Hyperfine and spin-orbit interactions in semiconductor Nanostructures

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Time is the wisest councellor of all.
-Pericles

Abstract

Understanding the hyperfine and spin-orbit interactions is important for e.g. quantum information processing with spin qubits. In this thesis, we investigate these interactions in various semiconductor nanostructures. While the methods developed here have been applied to specific nanostructures, they can be generalized to understand interactions (hyperfine, spin-orbit, and potentially others) in other systems and/or materials.

This thesis includes an introductory chapter where we derive the hyperfine and spin-orbit interactions from the Dirac equation and discuss the main theoretical tools used throughout the text, $\mathbf{k} \cdot \mathbf{p}$ theory and density-functional theory. In the succeeding chapter, we calculate the hyperfine couplings for electrons and holes in GaAs and silicon through first-principles densityfunctional theory. Our results are consistent with Knight-shift measurements for electrons. For holes, experimental results are still limited and a direct comparison to experiment is not possible. In the third chapter, we relate the dynamics of a hole spin after a spin echo pulse sequence to the hole hyperfine coupling. In particular, we demonstrate how the hole hyperfine couplings can be determined from measurements of hole spin echo envelope modulations. We apply this concept to a boron acceptor in silicon, where the value of the hyperfine coupling remains an open question. We show that direct measurements of boron-acceptor hyperfine couplings can be obtained by modifying the direction of the applied magnetic field in existing experiments. Finally, in the fourth chapter, we extend $k \cdot p$ theory beyond the envelope function approximation. In doing so, we find a novel 'dipolar' heavy-hole spin-orbit coupling in III-V semiconductor asymmetric quantum wells. This spin-orbit coupling is parametrized by the heavy-hole/light-hole electric-dipole matrix element. We calculate this matrix element and show that in GaAs, the dipolar spin-orbit coupling can represent a significant portion of the linear Dresselhaus spin-orbit coupling.

Résumé

La compréhension des interactions hyperfines et spin-orbite est importante pour, par exemple, le traitement de l'information quantique avec les qubits de spin. Dans cette thèse, nous étudions ces interactions dans diverses nanostructures de semi-conducteurs. Bien que les méthodes développées ici aient été appliquées à des nanostructures spécifiques, elles peuvent être généralisées pour comprendre les interactions (hyperfines, spin-orbite et potentiellement d'autres) dans d'autres systèmes et/ou matériaux.

Cette thèse comprend un chapitre d'introduction dans lequel nous dérivons les interactions hyperfines et de spin-orbite de l'équation de Dirac et discutons des principaux outils théoriques utilisés tout au long du texte, la théorie $\mathbf{k} \cdot \mathbf{p}$ et la théorie de la fonctionnelle de la densité. Dans le chapitre suivant, nous calculons les couplages hyperfins pour les électrons et les trous dans le GaAs et le silicium par le biais des premiers principes de la théorie de la fonctionnelle de la densité. Nos résultats sont conformes aux mesures du Knight-shift pour les électrons. Pour les trous, les résultats expérimentaux sont encore limités, et une comparaison directe avec l'expérience n'est pas possible. Dans le troisième chapitre, nous mettons en relation la dynamique d'un spin de trou après une séquence d'impulsions d'écho de spin avec le couplage hyperfin du trou. En particulier, nous démontrons comment les couplages hyperfins des trous peuvent être déterminés à partir des mesures des modulations de l'enveloppe de l'écho de spin du trou. Nous appliquons ce concept à un accepteur de bore dans le silicium, où la valeur du couplage hyperfin demeure une question ouverte. Nous montrons que des mesures directes de couplages hyperfins accepteur de bore peuvent être obtenues en modifiant la direction du champ magnétique appliqué dans les expériences existantes. Enfin, dans le quatrième chapitre, nous étendons la théorie $\mathbf{k} \cdot \mathbf{p}$ au-delà de l'approximation de la fonction d'enveloppe. Ce faisant, nous trouvons un nouveau couplage spin-orbite 'dipolaire' à trous lourds dans des puits quantiques asymétriques de semi-conducteurs III-V. Ce couplage spin-orbite est paramétré par l'élément de matrice électrique-dipôle à trous lourds et à trous légers. Nous calculons cet élément de matrice et démontrons qu'en GaAs, le couplage spin-orbite dipolaire peut représenter une partie significative du couplage spin-orbite Dresselhaus linéaire.

