of 3C-SiC. The individual contributions to the PL spectra are shown below the cumulative one. (b) A comparison of the PL spectra coming from the m7 shell of Al-N pairs in bulk (blue dashed line) and near a (2x1) H-terminated surface (Hsur) of 3C-SiC (black dashed line). The zero-phonon line (ZPL) values are computed using the HSE functional, and the phonon sidebands are computed using a scaling factor based on the PBE functional (see text). The near-surface ZPL value is aligned to match the ZPL value computed in the bulk for comparison (see text).

slab configuration (see Figure 4.5b).

In summary, the key distinction between surface and bulk Al-N DAPs lies in a moderate increase in electron-phonon coupling, as indicated by higher ΔQ and HR factors near the surface. Despite this, the essential properties - well defined ZPLs, moderate Debye-Waller factors, and large dipole moments - are retained. These features make surface-adjacent DAPs highly promising for quantum technologies. Their large intrinsic dipole moments confer exceptional Stark tunability, which can be exploited for electric field sensing. Furthermore, their proximity to the surface enables direct integration with nanophotonic devices such as waveguides or cavities, offering enhanced light-matter interaction and a pathway for device-scale quantum emitter networks.

4.3.3 *Surface-Defect Pairs Near OH-Terminated SiC surfaces*

In this section, we investigate a novel class of optically active defects we call surface-defect pairs (SDPs), formed by pairing a near-surface defect to the occupied surface states introduced by the OH-termination of SiC surfaces. These SDPs constitute an emergent donor-acceptor-like excitation. While in DAPs the electron is bound to the donor and the hole to the acceptor, in SDPs, the hole is a surface state near the VBM and the excited electron is localized on the defect. In this case, we use the transition metal impurity vanadium (V_{Si}^{4+} , hereafter referred simply as V) as the substitutional defect we pair with these surface states. This is because vanadium is an amphoteric defect center with three stable charge states in SiC: V^{3+} , V^{4+} , and V^{5+} [145–147]. Unlike conventional DAPs in the bulk, where the dipole orientations are distributed isotropically throughout the crystal, SDPs exhibit strongly aligned dipole moments perpendicular to the surface, as we verify below. This intrinsic alignment unlocks new functionalities for directional coupling and array-based sensing platforms. Here, we examine the electronic origin, dipole alignment, structural and spectral signatures as well as implications of this new surface-defect pair configuration.

The electronic structure of Vanadium in bulk SiC is well studied. [146, 148–151] In Figure 4.6 we show the atomic slab model used to compute the electronic structure of a near-surface V defect, as well as the resulting electronic structure, which is similar to that of V in bulk. The presence of occupied surface states just above the VBM does not substantially affect the V electronic structure. Vanadium is stable as a neutral defect in a wide range of doping levels [147] and has a spin doublet ground state. [149–151] It introduces two degenerate e states, of which only one is singly occupied in the band gap. These e states are energetically much higher than those of the occupied surface states introduced by the OH surface termination. The excitation from the occupied surface states into one of the unoccupied e states corresponds to the lowest possible optical excitation.

The difficulty of accurately modeling transition metal defect states - particularly those

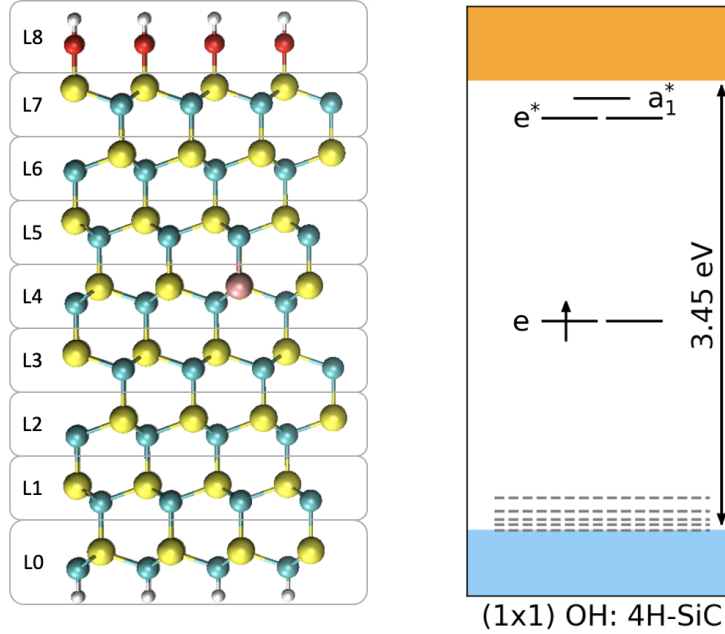


Figure 4.6: The atomistic structure of the Si-rich (0001) surface of 4H-SiC with a (2x1) surface reconstruction terminated with OH groups. The slab contains 9 bilayers and a V atom in the middle of the slab (L4 layer). The resulting electronic structure is shown on the right. The blue and orange regions indicate the valence and conduction bands. Occupied surface states are labeled with gray dashed lines, and V^{4+} defect levels are shown in the bandgap. V^{4+} has a doublet ground state with only one unpaired electron occupying one of the degenerate e states in the bandgap.

involving localized d orbitals - with the PBE and HSE functionals has been extensively discussed in the literature [146, 147]. These shortcomings are primarily due to the incomplete cancellation of self-interaction errors and insufficient screening of the Coulomb interaction between localized d orbitals. In the present study, we adopt the DDH functional for describing the electronic structure of near-surface V defects. Compared to HSE, DDH offers a more reliable treatment of the energetic placement of V 's CTLs without the need for a non-Koopman's correction scheme [146].

Experimental measurements of V in 4H-SiC place the (+/0) and (0/-) CTLs at roughly 1.6-1.7 eV and 2.2-2.3 eV above the valence band [148, 152]. In our study, we find the (+/0) and (0/-) CTLs to be 1.18 (1.32) and 1.98 (2.09) eV using the HSE (DDH) functional in

bulk 4H-SiC. The DDH predictions in particular align much more closely with experiment and highlight the functional’s improved accuracy for systems dominated by transition-metal character. Moreover, when comparing these levels across polytypes and environments - including bulk 3C-SiC and near-surface slab models - we find that the variation is modest. In all cases, the CTLs remain within approximately 0.1 eV of the aforementioned bulk 4H-SiC values, supporting the notion that V ’s defect levels are relatively robust with respect to crystallographic environment and surface proximity.

Turning to optical excitation energies, we find that V -based SDPs in 3C-SiC yield a ZPL energy of approximately 1.38 when computed using the DDH functional. However, this energy lies above the ionization threshold for the neutral V defect. The relevant ionization process corresponds to promoting the single electron occupying the e defect level into the conduction band. Energetically, this threshold is given by the difference between the CBM and the $(+/0)$ CTL, which we calculate to be ~ 1.0 eV, given the 2.35 eV bandgap obtained at the DDH level. Since the ZPL exceeds this ionization energy, optical excitation into the defect’s excited state would render the SDP unstable in 3C-SiC, making it vulnerable to spontaneous ionization and thus photoluminescent quenching.

To overcome this challenge, we explore an alternative host material, namely 4H-SiC, which offers a larger bandgap, which helps in increasing this ionization threshold and enhance SDP stability. The DDH functional accurately reproduces the experimental gap of this hexagonal polytype, yielding a value of 3.23 eV. Within this host, the computed ZPL of V -based SDPs is increased to approximately 1.47 eV. Crucially, the corresponding $(+/0)$ and $(0/-)$ CTLs now lie at 1.32 eV and 2.09 eV above the VBM, respectively. This mean the energy differences defining the ionization thresholds, $\text{CBM} - (+/0) \approx 1.9$ eV and $(0/-) - \text{VBM} \approx 2.1$ eV, comfortably exceed the ZPL energy of 1.47 eV. Even after accounting for potential underestimations due to finite-size errors or minor inaccuracies in the functional (on the order of 0.2-0.3 eV), the ZPL remains well below the threshold of ionization. These results

collectively suggest that V -based SDPs near (1x1) OH-terminated surfaces of 4H-SiC are optically stable and viable candidates for quantum photonic applications. Their excitation energies are well-positioned within the gap, avoiding unwanted transitions to continuum states, and their use of a wide gap host eliminates the need for external stabilization and or complex band engineering.

We now characterize the most compelling features of SDPs: the strong and intrinsic alignment of their electric dipole moments perpendicular to the surface plane. This directional consistency not only contrasts starkly with the random orientations found in bulk DAPs, but also introduces a number of practical advantages for their incorporation into engineered quantum platforms. Moreover, unlike traditional DAPs, where the static electric dipole moment exists in the ground state and vanishes upon excitation into the excited state, SDPs feature the opposite behavior: the dipole moment emerges only in the excited. This inversion is particularly advantageous for quantum applications, as it enables optical control over the interaction more akin to how it is done with trapped-atom Rydberg systems. In doing so, SDPs circumvent a key limitation of bulk DAPs, where persistent dipole interactions in the ground state can lead to unwanted background interactions.

To quantify the directionality of these dipoles, once more we employ the modern theory of polarization [99,100], implemented through the use of maximally localized Wannier functions (MLWFs) as provided by the Wannier90 code [101]. This formalism allows us to calculate the dipole moments with precision, capturing both their magnitude and vectorial orientation across different slab geometries.

In Figure 4.7, we present the evolution of the electric dipole moment associated with V -based SDPs as a function of the V defect's depth beneath the surface. The V atoms are embedded in varying bilayers (*e.g.* L3, L4, etc.). Our results show that the out-of-plane (z) component of the dipole increases linearly with the defect's distance from the surface. This behavior is consistent with a DAP-like dipole model, where increasing the separation

between the positively and negatively charged components (in the case of DAPs, the inter-defect distance, R_m) leads to an increased dipole moment along the axis of separation.