Preface

Contribution to original knowledge

This thesis is written in manuscript based format. The main portions of Chapters 2, 3, and 4 are manuscripts that have been published (Chapters 2 and 3) or have been submitted for publication (Chapter 4). Thus, each of these chapters has its own introduction, conclusion, and appendices. In addition, the addendum to Chapter 2 presents work that we intend to submit as part of a future publication. In accordance with the McGill thesis regulations, each manuscript (main portions of Chapters 2, 3, and 4 and the addendum to Chapter 2) contains its own reference list. A master reference list is also provided at the end of the thesis which includes all the references cited in the introduction, connecting material (prefaces to Chapters 2, 3, and 4) and conclusion of this thesis. Below, we give the reference for each completed manuscript and list the specific contributions to original knowledge from each chapter.

First-principles hyperfine tensors for electrons and holes in GaAs and silicon

Pericles Philippopoulos, Stefano Chesi, and W. A. Coish Phys. Rev. B 101, 115302 (2020). Chapter 2

The contributions to original knowledge of Chapter 2 are:

- theoretically establishing the strength and symmetry of the hyperfine interaction for electrons and holes in GaAs and silicon.
- developing DFT+ $k \cdot p$ to compute Bloch waves for bands whose extrema are off-zone center.
- calculating the hole hyperfine constants for holes in germanium (Addendum to Chapter 2).

Hole spin echo envelope modulations

Pericles Philippopoulos, Stefano Chesi, Joe Salfi, Sven Rogge, and W. A. Coish *Phys. Rev. B* **100**, 125402 (2019). Chapter 3

The contributions to original knowledge of Chapter 3 are:

- estimating the boron-acceptor hyperfine coupling based on empirical data and without relying on the envelope function approximation.
- calculating hole-spin echo envelope modulations accounting for the anisotropic light-hole g-tensor and hyperfine tensor.

Pseudospin-electric coupling for holes beyond the envelope-function approximation Pericles Philippopoulos, Stefano Chesi, Dimitrie Culcer, and W. A. Coish arXiv:2005.08821 (2020). Submitted for consideration in Phys. Rev. B Chapter 4

The contributions to original knowledge of Chapter 4 are:

- calculating $\mathbf{k} \cdot \mathbf{p}$ parameters and matrix elements of the Zeeman Hamiltonian for GaAs using ELK, an all electron density-functional theory code.
- calculating the GaAs valence-band electric-dipole matrix elements from first principles.
- deriving the dipolar spin-orbit coupling.
- demonstrating that the dipolar spin-orbit coupling is important for understanding the GaAs linear Dresselhaus spin-orbit coupling in asymmetric quantum wells.

Contributions of authors

- The work presented in this thesis was completed during the Ph. D. studies of the author at McGill University under the supervision of Prof. W. A. Coish.
- This thesis was written by the author with the help of Prof. Coish.
- The theory presented in Chapters 2, 3, and 4 was developed by the author with the help of Prof. Coish and Prof. S. Chesi of the Beijing Computational Science Research Center (CSRC).
- The calculations presented in Chapters 2, 3, and 4 were performed by the author.
- The work presented in Chapter 3 was performed in collaboration with Prof. J. Salfi of the University of British Columbia (UBC) and Prof. S. Rogge of the University of New South Wales (UNSW). Prof. Salfi and Prof. Rogge provided insights on the potential application of the theory to experiment.
- The work presented in Chapter 4 was performed in collaboration with Prof. D. Culcer of the University of New South Wales (UNSW). Prof. Culcer provided theoretical input and helped place the work in the context of past research.