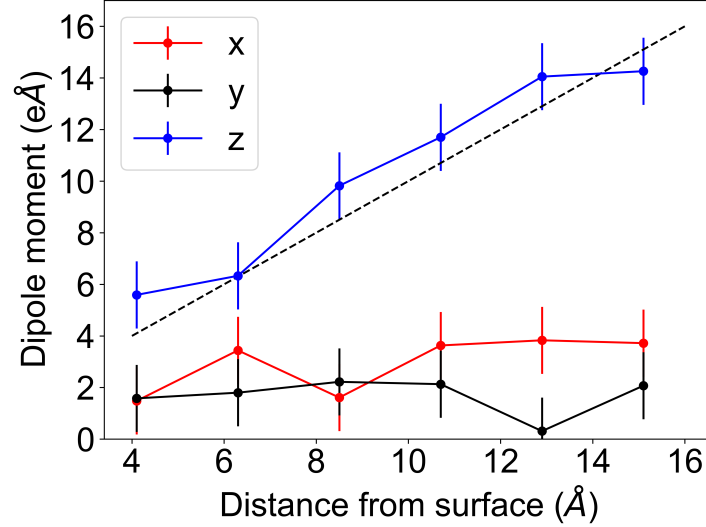


Figure 4.7: Transverse (x & y) and longitudinal (z) components of the electric dipole moment of surface-defect pairs formed between Vanadium and the (1x1) OH-terminated surface of 4H-SiC. The transverse components remain almost unchanged and the longitudinal component scales linearly with the distance of Vanadium from the surface. The black dashed line is a $y = x$ line meant as a guide to the eye.

Importantly, the in-plane components of the dipole (x and y directions) remain nearly constant and exhibit minimal fluctuations, comparable in magnitude to those observed in the isotropic dipole distributions of bulk DAPs [3]. The x-dominance of the dipole vector reflects a geometric asymmetry unique to the surface-defect configuration: while the defect center (the V site) is embedded several atomic layers deep, the corresponding hole state resides at the OH-terminated surface, producing a well-separated and vertically oriented charge separation. The near-uniformity of this z-alignment across different defect depths strongly suggests that SDPs form an array of parallel dipoles normal to the surface.

This degree of dipolar alignment represents a key asset for application where long-range dipole-dipole interaction are desired. Unlike bulk DAPs - where the 3D random orientation of dipole vectors averages out coupling in an ensemble - the SDPs here can exhibit

constructive, cooperative behavior in dipole-coupled networks. The consistent out-of-plane alignment ensures maximal coupling strength when the emitters are arranged laterally across the surface. This facilitates the implementation of conditional quantum logic gates based on dipole blockade and field-sensitive detection schemes with minimal angular averaging losses.

In tandem with the orientation analysis, we also compute the mass-weighted displacement ΔQ for the V -based SDPs, obtaining a value of $0.606 \text{ amu}^{1/2} \text{ \AA}$. This corresponds to a Huang-Rhys (HR) factor of ~ 2.6 , placing the SDP's electron-phonon coupling in an intermediate regime. We show the computed PL spectrum of V -based SDPs (with V defect placed in the L5 layer) in Figure 4.8. Although this HR factor is higher than that of the shallow Al-N DAPs examined in the previous section - many of which showed values ranging from 0.35 to 1.9 - it remains notably lower than that of the NV-center in diamond, which has an HR factor of ~ 3.6 . This indicates that while SDPs exhibit moderately broadened emission due to phonon sidebands, the ZPL remains spectrally distinct and potentially useful for optical applications.

Taken together, these findings underscore the viability of V -based SDPs as robust quantum emitters with built-in dipole directionality and acceptable optical performance. The alignment of the dipole moment along the surface normal enhances their utility for surface-integrated photonics, including cavities, antennas, and waveguides that operate with vertically coupled fields. In addition, the consistent dipole orientation across a surface array suggests that SDPs may be ideally suited for large-scale quantum sensing platforms, where uniform field response and tunable interactions are critical. Such architectures would benefit from the deterministic alignment and spacing of the SDPs, circumventing the disorder limitations that plague bulk defect arrays.

Moreover, the combination of moderate HR coupling and strong dipolar orientation makes these emitters compatible with emerging strategies for on-chip entanglement generation, electric field tuning, and hybrid quantum-classical interfacing. By anchoring both the optical

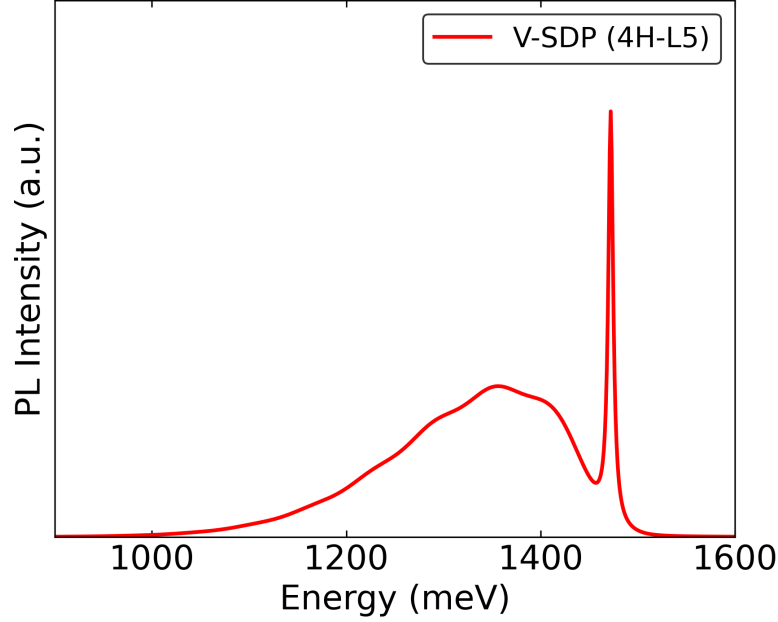


Figure 4.8: The computed photoluminescence (PL) spectra for a Vanadium surface-defect pair (SDP) near the (1x1) OH-terminated surface of 4H-SiC. The V defect is placed at the L5 layer of the slab, and the PL spectra is computed using the 1D configurational coordinate model. It resides in the intermediate electron-phonon coupling regime, with a Huang-Rhys factor of ~ 2.6 .

and electrostatic properties in a fixed geometric axis (perpendicular to the surface), SDPs offer a rare balance between precise optical control and scalability, hallmarks of practical quantum information systems.

4.3.4 Photoionization and Stimulated Emission Cross Sections

$\mathcal{E}$ Polarization Control

A defining feature of optically addressable quantum defects is their ability to efficiently couple with electromagnetic fields. Quantifying this coupling strength is critical not only for understanding spontaneous and stimulated emission processes, but also for engineering interactions in complex quantum architectures. Two central quantities in this context are the stimulated emission cross section, which describes the probability of induced photon

emission upon optical excitation, and the photoionization cross section, which characterizes the likelihood of an electron being promoted from a lower-lying state (*e.g.* a valence surface state) into an unoccupied defect level. These quantities directly govern the efficiency of excitation, readout, and charge-state manipulation of quantum emitters.

In the case of surface-defect pairs (SDPs), formed by V defects close to OH-terminated surfaces in 4H-SiC, optical cross sections acquire an additional layer of complexity: their strength becomes highly sensitive to the spatial separation of the V defect and the polarization of incident laser light. This sensitivity originates from the spatial separation of the electron and hole states - namely a hole localized on the surface and an electron residing in the V defect orbital. For the ZPL transition, which represents the lowest energy optical excitation, the transition dipole moment exhibits a pronounced alignment nearly perpendicular to the surface. This directional character strongly influences the polarization dependence of optical processes like stimulated emission and photoionization.

However, it is important to note that this directional anisotropy primarily characterizes the ZPL transition. Higher energy transitions, involving excitations from lower-lying states deeper in the valence band may not retain this preferential alignment. Their associated dipole moments can have broader spatial components and less deterministic orientation. Therefore, while the polarization control offered by SDPs is a unique feature, it is most pronounced in the first optical transition and should not be assumed to generalize across the entire absorption or emission spectrum.

This nuanced behavior distinguishes SDPs from conventional bulk point defects or DAPs, where the orientation of optical dipoles is randomly distributed across an ensemble, and polarization control is effectively lost. In contrast, the aligned ZPL dipole of SDPs enables field-resolved modulation of emission and absorption processes, paving the way for integration with polarization-selective photonic elements and directional quantum sensors. Additionally, the magnitude of stimulated emission and photoionization cross sections provide

insight into device viability. A high stimulated emission cross section can enhance coupling to optical cavities and waveguides, while a suppressed photoionization cross section minimizes the risk of charge-state instability under operational conditions. These optical metrics are not merely theoretical constructs, they define the practical design space for SDP-based emitters and sensors operating at the SiC surface. In this section, we analyze the computed cross sections for V -based SDPs, emphasizing their spatial, spectral, and polarization-dependent behavior.

To compute the optical cross sections of SDPs, we adopt a first-principles framework based on the methods laid out in Section 2.5.3. Within this framework, the central quantity governing interaction strength is the optical transition dipole moments, which we compute using the WEST code [8,9]. In the case of stimulated emission, the transition occurs between an excited SDP configuration, where the electron resides on the V defect and the hole resides at the OH-terminated surface. For photoionization, the transition originates from an occupied state (typically on the surface or in the valence band) and transitions into the V -based e states in the bandgap. Both processes involve Franck-Condon transitions mediated by electron-phonon coupling. To model these vibronic effects, we employ the 1D configurational coordinate (CC) model, and use the electron-phonon spectral function $A(\hbar\omega, T)$ to quantify the distribution of optical transition strength across different vibronic channels. The cross sections for both stimulated emission and photoionization are written in the general form:

$$\sigma_s(\hbar\omega, T) = \frac{4\pi^2\alpha}{n_r} \hbar\omega |\vec{\mu}_{eg}|^2 A(\hbar\omega, T) \quad (4.3)$$

$$\sigma_{ion}(\hbar\omega, T) = \frac{4\pi^2\alpha}{n_r} \hbar\omega \sum_i |\vec{\mu}_{id}|^2 A_i(\hbar\omega - E_i, T) \quad (4.4)$$

where $\vec{\mu}_{eg}$ and $\vec{\mu}_{id}$ are the optical transition dipole moments. In the case of stimulated emission, it is between the occupied V -based e state and the surface hole state, and in the

case of photoionization, between lower-lying surface or valence band states and the V -based e state. E_i are the energies of those transitions, the lowest of which is the ZPL energy.

For polarization control, we consider the real-space projection of the optical dipole matrix elements onto the polarization direction of the laser as shown in Figure 4.9. The polarization dependence of the cross sections are then determined by:

$$|\vec{\mu}_i|^2 = |\vec{e} \cdot \vec{\mu}_i|^2 = |\cos \delta(\vec{e}_{\parallel} \cdot \vec{\mu}_i) + \sin \delta(\vec{e}_{\perp} \cdot \vec{\mu}_i)|^2 \quad (4.5)$$

Here $\vec{e}$ is the unit vector describing the laser polarization, and δ is the polarization angle. This decomposition allows us to trace out the angular dependence of the cross sections and determine the optimal excitation or emission polarization angles for each configuration.

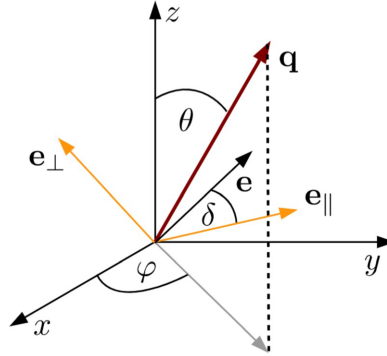


Figure 4.9: A representation of the photon wavevector $\mathbf{q}$ and the two polarization vectors $\vec{e}_{\parallel}$ and $\vec{e}_{\perp}$ in polar coordinates.

Figure 4.10 presents the calculated stimulated emission cross sections for V -based SDPs. The figure is organized by the direction of the incident laser light: the left panel corresponds to incident light parallel to the z axis (perpendicular to the surface) while the right panel shows the case for light perpendicular to the z axis (in-plane). In this case, only the dipole transition from the surface-localized hole state to the singly occupied e orbital of V contributes to the stimulated emission. This transition defines the ZPL and is the dominant radiative channel.

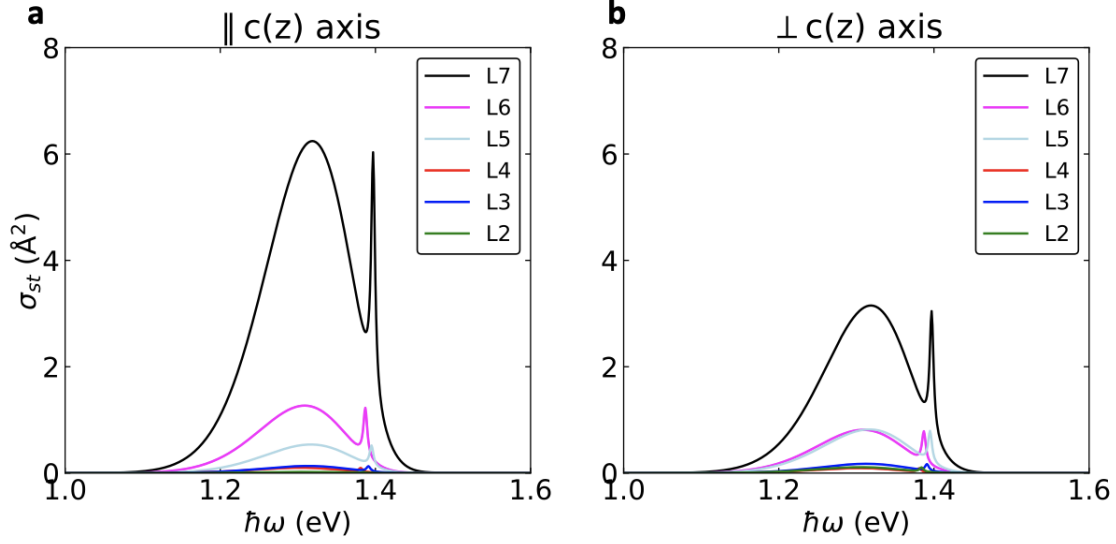


Figure 4.10: The stimulated emission cross sections ($\sigma_s \cdot 10^{-3}$) for Vanadium surface-defect pairs near OH-terminated SiC surfaces for incident exciting laser (a) parallel to the z axis and (b) perpendicular to the z axis. Stimulated emission cross sections from slabs containing V defect at different bilayers (see Figure 4.1) from L2 to L7 are shown together in both panels. We use a one-dimensional approach to compute the electron-phonon spectral function $A(\hbar\omega, T)$ and compute the transition dipole matrix elements using the WEST code [8, 9].

As anticipated, the strength of this dipole transition, and thus the magnitude of the stimulated emission cross section, is highly sensitive to the depth of the V atom relative to the surface. When the defect resides in the uppermost bilayers (specifically L6 and L7), where the spatial overlap between the defect states and the surface hole state is maximal, the transition strength peaks. However, this coupling drops off steeply as the V atom is positioned deeper into the slab. Shifting the V atom even a few Angstroms away from the surface can reduce the cross section by more than an order of magnitude.

Turning to the photoionization spectra shown in Figure 4.11, we observe a qualitatively different dependence on defect depth. Unlike the case of stimulated emission, which involves a single well-defined transition, photoionization involves multiple possible initial states. The contributing matrix elements change significantly as the V depth varies. When V is located near the surface (*e.g.* L6-L7), the ZPL transition remains dominant in the photoionization process, giving rise to a clear low-energy feature near 1.50 eV. This reflects a transition in

which the electron is excited from the surface hole state into the e that of the V defect, echoing the configuration for stimulated emission. However, for deeper V placements, (*e.g.* in bilayers L3-L5), this low-energy channel becomes suppressed. In these configurations, the dominant photoionization pathway shifts to higher energy transitions involving deeper lying surface states or valence band states, thereby pushing the absorption onset to higher photon energies in the spectrum.

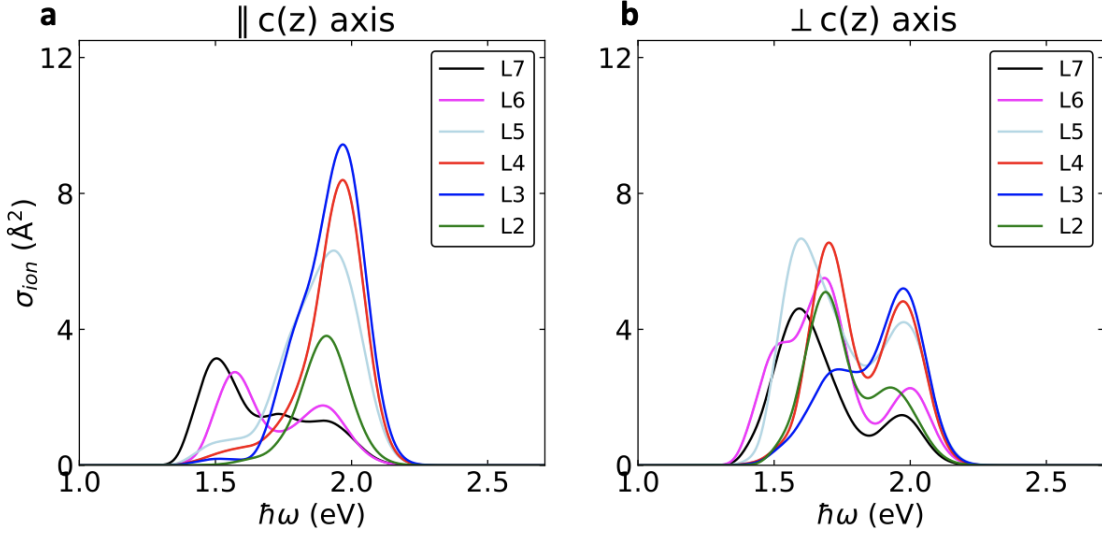


Figure 4.11: The photoionization cross sections ($\sigma_{ion} \cdot 10^{-3}$) for Vanadium surface-defect pairs near OH-terminated SiC surfaces for incident exciting laser (a) parallel to the z axis and (b) perpendicular to the z axis. Photoionization cross sections from slabs containing V defect at different bilayers (see Fig. 2.2) from L2 to L7 are shown together in both panels. We use a one-dimensional approach to compute the electron-phonon spectral function $A(\hbar\omega)$ and compute the transition dipole matrix elements using the WEST code [8,9].