Pericles Philippopoulos

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1 Introduction

Understanding spin interactions in semiconductor nanostructures is important for a broad range of applications. These applications include, but are not limited to, nuclear magnetic resonance (NMR), spintronics, and sensing. Spin interactions can also be important for fundamental studies of topological and other material properties. One of the most interesting areas of current research related to semiconductor spin interactions is the development of a quantum computer.

Quantum computers offer an exponential speedup over their classical counterparts in performing certain tasks. These tasks include simulating quantum systems [1, 2], which could lead to the discovery of new drugs, catalysts, and materials [3–5] and solving discrete-log problems [6], which have been used to guarantee security in multiple cryptographic algorithms [7–10]. The exponential improvement in performing these and other quantum-information-processing tasks has acted as a major motivator for the development of quantum computers. However, before a quantum computer can be developed, a physical qubit must be established. The qubit (or quantum bit) is the fundamental unit of quantum information: a quantum-mechanical two-level system which encodes quantum information. The qubit is therefore the quantum analogue to the classical bit which encodes classical information.

Various proposals have nominated different physical systems as viable qubit candidates [11-23]. Here, we focus on systems where the qubit is realized by two spin (or pseudospin) states of an electron (or hole) confined to a semiconductor nanostructure. Because electrons are spin-1/2 particles, their spin degree of freedom provides a natural choice for a qubit (quantum two-level system). This type of qubit is commonly referred to as a 'spin qubit'. However, 'spin qubit' can also refer to a qubit comprised of a more general pseudospin.

If spin qubits are to be used for quantum information processing, the interactions that influence the spin (or pseudospin), must be understood. In this thesis, we focus on two of these interactions. The first is the magnetic dipole-dipole interaction between the electron magnetic moment and the nuclear spins that make up the nanostructure host material: the hyperfine interaction. The second is the coupling between the spin and orbital degrees of freedom of the electron: the spin-orbit interaction. In short, the goal of this thesis is to calculate and understand hyperfine and spin-orbit interactions in various GaAs and silicon nanostructures. Although we focus the analysis on specific nanostructures, the methods employed can be extended to understand these interactions in other systems.

The remainder of this introductory chapter is organized as follows: In Sec. 1.1 we derive the hyperfine and spin-orbit interactions from the Dirac Hamiltonian. In Secs. 1.2 and 1.3 we discuss the main theoretical methods employed in the remaining chapters. In Sec. 1.2 we focus on $\mathbf{k} \cdot \mathbf{p}$ theory under the envelope function approximation. Finally, in Sec. 1.3 we discuss density-functional theory.

1.1 Dirac Equation

The aim of this section is to derive the hyperfine and spin-orbit interactions from the Dirac Hamiltonian. The derivation given here is based on the analysis of the Dirac equation presented in the book by Weissbluth, Ref. [24]. Similar derivations are presented in Refs. [25–27].

The Dirac equation is the relativistic equivalent to the Schrödinger equation. For an electron in the presence of an electromagnetic field described by a scalar potential ϕ and a vector potential \mathbf{A} , the Dirac Hamiltonian is given by

$$H = c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta mc^2 - e\phi. \tag{1.1}$$

Here, $\boldsymbol{\pi} = \boldsymbol{p} + e\boldsymbol{A}$ is the canonical momentum operator (\boldsymbol{p} is the momentum operator), the electron charge and rest mass are -e and m respectively, and