Furthermore, the magnitude and character of these transitions also depend on the angle of polarization of the incident laser light. As suggested by Equation 4.5, the projection of the transition dipole moment along the light polarization direction modulates the cross section strength. Consequently, both stimulated emission and photoionization are not only geometry dependent, but also polarization sensitive, introducing a tunable degree of control in photonic applications. We analyze this polarization dependence by inserting Equation 4.5 into Equations 4.3 and 4.4, expand all the terms to arrive at:

$$\sigma(\delta) = A \cos^2 \delta + B \sin^2 \delta + 2C \cos \delta \sin \delta \quad (4.6)$$

where the coefficients A , B , and C are given by:

$$\begin{aligned} A &= \frac{4\pi^2\alpha}{n_r} \hbar\omega \sum_i A_i |\vec{e}_{\parallel} \cdot \vec{\mu}_i|^2 \\ B &= \frac{4\pi^2\alpha}{n_r} \hbar\omega \sum_i A_i |\vec{e}_{\perp} \cdot \vec{\mu}_i|^2 \\ C &= \frac{4\pi^2\alpha}{n_r} \hbar\omega \sum_i A_i (\vec{e}_{\parallel} \cdot \vec{\mu}_i)(\vec{e}_{\perp} \cdot \vec{\mu}_i) \end{aligned}$$

where we used the short-hand notation A_i for the electron-phonon spectral function $A_i(\hbar\omega - E_i, T)$ centered at transition energy E_i . In the case of stimulated emission, there's no need for the summation, as the only contributor is the ZPL transition, so the expression is even simpler.

The extrema of this polarization dependent cross section - namely, the angles that maximize and minimize optical response - are given analytically by:

$$\begin{aligned} \delta_{max} &= \frac{1}{2} \tan^{-1} \left(\frac{2C}{A-B} \right) + n\pi \\ \delta_{min} &= \frac{1}{2} \tan^{-1} \left(\frac{2C}{A-B} \right) + \frac{\pi}{2} + n\pi \end{aligned}$$

And consequently, the peak and trough (maximum and minimum points) for the cross sections $\sigma(\delta)$ are given by:

$$\begin{aligned} \sigma(\delta_{max}) &= \frac{A+B}{2} + \sqrt{\left(\frac{A-B}{2}\right)^2 + C^2} \\ \sigma(\delta_{min}) &= \frac{A+B}{2} - \sqrt{\left(\frac{A-B}{2}\right)^2 + C^2} \end{aligned}$$

This angular dependence is not merely a small perturbation, it enables substantial mag-

nitude modulation over the cross sections for both photoionization and stimulated emission. For V -based SDPs near OH-terminated 4H-SiC surfaces, cross section modulations of up to a factor of 100 are observed when tuning the polarization angle δ . This is an extremely useful level for optical control, especially in integrated systems where photon energy and direction are fixed but polarization can be varied with minimal effort. Such polarization-based modulation provides an effective means to selectively address or suppress specific optical processes in engineered defect arrays. For instance, one could suppress unwanted photoionization while enhancing stimulated emission by aligning the laser polarization with the preferred dipole axis of the defect. This is particularly powerful for surface-defect systems where the dipole orientation is strongly aligned.

These findings underscore the value of polarization engineering as a practical knob for defect-based quantum device operation, from qubit readout to spin-photon interfacing and even dipolar coupling-based quantum gates. Since the entire dependence is derived from transition dipole projections and phonon coupling - quantities accessible via first-principles simulation - this modulation strategy is also predictive, enabling design and optimization *a priori*.

4.4 Summary and Conclusions

In this chapter, we examined how the structural, electronic, and optical properties of DAPs and SDPs evolve in the presence of hydrogen-terminated and hydroxyl-terminated surfaces of 3C- and 4H-SiC. Our analysis, grounded in first-principles calculations, provides a comprehensive picture of the defect-surface interactions and identifies several critical advantages and limitations associated with placing quantum defects in near-surface environments.

We began by characterizing the electronic structure of various surface terminations, noting that hydrogenated (2x1) SiC surfaces preserve semiconducting character with moderate electron affinity, while hydroxyl (OH) termination introduces surface states above the valence

band. These electronic surface states allow the formation of tightly bound defect-surface complexes, demonstrated in the SDP configurations.

Charge transition levels (CTLs) of isolated near-surface donors and acceptors, particularly N_C and Al_{Si} were found to remain close to their bulk values when finite size corrections were properly accounted for. This suggests that the shallow or deep character of these defects is preserved near the surface, allowing for the controlled assembly of DAPS without significant disruption to their ionization thermodynamics. Using 9-bilayer slabs, we estimate bandgap and CTL shifts on the order of 0.1-0.2 eV due to confinement effects, but extrapolated trends confirmed the near-surface values are mostly consistent with bulk behavior.

The ZPL energies and PL spectra of Al-N DAPS placed near the H-terminated surface were shown to remain remarkably stable, with only minor shifts in energy compared to bulk configurations. However, a more noticeable impact was observed on the electron-phonon coupling: DAPs located in the topmost layers exhibit larger mass-weighted displacements (ΔQ) and enhanced Huang-Rhys (HR) factors, reducing their Debye-Waller factors and broadening the PL spectrum. Despite this increase in phonon sideband emission, many of these near-surface DAPs still preserve sharp ZPL peaks, offering potential compatibility with photonic devices.

Surface-defect pairs (SDPs) presented a new avenue for overcoming limitations inherent to bulk DAP systems. In contrast to bulk DAPs, which suffer from dipole orientation randomness due to uncontrolled thermal formation, SDPs exhibit robust dipole alignment perpendicular to the surface. This geometrical determinism is not only useful for creating uniform optical emission but also paves the way for deterministic dipole-dipole interaction strengths and enhanced optical addressability. Furthermore, the dipole moments of SDPs emerge in the excited state, rather than the ground state, resolving a conceptual drawback of DAPs, where persistent ground state dipoles can lead to uncontrolled crosstalk and decoherence.

We evaluated both photoionization and stimulated emission cross sections for SDPs and demonstrated their strong dependence on the defect’s proximity to the surface and the polarization of incident light. Stimulated emission rates were highest when the V defect was located close to the surface, with sharp declines occurring as the V was placed further from the surface. Polarization analysis revealed modulation factors up to one hundred, a degree of optical tunability that is hard to attain in bulk defects. This polarization dependence enables precise photonic control and positions SDPs as scalable building blocks for on-chip quantum optical networks, capable of integrations with nanophotonic platforms.

Altogether, this chapter underscores that near-surface defect architectures are not merely modifications of bulk systems but constitute a new design space with distinct advantages in dipole alignment, tunability, and photonic integration. By carefully engineering surface terminations and defect placements, it becomes possible design solid-state quantum emitters and sensors that combine atomic-scale precision with device-level controllability. Future work should focus on experimental validation of these computational predictions and explore strategies for deterministic implantation or site-controlled growth of SDPs in patterned SiC surfaces.

CHAPTER 5

GERMANIUM VACANCY CENTERS AS OPTICAL NANO-ANTENNAS

Adapted from Z. Li, X. Guo, Y. Jin, F. Andreoli, A. Bilgin, D. D. Awschalom, N. Deegan, F. J. Heremans, D. Chang, G. Galli, A. A. High. Nat. Photonics, 18, 1113-1120 (2024)

5.1 Introduction

In recent years, point defects in wide-bandgap semiconductors have emerged as versatile building blocks for quantum photonics, sensing and information processing platforms [14,15]. Among these, the Group-IV vacancy centers in diamond - such as silicon-vacancy (SiV), germanium-vacancy (GeV), and tin-vacancy (SnV) centers - have attracted particular attention due to their narrow optical emission linewidths, inversion symmetry, and compatibility with nanophotonic structures [39,48,153–156]. The GeV center, in particular, exhibits desirable optical properties including a sharp zero-phonon line (ZPL) near 602 nm, near-transform limited linewidths, and high Debye-Waller factors, making it a promising candidate for scalable quantum devices [153,157,158].

Despite these advantages, the ability to dynamically control the optical transition characteristics of individual color centers remains a critical challenge. While techniques such as strain tuning [39,159,160] and external electric fields [161] have been employed to shift emission frequencies, most efforts have focused on simple ZPL energy modulation. Less explored, but equally important, is the anisotropic nature these defect’s photophysics and their distance-dependent near and far-field implications under resonant and off-resonant laser illumination. After all, the directionally-dependent behavior of color centers plays a central role in coupling color centers to nanophotonic elements, such as waveguides and optical cavities, where mode matching depends critically on the emitter orientation.

In this chapter, we investigate the electric field response of the GeV center’s ZPL in diamond, with particular emphasis on its second-order Stark shift and the resulting implications for its use as a quantum sensor of nearby charge fluctuations and as an optical nano-antenna. Unlike nitrogen-vacancy (NV) centers, GeV centers possess inversion symmetry, and therefore lack a permanent electric dipole moment [161]. As a result, their Stark response is strictly quadratic in the applied field. This symmetry-imposed constraint allows us to probe their polarizability in a clean and unambiguous way, free from first-order contributions that typically dominate other systems.

The key motivation for this work stems from experimental observations made in previous studies [159, 162, 163]. There, GeV centers were found to exhibit discrete spectral jumps in their ZPL energies, even in the absence of externally applied fields. These jumps, while initially unexplained, motivated a detailed investigation into their origin. Several potential mechanisms were considered and systematically ruled out, including strain-induced Jahn-Teller distortions and dynamic hydrogen reorientation near the GeV centers. Through this process of elimination, and by comparing with theoretical models and experimental results, the most consistent explanation emerged: the observed spectral jumps are caused by fluctuating local electric fields, most likely originating from charge state transitions of nearby vacancies. These localized fields induce second-order Stark shifts in the GeV center’s ZPL energy, highlighting the need to model GeV’s direction-dependent sensitivity for second-order Stark shifts through its polarizability tensor.

To interpret and quantify these effects, our contribution centered on a first-principles approach using constrained density functional theory (DFT). We compute the ZPL energies of GeV centers under applied electric fields using constrained DFT, and the resulting shifts in emission energy are then fit to a second-order Stark shift model of the form:

$$\Delta E_{\text{ZPL}} = \frac{1}{2} \mathbf{E}^T \cdot \boldsymbol{\alpha} \cdot \mathbf{E} \quad (5.1)$$

where $\mathbf{E}$ is the applied electric field vector, and $\boldsymbol{\alpha}$ is the polarizability tensor of the defect. By varying the direction and magnitude of the electric field in our simulations, we extract all independent components of $\boldsymbol{\alpha}$, and use this information to generate polar maps of Stark shift sensitivity as a function of field angle and distance. These polar plots reveal a pronounced angular dependence in the Stark response, indicating that the GeV center’s emission energy is anisotropically sensitive to applied fields.

In the broader context of this thesis, this chapter demonstrated a novel framework for evaluating the polarizability of quantum defects and highlights how constrained DFT can be used to model subtle but important field-induced phenomena. By focusing on a defect that lacks a permanent dipole, we emphasize the power of higher-order modeling to uncover emergent tunability and field response mechanisms. These insights pave the way for designing photonic structures and quantum devices that harness not just the emission wavelength of quantum emitters, but also their highly directional properties, such as polarizability.

In the following sections, we describe the computational methodology employed for these constrained DFT simulations, followed by a detailed presentation of our results, including understanding the polarizability tensor, creating a polar Stark shift mapping of the GeV center, and a discussion on future quantum technologies based on Group-IV centers.

5.2 Computational Methods

To investigate the origin of discrete spectral jumps in the zero-phonon lines (ZPLs) of the negatively charged GeV center in diamond, we conducted a series of DFT calculations using the Quantum ESPRESSO [79–81] software package. All simulations employed the PBE [10] functional, together with SG15 optimized norm-conserving Vanderbilt pseudopotentials [82, 83]. The kinetic energy cutoff for the plane-wave basis set is set to 90 Ry, ensuring full convergence for both total energies and forces. Structural relaxations and total energy evaluations are performed with a lattice constant of 3.568 Å.

The GeV defect is modeled in a 3x3x3 cubic diamond supercell, comprising 214 carbon atoms and one germanium atom, with Γ -point sampling used for Brillouin zone integration. The Ge atom is placed in a split-vacancy configuration, forming the characteristic D_{3d} symmetry of the GeV center. Structural optimization is performed until the forces on all atoms are below 10 meV/Å, and spin polarization is included throughout.

To compute the electric field response of the ZPL, we employ constrained-occupation DFT (Δ SCF). The ZPL is obtained as the total energy difference between the relaxed ground and excited state geometries. External electric fields (compatible with periodic boundary conditions) are applied along multiple directions, enabling extraction of the second-order Stark shift tensor (*i.e.* the polarizability tensor). These tensor components quantify the quadratic dependence of the ZPL energy on field strength and orientation, which is the leading-order effect in GeV due to the inversion symmetry of the defect eliminating any permanent electric dipole moment.

In addition to field-based modeling, we perform a broader suite of DFT calculations to systematically eliminate several alternative mechanisms that could underlie the observed spectral instability. First, we explore strain-induced perturbations by applying strain along different crystallographic axes to the 3x3x3 supercell. These simulations aim to probe potential Jahn-Teller-related symmetry breaking effects, which could lift orbital degeneracies and shift excited state energies. For each strain configuration, we relax atomic positions and evaluate the ZPL via Δ SCF, monitoring any abrupt changes in excitation energy.

Second, we explore the possibility of metastable hydrogen configurations near the GeV center as a source of spectral variation. These calculations are performed considering four degenerate configurations of vacancy-hydrogen (VH) complexes, reflecting the four possible ways a hydrogen atom could bond with one of the four carbon atoms in a carbon tetrahedron. The hydrogen reorientation process involves breaking the old C-H bond and forming a new one with another carbon atom, resulting in local strain in the diamond lattice that could shift

the ZPL energy of the nearby GeV center. In our calculations, we implement the negatively charged VH center, considering that in the range of Fermi levels that stabilize the GeV in its negative charge state, the VH is also most stable in this charge state [164, 165]. We study the path of the reorientation of the hydrogen atom in an isolated VH center using a nudged elastic band calculation in a 4x4x4 diamond supercell and obtain a magnitude for the potential barrier the H atom needs to overcome through quantum tunneling.

Together, these modeling efforts serve a dual purpose: they establish the field-induced quadratic Stark response as the dominant mechanism for observed ZPL shifts, and they rule out competing scenarios based on strain-induced symmetry breaking or dynamic hydrogen rearrangement. This comprehensive approach allows for a robust interpretation of the GeV's spectral behavior in terms of local charge fluctuations, which is further corroborated by experimentally demonstrated charge initialization through resonant pumping of either of the split ZPL peaks of GeV center.

5.3 Results and Discussion

5.3.1 Strain-Induced Degeneracy Breaking of Jahn-Teller Configurations

The germanium-vacancy (GeV) center in diamond is known to possess degenerate electronic orbitals that are susceptible to Jahn-Teller distortions in both its ground and excited states [165]. Specifically, there is one unpaired electron occupying the degenerate e_g (e_u) orbitals when the system is the ground (excited) state. This symmetry in the electronic structure makes the system prone to spontaneous symmetry breaking distortions, known as Jahn-Teller effects, which lower the system's total energy.

First-principles calculations confirm that there exist three equivalent Jahn-Teller distorted configurations for both the ground and excited states of the GeV center. In each of these configurations, two of the Ge-C bonds are elongated, while the other four are com-

pressed, leading to structures with reduced point-group symmetry (C_{2h}), even though the average symmetry across all three configurations remains D_{3d} . Under ambient conditions, transitions between these configurations average out, yielding a single observed ZPL. However, the application of an external strain field could, in principle lift this degeneracy and result in distinguishable ZPL energies corresponding to different initial and final geometries.

To investigate this possibility, we performed DFT calculations by applying external strain along crystallographic directions, particularly the [100] direction, to artificially break the symmetry. These calculations showed that even a small uniaxial strain on the order of 0.01% could split the ZPL into two distinct branches, as seen in Figure 5.1. This splitting arises due to the removal of the degeneracy between the Jahn-Teller configurations, which modifies the potential energy surface differently for the ground and excited states.

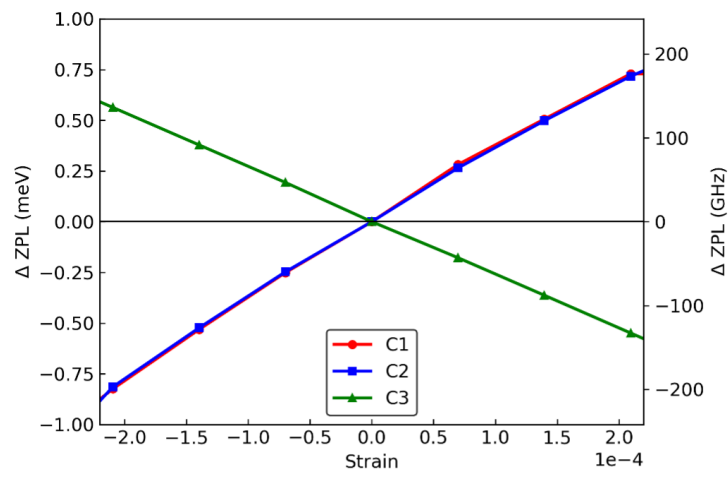


Figure 5.1: Splitting of the zero-phonon line (ZPL) by strain in the [100] direction obtained from density functional theory (DFT) calculations. C1, C2, and C3 refer to three Jahn-Teller configurations, which break into two groups upon [100] strain.

However, several observations undermine this mechanism as a plausible explanation for the ZPL spectral switching observed experimentally. Firstly, the calculated ZPL splitting is on the order of 100 GHz when strain is around 0.01%, which is much smaller than the strains present in experimental samples. More importantly, no strong correlation is observed

between the measured strain and the occurrence or magnitude of spectral switching, casting doubt on the assumption that strain is the driving factor. Experimental observations of spectral splitting exceeding twofold, namely four and eight-fold splittings, also remain unexplained by this mechanism, which predicts only a twofold splitting under strain.

Beyond energetic arguments, the dynamics of spectral switching provide further evidence against a strain-induced Jahn-Teller mechanism. Here, the hypothesis is that the observed switching arises from the GeV center dynamically hopping between its three Jahn-Teller-distorted configurations. To evaluate this, we estimate the rate of such hopping using an Arrhenius model:

$$r = Ae^{-\frac{E_{\text{barrier}}}{k_B T}} \quad (5.2)$$

where E_{barrier} is the energy barrier for the configurational transition and A is the attempt frequency, associated with the phonon mode driving the distortion. Previous DFT calculations yield an energy barrier of 2.0 meV for the ground state and 5.4 meV for the excited state [165]. Corresponding phonon energies (used for estimating A), are 82.2 meV and 73.0, respectively. using these parameters at a cryogenic temperature of 4K, the predicted hopping rates are $\sim 6 \times 10^{10} \text{ s}^{-1}$ for the ground state and $\sim 3 \times 10^6 \text{ s}^{-1}$ for the excited state. This is several orders of magnitude larger than the observed experimental switching rates of 0.01 to 1 s^{-1} .