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$$
(1.2)

are four-dimensional matrices constructed from the Pauli matrices, σ_i , and the two-dimensional identity matrix, I_2 . Because the Dirac Hamiltonian is a 4×4 matrix, a solution, ψ , to the

eigenvalue equation, $H\psi = \epsilon\psi$, is a four-component Dirac spinor

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \tag{1.3}$$

where ψ_1 is a two-component spinor that describes the electron and ψ_2 is a two-component spinor that describes its anti-particle. The eigenvalue equation for H can be reduced to two coupled matrix equations,

$$(\epsilon' + e\phi)\psi_1 - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi}\psi_2 = 0 \tag{1.4}$$

and

$$\left(\epsilon' + 2mc^2 + e\phi\right)\psi_2 - c\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\psi_1 = 0, \qquad (1.5)$$

where $\epsilon' = \epsilon - mc^2$ is the electron energy relative to its rest-mass energy. From Eq. (1.4), we can estimate the relative magnitude of ψ_1 and ψ_2 . Approximating $\epsilon' + e\phi \sim \frac{1}{2}mv^2$ (kinetic energy) and $\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \sim p = mv$, where v is the electron velocity, we obtain

$$\psi_1 \sim \frac{c}{v} \psi_2. \tag{1.6}$$

For non-relativistic electrons $(c/v \gg 1)$, ψ_1 is the important component of the Dirac spinor. Therefore, we solve Eq. (1.5) for ψ_2 and insert the result in Eq. (1.4) to obtain an equation for ψ_1 alone

$$H_1\psi_1 := \left[-e\phi + \frac{1}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{\pi} K\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\right]\psi_1 = \epsilon'\psi_1, \qquad (1.7)$$

where

$$K = \frac{2mc^2}{\epsilon' + 2mc^2 + e\phi}.$$
(1.8)

The result is an eigenvalue equation, $H_1\psi_1 = \epsilon'\psi_1$, where the eigenstates are the electron component of the Dirac spinors, ψ_1 , with associated eigenenergies ϵ' . The Hamiltonian associated with this eigenvalue equation, H_1 , can be rewritten in terms of the electric field, $\boldsymbol{E} = -\boldsymbol{\nabla}\phi, \text{ as:}^{1}$ $H_{1} = K \frac{p^{2}}{2m} - e\phi + H_{c} + H_{a} + H_{L} + H_{SO} + H', \qquad (1.9)$

where

$$H_c = \frac{e^2 \hbar c^2}{(\epsilon' + 2mc^2 + e\phi)^2} \boldsymbol{\sigma} \cdot \boldsymbol{E} \times \boldsymbol{A} \quad \rightarrow \text{ contact hyperfine,}$$
(1.10)

$$H_d = \frac{e\hbar c^2}{\epsilon' + 2mc^2 + e\phi} \boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} \times \boldsymbol{A}) \quad \rightarrow \text{ dipolar hyperfine,}$$
(1.11)

$$H_L = \frac{2ec^2}{\epsilon' + 2mc^2 + e\phi} \mathbf{A} \cdot \mathbf{p} \qquad \rightarrow \text{ nuclear-orbital interaction}, \qquad (1.12)$$

$$H_{SO} = \frac{\hbar ec^2}{(\epsilon' + 2mc^2 + e\phi)^2} \boldsymbol{E} \times \boldsymbol{p} \cdot \boldsymbol{\sigma} \qquad \rightarrow \text{ spin-orbit interaction.}$$
(1.13)

The term H' contains relativistic effects that do not depend on the spin, σ , of the electron (e.g. the Darwin term, see Chapter 15 of Ref. [24] for more details). Throughout the remainder of this thesis we neglect the spin-independent effects described by H' and focus instead on the terms of Eqs. (1.10)-(1.13).