These hopping rates remain much too fast to account for the slow dynamics observed in the experiments. This discrepancy effectively rules out the Jahn-Teller switching mechanism as the origin of the spectral jumps. As such, while strain can influence the ZPL energetics in principle, it is insufficient to explain the discrete, long-time scale spectral switching behavior seen in GeV centers, necessitating further investigation into alternative mechanisms.

5.3.2 Hydrogen Reorientation of the VH center

Another potential mechanism considered to explain the discrete spectral switching observed in GeV centers involved the reorientation dynamics of the vacancy-hydrogen (VH) complexes in the vicinity of the emitter. VH complexes are known to be prevalent in diamond thin films, where hydrogen atoms passivate carbon vacancies by forming C-H bonds. Structurally, the VH center consists of a hydrogen atom situated within a carbon vacancy and can exist in one of four energetically favorable configurations, corresponding to bonding with one of the four neighboring carbon atoms forming the vacancy's tetrahedral environment.

Reorientation of the hydrogen atom between these configurations involves breaking an existing C-H bond and forming a new one, effectively relocating the hydrogen atom within the tetrahedron, as illustrated in Figure 5.2. This hopping process introduces local lattice strain, which in turn could modulate the electrostatic and strain environment around a nearby GeV center, potentially resulting in shifts in the ZPL. Given the sensitivity of color centers to their local environment, even modest strain perturbations may lead to observable optical shifts.

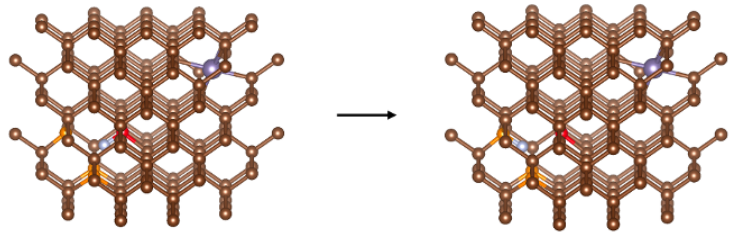


Figure 5.2: The schematic plot depicts the reorientation of a VH center in the vicinity of a GeV center. The germanium atom and the hydrogen atom are represented by purple and silver spheres, respectively. In the left plot, the hydrogen atom is linked to the red carbon atom, while in the right plot, it is repositioned to the orange carbon atom. The reorientation process may cause local strain in the diamond lattice, which could shift the zero-phonon line (ZPL) of the GeV center.

To assess the plausibility of this mechanism, the intrinsic properties of the VH complex were evaluated using DFT. Prior studies [164] indicate that the VH center is stable in the

negatively charged state when the Fermi level lies between approximately 1.5 and 3.3 eV above the valence band maximum. Meanwhile, as established in earlier calculations [165], the negatively charged state of the GeV center is energetically favorable when the Fermi level resides between 1.9 and 2.7 eV. Considering the overlap in charge state stability regions and the fact the GeV centers used here are also negatively charged, we justify modeling the VH center in its negatively charged configuration.

A direct evaluation of the ZPL shift caused by the hydrogen reorientation in a large supercell containing both the GeV and the VH center is prohibitively expensive computationally, especially considering the long-range elastic and electrostatic interactions. Instead, we take a more tractable approach by modeling the reorientation pathway of the hydrogen atom in an isolated VH center using the nudged elastic band (NEB) method. We carry these calculations out in a large 4x4x4 diamond supercell containing 511 carbon atoms and one hydrogen atom. These calculations revealed a reorientation barrier of 810 meV and an associated phonon frequency along the reaction coordinate of 93 meV.

To quantify the reorientation dynamics, including quantum tunneling effects, which are especially relevant at cryogenic temperatures, we use the WKB approximation, and write the reorientation rate with the following expression:

$$\nu_t = \frac{\omega}{2\pi} \exp\left(-\frac{1}{\hbar} \int_{-x_0}^{x_0} \sqrt{2m\left[V(x) - \frac{1}{2}\hbar\omega\right]} dx\right) \quad (5.3)$$

Here, ω is the effective phonon frequency, $V(x)$ is the reorientation potential (as shown in Figure 5.3) and x_0 defines the limits of the classically forbidden region. The system is assumed to reside in its vibrational ground state at $T = 4\text{K}$. Based on this model, the calculated reorientation rate is found to be approximately 3 s^{-1} , a value comparable to experimentally observed spectral switching rates in GeV centers. This agreement initially suggested VH reorientation as a plausible explanation.

To experimentally test this hypothesis, a targeted control experiment was performed.

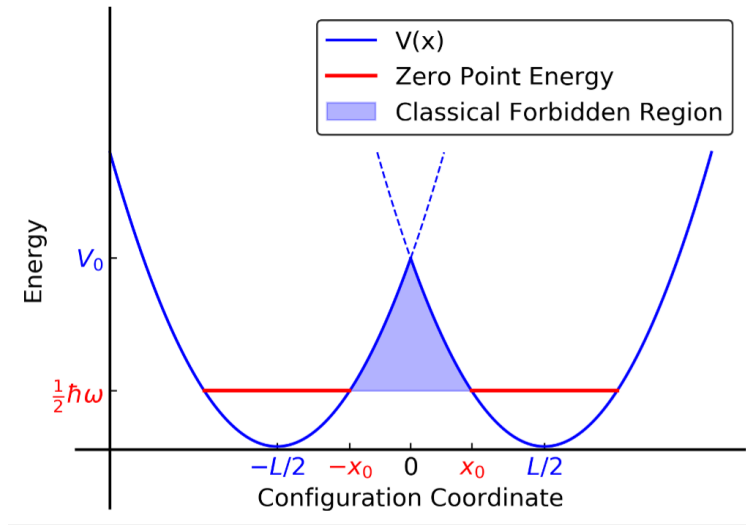


Figure 5.3: Effective potential used in the WKB approximation. The potential energy curve is approximated as the concatenation of two parabolas whose curvature is determined by the effective phonon frequency. V_0 is the height of the barrier, and $\frac{1}{2}\hbar\omega$ is the zero point energy. The distance between two local minima is L . The classically forbidden region is shown as the shaded area between $[-x_0, x_0]$.

Seventeen GeV centers were individually characterized via photoluminescence excitation (PLE) spectroscopy at 4K, using a confocal microscope setup. Subsequently, the sample was warmed to room temperature and exposed to ambient air for four hours - a treatment expected to allow significant hydrogen diffusion away from vacancy sites. After re-cooling the sample to 4K, the same 17 GeVs were re-characterized.

Crucially, no significant change in the number of observable ZPL peaks, their splitting magnitudes, or the overall spectral dynamics was observed after this thermal cycle. This lack of correlation between thermal treatment and spectral behavior rules out hydrogen reorientation in VH centers as the primary mechanism behind the ZPL switching in GeV centers.

5.3.3 Characterizing the Second Order Stark Shift Through

the Polarizability Tensor

The inversion symmetry of the GeV center in diamond leads to a vanishing permanent dipole moment, meaning that first-order Stark shifts are forbidden. Consequently, any shift in the ZPL under electric fields must arise from second-order effects. These are described through a polarizability tensor $\boldsymbol{\alpha}$, which captures the quadratic coupling of an external electric field to the electronic energy levels of the system. The second-order Stark shift of the GeV's ZPL can be expressed as:

$$\begin{aligned}\Delta E_{\text{ZPL}} &= \frac{1}{2} \mathbf{E}^T \cdot \boldsymbol{\alpha} \cdot \mathbf{E} \\ &= \frac{1}{2} \begin{pmatrix} E_x & E_y & E_z \end{pmatrix} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}\end{aligned}\tag{5.4}$$

where $\mathbf{E} = (E_x, E_y, E_z)$ is the applied electric field vector, and $\boldsymbol{\alpha}$ is a symmetric second-rank tensor with units of volume ($\text{\AA}^3$). The matrix elements of α_{ij} describe the induced energy shift per unit square electric field in directions i and j . Since $\boldsymbol{\alpha}$ is symmetric ($\alpha_{ij} = \alpha_{ji}$), it has six independent components.

To compute the components of $\boldsymbol{\alpha}$, we carried out DFT simulations with the PBE functional within a 3x3x3 supercell (214 carbon atoms and 1 Ge atom). The excited state was modeled via ΔSCF , in which one electron was manually promoted to the e_u orbital, mimicking the first bright transition. External electric fields were applied in six linearly independent directions to extract both the diagonal and off-diagonal terms of the polarizability tensor. To align the coordinate system with the defect symmetry, we define the axes as follows:

- z-axis along the $[111]$ direction (GeV axis)
- y-axis along $[11\bar{2}]$

- x-axis along $[1\bar{1}0]$

It is straightforward to apply electric fields along these three directions and obtain the diagonal components of the polarizability tensor. For the off-diagonal components, we apply electric fields three additional directions, namely the $[100]$, $[110]$, and $[101]$ directions. From each of these configurations we can extract linear combinations of the off-diagonal components and solve three linear equations for the three unknown components. Following those steps, we obtain the full polarizability tensor as follows:

$$\boldsymbol{\alpha} = \begin{pmatrix} 2.589 & 0.028 & -0.402 \\ 0.028 & 2.688 & -0.216 \\ -0.402 & -0.216 & 13.90 \end{pmatrix} (\text{\AA}^3) \quad (5.5)$$

This tensor reveals several insights. The component along the GeV's axis α_{zz} is significantly larger than α_{xx} and α_{yy} , indicating a stronger sensitivity along the GeV's axis and off-diagonal components are small. The similarity of α_{xx} and α_{yy} and the small sizes of α_{xz} and α_{yz} justify an approximate cylindrical symmetry assumption about the z-axis.