1.1.1 Hyperfine interaction

Contact hyperfine interaction

The contact hyperfine interaction is given by Eq. (1.10):

$$H_c = \frac{e^2 \hbar c^2}{(\epsilon' + 2mc^2 + e\phi)^2} \boldsymbol{\sigma} \cdot \boldsymbol{E} \times \boldsymbol{A}.$$
 (1.14)

In semiconductor nanostructures, the electron wavefunction is spread over many nuclei of the underlying material (see Sec. 1.2.3, below). In general, each of these nuclei is charged and may have a finite spin. The electromagnetic fields generated by a nuclear spin with charge

^{1.} The property $(\boldsymbol{\sigma} \cdot \boldsymbol{O}_1)(\boldsymbol{\sigma} \cdot \boldsymbol{O}_2) = \boldsymbol{O}_1 \cdot \boldsymbol{O}_2 + i\boldsymbol{\sigma} \cdot \boldsymbol{O}_1 \times \boldsymbol{O}_2$ for two vector operators \boldsymbol{O}_1 and \boldsymbol{O}_2 is used to rewrite H_1 .

Ze and magnetic moment μ_I can be written as:

$$\phi(\mathbf{r}) = \frac{Ze}{4\pi\epsilon_0 r}, \quad \mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) = \frac{Ze}{4\pi\epsilon_0 r^3}\mathbf{r}, \tag{1.15}$$

and

$$\boldsymbol{A}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \frac{\gamma \boldsymbol{I} \times \boldsymbol{r}}{r^3},\tag{1.16}$$

where we have written $\mu_I = \gamma I$ in terms of the nuclear gyromagnetic ratio, γ and the nuclear-spin operator, I. For a non-relativistic electron ($\epsilon' \ll mc^2$) in the presence of these fields, we can approximate the contact hyperfine interaction by:

$$H_c \simeq \mu_0 \mu_B \gamma \delta_{\rm T}(r) \left[\boldsymbol{\sigma} \cdot \boldsymbol{I} - (\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}}) (\boldsymbol{I} \cdot \hat{\boldsymbol{r}}) \right].$$
(1.17)

Here, $\hat{\boldsymbol{r}} = \boldsymbol{r}/r$ is a radial unit vector, $\mu_B = \frac{e\hbar}{2m}$ is the Bohr magneton, and

$$\delta_{\rm T}(r) = \frac{1}{4\pi r^2} \frac{r_{\rm T}/2}{(r + r_{\rm T}/2)^2},\tag{1.18}$$

where $r_T = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{mc^2} = Z\alpha^2 a_0$ is the Thomson radius and a_0 is the Bohr radius.

We now consider matrix elements of H_c with respect to two arbitrary states, $|a\rangle$ and $|b\rangle$,

$$\langle a | H_c | b \rangle = \mu_0 \mu_B \gamma \int d\boldsymbol{r} \delta_{\mathrm{T}}(r) \psi_a(\boldsymbol{r})^* \left[\boldsymbol{\sigma} \cdot \boldsymbol{I} - (\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}}) (\boldsymbol{I} \cdot \hat{\boldsymbol{r}}) \right] \psi_b(\boldsymbol{r}), \qquad (1.19)$$

where $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are spinors with components $\psi_a^{\sigma}(\mathbf{r}) = \langle \mathbf{r}\sigma | a \rangle$ and $\psi_b^{\sigma}(\mathbf{r}) = \langle \mathbf{r}\sigma | b \rangle$. Due to $\delta_{\mathrm{T}}(r)$, the important contribution to this integral is from the region $r \leq r_{\mathrm{T}}$. The only orbitals that have substantial weight in this region are the $s_{1/2}$ and $p_{1/2}$ solutions to the Dirac equation (the subscript indicates the total angular momentum of the states, J = 1/2in this case) [28]. The contact hyperfine interaction is therefore vanishingly small for all other orbitals. The orbitals we will consider in the remainder of this thesis will either have ssymmetry (a reasonable approximation for conduction-band electrons in III-V semiconductors) or p symmetry with total angular momentum, J = 3/2 (e.g. valence-band holes in III-V or group IV semiconductors). For this reason, we focus on the contact hyperfine interaction specifically for s orbitals. Since s orbitals are isotropic, the angular part of the integral in Eq. (1.19) results in:

$$\int d\Omega [\boldsymbol{\sigma} \cdot \boldsymbol{I} - (\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}}) (\boldsymbol{I} \cdot \hat{\boldsymbol{r}})] = \frac{8\pi}{3} \boldsymbol{\sigma} \cdot \boldsymbol{I}.$$
(1.20)