To visualize the angular dependence of the Stark shift, we model the ZPL energy shift from a nearby point charge by computing the local electric field it generates and applying Equation 5.4. Assuming the position of the carbon vacancy relative to GeV is:

$$\mathbf{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (5.6)$$

the electric field generated by the negative point charge is:

$$\mathbf{E} = -\frac{e}{4\pi\epsilon_0\epsilon_r} \frac{\mathbf{r}}{r^3} \quad (5.7)$$

and the ZPL shift is given by:

$$\Delta E_{\text{ZPL}} = \frac{1}{2} \mathbf{E}^T \cdot \boldsymbol{\alpha} \cdot \mathbf{E}$$

$$\Delta E_{\text{ZPL}} = \frac{1}{2} \left(\frac{e}{4\pi\epsilon_0\epsilon_r} \right)^2 \frac{1}{r^4} \begin{pmatrix} \sin\theta \cos\phi & \sin\theta \sin\phi & \cos\theta \end{pmatrix} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix}$$

$$\Delta E_{\text{ZPL}} = \frac{1}{2} \left(\frac{e}{4\pi\epsilon_0\epsilon_r} \right)^2 \frac{1}{r^4} \left(\alpha_{xx} \sin^2\theta \cos^2\phi + \alpha_{yy} \sin^2\theta \sin^2\phi + \alpha_{zz} \cos^2\theta \right. \\ \left. + 2\alpha_{xy} \sin^2\theta \sin\phi \cos\phi + 2\alpha_{xz} \sin\theta \cos\theta \cos\phi + 2\alpha_{yz} \sin\theta \cos\theta \sin\phi \right) \quad (5.8)$$

As justified above, if we assume a cylindrical symmetry, we have $\alpha_{xx} = \alpha_{yy}$ and $\alpha_{xz} = \alpha_{yz}$. By further neglecting the off-diagonal elements and solving the equation for a fixed ΔE_{ZPL} , or alternatively, solving the equation for a fixed GeV-vacancy distance, we arrive at two relations that give us polar plots of the GeV's polarizability dependence:

- For fixed distance r from the GeV:

$$\Delta E_{\text{ZPL}} = \frac{1}{2} \left(\frac{e}{4\pi\epsilon_0\epsilon_r} \right)^2 \frac{1}{r^4} [(\alpha_{xx} - \alpha_{zz}) \sin^2\theta + \alpha_{zz}] \quad (5.9)$$

- For fixed ΔE_{ZPL} :

$$r^4 = \frac{1}{2} \left(\frac{e}{4\pi\epsilon_0\epsilon_r} \right)^2 \frac{1}{\Delta E_{\text{ZPL}}} [(\alpha_{xx} - \alpha_{zz}) \sin^2\theta + \alpha_{zz}] \quad (5.10)$$

The resulting polar plots from Equation 5.9 and 5.10 are shown in Figure 5.4. Additionally, we also show the expected Stark shift ΔE_{ZPL} experienced by the GeV's ZPL as a function of the distance from the GeV center for various different angles with respect to the z-axis in Figure 5.5

The results confirm that GeV centers are indeed relatively insensitive to electric field noise, with second-order Stark shifts that are nearly three orders of magnitude smaller than

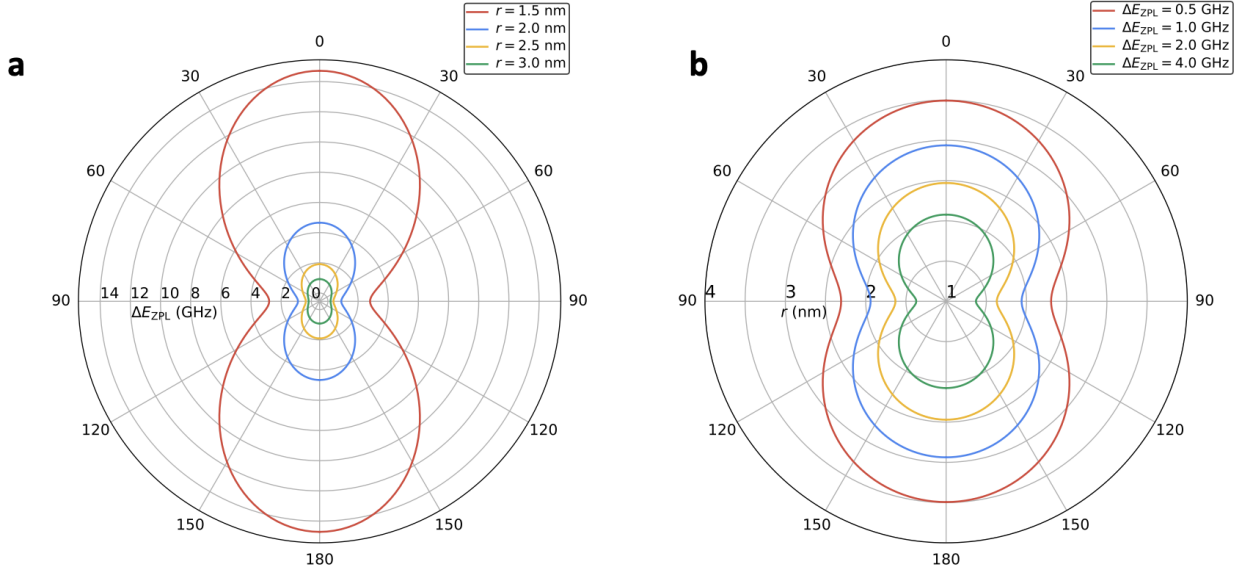


Figure 5.4

. (a) The second-order Stark shift of the GeV's ZPL as a function of the polar angle θ from the z-axis (defined as the [111] direction) for a given distance r between the vacancy and the GeV. (b) The distance between the GeV and the vacancy as a function of the polar angle θ for a given Stark shift ΔE_{ZPL}

first-order shifts observed in NV centers [40]. Nevertheless, the directional dependence of the shift provides a diagnostic tool for identifying the orientation and proximity of nearby fluctuating charges at vacancy sites - essential for understanding the noise environment near GeV centers.

The second-order Stark mechanism revealed here offers a compelling explanation for the experimentally observed discrete spectral jumps of GeV centers in diamond. These abrupt changes in the ZPL energy are consistent with electric field fluctuations originating from nearby trapped charges in vacancy complexes. The calculated polarizability tensor provides a quantitative link between the orientation and magnitude of such localized fields and the resulting energy shift.

Unlike many defect systems where electric field sensitivity is dominated by a permanent dipole moment and first-order Stark shifts, the GeV's inversion symmetry suppresses this

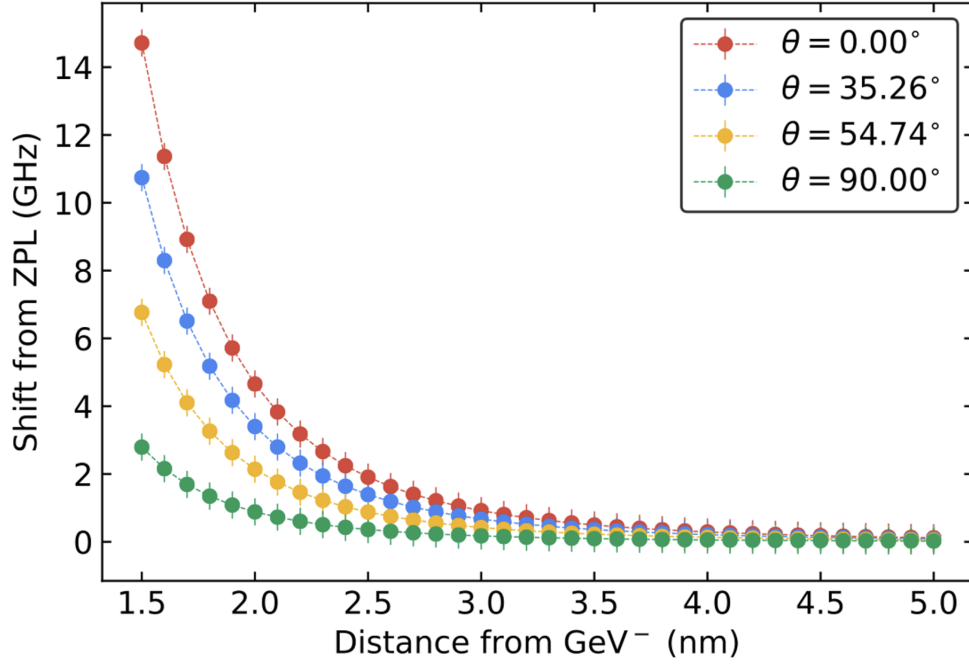


Figure 5.5: The Stark shift of the GeV's ZPL as a function of the distance r between the GeV and the localized electron at a vacancy for different polar angles θ .

pathway. This leads to an important conclusion: The shift magnitude depends strongly on both the field intensity and its alignment relative to the GeV axis, explaining why only some GeV centers exhibit switching behavior while others remain spectrally stable - even within the same sample. Some GeV's may not have any vacancies within a $\sim 3\text{-}5$ nm radius, or even if they do, these vacancies might not be strongly aligned along the GeV's axis to induce Stark shifts of enough magnitude to be detectable.

Importantly, this mechanism also aligns with the failure of alternative hypotheses. Strain-induced Jahn-Teller or hydrogen reorientation in nearby VH centers predict either incorrect spectral scales or behaviors that are not borne out experimentally. In contrast, the electric field induced Stark shift model derived here is both physically plausible and quantitatively consistent with the observed ZPL fluctuations, establishing it as the most viable explanation among those considered.