Therefore, in a subspace spanned by s orbitals [i.e. if $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are both s orbitals], the contact hyperfine interaction reduces to

$$H_c \simeq \frac{8\pi}{3} \frac{\mu_0}{4\pi} \mu_B \gamma \delta_T(r) \boldsymbol{\sigma} \cdot \boldsymbol{I}.$$
(1.21)

Dipolar hyperfine and nuclear-orbital interactions

The dipolar hyperfine interaction [Eq. (1.11)],

$$H_d = \frac{e\hbar c^2}{\epsilon' + 2mc^2 + e\phi} \boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} \times \boldsymbol{A}), \qquad (1.22)$$

depends on the magnetic field generated by the nuclear magnetic moment, μ_I :

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} = \frac{\mu_0}{4\pi r^3} \left[3\hat{\boldsymbol{r}} \left(\boldsymbol{\mu}_I \cdot \hat{\boldsymbol{r}} \right) - \boldsymbol{\mu}_I \right].$$
(1.23)

For a non-relativistic electron, substituting Eq. (1.23) and $\boldsymbol{\mu}_{I} = \gamma \boldsymbol{I}$ into Eq. (1.22), we obtain

$$H_d \simeq \frac{\mu_0}{4\pi} \mu_B \gamma f_{\rm T}(r) \frac{3 \left(\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}}\right) \left(\boldsymbol{I} \cdot \hat{\boldsymbol{r}}\right) - \boldsymbol{\sigma} \cdot \boldsymbol{I}}{r^3},\tag{1.24}$$

where

$$f_{\rm T}(r) = \frac{r}{r + r_T/2}.$$
 (1.25)

Finally, the nuclear-orbital interaction [Eq. (1.12)],

$$H_L = \frac{2ec^2}{\epsilon' + 2mc^2 + e\phi} \boldsymbol{A} \cdot \boldsymbol{p}, \qquad (1.26)$$

describes the coupling between a nuclear magnetic moment and an electron orbital magnetic moment. For a non-relativistic electron, inserting Eq. (1.16) into Eq. (1.26) we have

$$H_L \simeq \frac{\mu_0}{4\pi} \frac{2\mu_B \gamma}{r^3} f_{\rm T}(r) \boldsymbol{L} \cdot \boldsymbol{I}, \qquad (1.27)$$

where $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is the electron orbital angular momentum operator.

We now repeat the procedure of Sec. 1.1.1 and consider matrix elements of H_d and H_L with respect to s orbitals. The matrix elements of H_L vanish identically because, by definition, s orbitals have a vanishing orbital angular momentum (l = 0). Because s orbitals are isotropic, we can again compute the angular part of the integral originating from the matrix element of H_d . In this case the result is:

$$\int d\Omega[3\left(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{r}}\right)\left(\boldsymbol{I}\cdot\hat{\boldsymbol{r}}\right)-\boldsymbol{\sigma}\cdot\boldsymbol{I}]=0.$$
(1.28)

Therefore, the dipolar hyperfine interaction also vanishes identically for s orbitals. Thus, while only the contact hyperfine coupling will be relevant for s orbitals, the dipolar hyperfine and nuclear-orbital interactions will be relevant for all other orbitals.

Total hyperfine Hamiltonian

The hyperfine interaction (the sum of three terms discussed above) couples the electron magnetic moment (characterized by $\boldsymbol{\sigma}$ and \boldsymbol{L}) and the nuclear magnetic moment (characterized by \boldsymbol{I}). This interaction is suppressed relative to the typical atomic (Bohr) energies by a factor of α^2 [29], where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}$ is the fine structure constant. Accordingly, in a nanostructure, the hyperfine interaction is usually too weak (relative to the Coulomb interaction) to couple the electron orbital states. However, it can couple the low-energy degrees of freedom that are typically used to define a spin qubit. Therefore, in a nanostructure, where the electron wavefunction is spread over $\gtrsim 10^4$ nuclei [30], the hyperfine interaction can have a significant impact on the spin dynamics.

In this thesis, we focus mainly on spin qubits formed by semiconductor conduction-band states or valence-band states. The conduction-band electrons in the semiconductors we consider (III-V and group IV materials) have approximate s symmetry, while the valenceband holes transform like p states with total angular momentum J = 3/2. Therefore, as discussed above, the contact hyperfine interaction is relevant only for conduction-band electrons, while the dipolar and nuclear-orbital interactions are relevant only for valence-band holes. In the remainder of this thesis, we write the total hyperfine interaction as

$$H_{hf} = H_c + H_a + H_L \tag{1.29}$$

$$= \frac{\mu_0}{4\pi} \mu_B \gamma \left[\frac{8\pi}{3} \delta_T(r) \boldsymbol{\sigma} + f_{\rm T}(r) \frac{3 \left(\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}} \right) \hat{\boldsymbol{r}} - \boldsymbol{\sigma} + \boldsymbol{L}}{r^3} \right] \cdot \boldsymbol{I}.$$
(1.30)

The hyperfine interaction results in an effective magnetic field experienced by the electron spin (pseudospin) due to the nuclear spins in the surrounding lattice. This effective magnetic field is called the Overhauser field. Conversely, the effective magnetic field due to the electron magnetic moment acting on the nuclear spins is called the Knight field. The Overhauser field can fluctuate as a result of nuclear dipole interactions and the hyperfine interaction [30, 31]. Consequently, at a given instant in time, an electron confined to a nanostructure experiences a random (and unknown) magnetic field. This random magnetic field leads to a randomization of the electron spin along with a decay of any encoded quantum state. This randomization/decay occurs on a decoherence time, typically denoted T_2^* . The hyperfine interaction has been shown to be a major factor in limiting spin decoherence times for electron- and hole-spin qubits [31–37]. Understanding the hyperfine interaction is therefore crucial when considering spin dynamics in semiconductor nanodevices and associated applications in e.g. classical spintronics, sensing, and quantum information processing.

1.1.2 Spin-orbit interaction

The last term originating from the Dirac equation that we consider is the spin-orbit interaction [Eq. (1.13)]. In the non-relativistic limit, this term can be written as

$$H_{SO} = \frac{\hbar e c^2}{(\epsilon' + 2mc^2 + e\phi)^2} \boldsymbol{E} \times \boldsymbol{p} \cdot \boldsymbol{\sigma} \simeq \frac{\hbar e}{4m^2c^2} \boldsymbol{E} \times \boldsymbol{p} \cdot \boldsymbol{\sigma}.$$
 (1.31)

As the name suggests, the spin-orbit interaction couples the spin degrees of freedom (σ) of the electron to its orbital degrees of freedom (p). In the presence of the electric field generated by a charged nucleus [see Eq. (1.15)], the spin-orbit coupling takes the well-known $\sim L \cdot \sigma$ form [29]:

$$H_{SO} = \frac{\mu_B}{2e} \frac{r_T}{r(r+r_T/2)^2} \boldsymbol{L} \cdot \boldsymbol{\sigma} \simeq \frac{\mu_B r_T}{2er^3} \boldsymbol{L} \cdot \boldsymbol{\sigma}, \qquad (1.32)$$

where the last approximation holds when the atomic wavefunction does not vary on the scale of the Thomson radius, r_T .