5.4 Summary and Conclusions

In this chapter, we examined the optical behavior of the negatively charged germanium vacancy (GeV-) center in diamond, with a particular emphasis on understanding and modeling the discrete spectral switching phenomena observed in its ZPL under static conditions. This study, stemming from the collaborate effort presented in our recent work on "Atomic Optical Antennas in Solids" [166], integrates DFT modeling of the Stark effect in systems with inversion symmetry. The findings presented here build toward a comprehensive microscopic interpretation of GeV spectral instability, while also developing a predictive, designable framework for electric-field sensitive color centers in solid-state hosts.

We began the chapter by contextualizing the GeV center as a member of the Group-IV vacancy family of color centers in diamond, which have attracted substantial interest due to their excellent optical properties. While the inversion symmetry of the GeV center suppresses linear electric dipole coupling, it has been that its ZPL undergoes abrupt spectral jumps under passive experimental conditions, suggesting a mechanism beyond simple strain or temperature modulation. These discrete shifts, though previously unaccounted for, have important implications for both quantum device stability and the underlying physics of point defects in solids.

To resolve the origin of these discrete ZPL jumps, we undertook a systematic process of elimination. In the first part of the chapter, we explored the hypothesis that strain-induced degeneracy breaking of Jahn-Teller configurations could produce multiple ZPL branches. Through DFT simulations of GeV centers under uniaxial strain, we confirmed that such strain does indeed split the ZPL; however, the magnitude of the effect was on the order of ~ 100 GHz for 0.01% strain, and did not match with strains present in experimental samples. Furthermore, the estimated hopping rates between Jahn-Teller configurations were several orders of magnitude faster than the observed spectral switching dynamics (which occur at rates on the order of $0.01\text{-}1\text{ s}^{-1}$), effectively ruling out this mechanism as a viable option.

Next, we investigated the potential impact of hydrogen reorientation in vacancy-hydrogen (VH) complexes near the GeV center. This hypothesis posited that motion of a nearby hydrogen atom bonded within a vacancy might locally perturb the strain field, thereby influencing the GeV's optical transition. We evaluated this through nudged elastic band (NEB) calculations. The calculated energy barrier of 810 meV and associated reorientation rate ($\sim 3 \text{ s}^{-1}$ at 4K) suggested a plausible mechanism from a dynamic standpoint. However, experimental testing through thermal cycling and air exposure - expected to help hydrogen atoms diffuse and change the local environment significantly - yielded no observable change in GeV ZPL splitting behavior. This result allowed us to definitely reject hydrogen reorientation as the primary cause of spectral switching.

Having excluded these mechanisms, the remainder of the chapter focused on the electric field induced Stark effect as the leading candidate. We constructed a polarizability-based model to describe the ZPL shift as a second-order function of the electric field, leveraging inversion symmetry of the GeV center, which eliminates the first-order contributions. By applying homogeneous electric fields along six different crystallographic directions, we extracted the full 3x3 polarizability tensor, including the off-diagonal elements. The values of the diagonal components, most notably $\alpha_{zz} \approx 13.9 \text{ \AA}^3$, highlight a pronounced anisotropic response to electric fields aligned along the defect symmetry axis ([111] direction). This anisotropy is further supported by the near-zero off-diagonal terms and small differences between α_{xx} and α_{yy} , indicating a near-cylindrical symmetry.

We then used this polarizability tensor to compute the Stark sensitivity of the GeV center under arbitrary field orientations. We produced polar plots of the resulting ZPL shifts as a function of position and orientation. These maps clearly showed that ZPL shifts on the order of several GHz, consistent with experimental jumps, can be produced by relatively modest field fluctuations originating within a few nanometers of the GeV center.

Together with experimental observations, this body of evidence builds a strong case

for the second-order Stark effect as the underlying mechanism for GeV spectral switching. Not only does this framework account for the magnitude, symmetry, and directionality of the observed ZPL jumps, it also explains why some GeV centers exhibit stability while others do not - depending on their proximity to local fluctuating charge traps at vacancies. Furthermore, it enables predictions of defect stability in nanostructured environments, a vital capability for the design of future quantum networks using GeV centers as coherent emitters.

In summary, this chapter has explored and evaluated competing hypotheses for the origin of GeV spectral switching, ultimately identifying the second-order Stark effect due to environmental charge fluctuations as the dominant contributor. Our approach, combining DFT simulations with corroborating experimental studies, provides a blueprint for diagnosing and mitigating spectral instabilities in other color center systems. By quantitatively linking microscopic charge distributions to optical line shifts, this work advances both our fundamental understanding and our capacity to engineer reliable, field-sensitive quantum emitters.

CHAPTER 6

CONCLUSIONS AND OUTLOOK

This thesis has explored the theoretical foundations and design principles for achieving tunable, optically controllable dipolar interactions in solid-state defect systems. Through an extensive series of first-principles studies on donor-acceptor pairs (DAPs), surface-defect pairs (SDPs), and inversion symmetric color centers in diamond, I have established a coherent understanding of how electronic structure, lattice environment, and external fields govern both the dipolar properties and the optical response of defects in wide-bandgap semiconductors. The findings presented here contribute to the fundamental physics of point defects and to the practical engineering of quantum systems based on defect architectures.

The first part of this thesis demonstrated that substitutional donor-acceptor pairs in bulk diamond and SiC can support large, tunable electric dipole moments and strong long-range interactions. By systematically mapping the charge transition levels, ZPL energies, radiative lifetimes, and electron-phonon coupling for a wide range of donor-acceptor combinations, I identified the necessary conditions for DAPs to exhibit sharp optical transitions. I showed that such DAPs can function as solid-state analogs of Rydberg atoms, capable of mediating conditional logic gates and non-local couplings on tens to hundreds of nanometers scales. These results establish DAPs as a promising materials platform for scalable quantum technologies - one that relies on intrinsic material properties rather than complex engineering of heterostructures.

Yet, the same calculations also revealed intrinsic limitations: in bulk crystals, DAP dipoles are randomly oriented due to the lack of control over defect positioning, and the inversion of dipole moments between ground and excited states introduces complications for optical control protocols. These issues, together with the need to understand DAPs in more realistic environments for integration with other nanophotonic structures motivated a shift in focus toward investigating the effects of surfaces.

In the second part of this thesis, I extended the DAP framework to surfaces, where defect alignment and environmental engineering can be exploited to stabilize useful dipole configurations. My calculations on DAPs and SDPs near SiC surfaces showed that surface termination can dramatically influence both the stability and optical properties of nearby defect complexes. In particular, I showed that hydrogen-terminated surfaces passivate the SiC surface, preventing any spurious interactions from complicating the control mechanisms of near-surface DAPs. Moreover, I showed that the desirable properties of near-surface DAPs are well-preserved and the physics of their operation is not significantly affected by the presence of the surface. Additionally, I also demonstrated that hydroxyl-terminated SiC surfaces can introduce surface states above the valence band that can be used to align the dipoles of SDPs perpendicular to the surface, enabling a pathway towards engineering deterministic dipole-dipole coupling in arrays. In the last part of this section, I computed the polarization-dependent stimulated emission and photoionization cross sections and shown how these optical processes can be selectively enhanced or suppressed by carefully choosing the polarization of the incident laser light. These findings suggest that SDPs architectures could overcome the bulk limitations of DAPs and form the basis for integrated quantum photonic devices.

Finally, the third part of this thesis is a collaborative work that addressed spectral instability in inversion-symmetric color centers, where I developed a predictive model for the Stark shift response of the GeV center in diamond. Through constrained DFT calculations, I computed the second-order Stark polarizability tensor of the GeV's ZPL and demonstrated how this response explains long-standing experimental observations of discrete spectral jumps. The calculated Stark response showed clear anisotropy and provided a natural mechanism for field-induced spectral diffusion in GeV-based devices. More broadly, this work established that second-order field interactions must be accounted for even in systems with inversion symmetry, and that controlling the nearby charge environment is still critical for stabilizing

these high-coherence emitters often thought to be insensitive to noise to first order.

Looking ahead, the work presented in this thesis opens several promising directions for future study. One immediate avenue is to extend surface-defect engineering to nanodiamonds, where surface termination can vary significantly from bulk or thin-film environments, and where the proximity of the surface to the defect is intrinsic to the system geometry. Such studies would benefit from improved phonon mode analysis beyond the one-dimensional configurational coordinate model used here. In particular, resolving vibrational modes more fully could reveal important coupling between surface vibrations and defect optical transitions, offering both opportunities and challenges for spectral stability in nanophotonic applications.

Another direction lies in achieving deterministic placement and alignment of DAPs and SDPs through advanced ion implantation or bottom-up synthesis techniques. Realizing patterned arrays with controlled dipole orientation would be a major step toward scalable, on-chip quantum networks based on dipolar interactions. Furthermore, extending the methods developed here to other wide-bandgap materials, such as GaN, hBN or emerging 2D materials with rich excitonic physics could reveal new defect classes with similarly tunable dipolar properties.

Finally, this thesis underscores the importance of developing integrated computational-experimental approaches to defect photophysics. The combined use of constrained excited-state calculations, polarizability mapping, and electrostatic modeling presented here offers a powerful toolkit for predicting the behavior of quantum emitters in realistic, noisy environments. By refining these tools and applying them to new systems, future work can further bridge the gap between idealized models and device-ready quantum defect platforms.

In summary, the results presented in this thesis advance both the fundamental understanding and the practical engineering of dipolar defect systems in wide-bandgap semiconductors. They lay a strong foundation for the continued development of scalable and tunable quantum architectures built from the bottom up, one defect at a time.

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