Various effective spin-orbit interactions can be derived from Eq. (1.31) for electrons and holes confined to semiconductor nanostructures [38–43]. In general, each of these effective spin-orbit interactions can couple states with different spin. This coupling allows electric field fluctuations to induce spin relaxation [31,42,44,45]. In carefully engineered nanodevices, the coupling to electric-field fluctuations of noisy external sources (e.g. fluctuations in gate potentials) is less important than the fluctuations produced by phonons [31]. In particular, phonon-assisted spin flips due to spin-orbit coupling can represent a dominant mechanism for spin relaxation [44–53].² Therefore, like the hyperfine interaction discussed above, the spin-orbit interaction can impact the spin dynamics in semiconductor nanodevices.

Another important feature of the spin-orbit interaction is that it enables electric manipulation of spins [54–58]. The most direct way of manipulating spins is through the use of time-varying magnetic fields. However, magnetic manipulations are slow and lead to difficulties associated with addressing individual spins [58–60]. Furthermore, generating strong oscillating magnetic fields requires ancillary components (e.g. a microwave cavity) which induce additional engineering constraints [55, 59, 61]. In contrast, generating oscillating electric fields can be achieved by modulating the voltage on local gates. This approach is simpler to implement and facilitates addressing individual spins [55]. Because the spin-orbit coupling provides a mechanism by which electric fields couple to spins, understanding the spin-orbit coupling can help to engineer better spin-qubit nanodevices.

In summary, the spin-orbit interaction may be important to achieve all-electric spin control in semiconductor nanodevices. In addition, the spin dynamics in these devices can be influenced by both the hyperfine and the spin-orbit interactions. The goal of this thesis is to gain a better understanding of these interactions. The approach we take is to calculate matrix elements of the corresponding Hamiltonians with respect to nanostructure eigenstates. In the next section, we describe a common procedure to obtain these eigenstates: $\mathbf{k} \cdot \mathbf{p}$ theory under the envelope function approximation.

^{2.} This relaxation occurs via a second order process. The spin-orbit coupling flips the spin while simultaneously placing the electron in an excited orbital state and the electron-phonon coupling allows the electron to relax back down to its orbital ground state. The net result is a spin-flip event (relaxation) in the orbital ground state.

1.2 Nanostructures

To use electron spins (or pseudospins) for quantum information processing or other applications, it is convenient (if not necessary) to first confine the electrons to some well-defined region of space. One way of achieving this confinement is with carefully designed semiconductor nanostructures. The semiconductor hosting the nanostructure provides a controlled environment that can be engineered to confine single spins [31, 62, 63]. Moreover, electrostatic gates can be precisely deposited on the semiconductor in the vicinity of the confined spins allowing for each one to be addressed (measured, manipulated) individually [31]. The nanostructures of interest in this thesis are quantum dots in GaAs and silicon and impurities in silicon (specifically, phosphorus donors and boron acceptors). While the techniques we discuss in the remainder of this introduction have been employed to understand these specific structures, they can be generalized and applied to other devices in different materials.

A quantum dot is a solid-state device that can be filled with electrons or holes. There are many ways these devices can be fabricated. For example, an electron can be confined to a GaAs gated lateral quantum dot [see Fig. 1.1 (a)]. In this architecture, a heterostructure is made of a layer of GaAs and a layer of n-doped AlGaAs [31]. Because the GaAs band gap is narrower than that of AlGaAs, there is band bending at the heterointerface [64]. Solving Poisson's equation, accounting for the band bending and the Coulomb interaction with the ionized dopants in the AlGaAs layer [see Fig. 1.1 (a)], leads to a potential well [see Fig. 1.1 (b) [64–66]. This potential well, known as a quantum well, has eigenstates that are localized (along z in Fig. 1.1) at the heterointerface and occupied by electrons supplied by the dopants in the AlGaAs layer [see Fig. 1.1] [31,65]. The result is the formation of a two-dimensional electron gas (2DEG) situated at the GaAs/AlGaAs interface. The quantum well therefore provides confinement along one dimension (z), limiting the electrons to planar motion (x-y)plane). Additional confinement (along x and y) can be achieved by applying voltages to electrostatic gates patterned on top of the heterostructure [see Fig. 1.1(a)] [31,65,67]. The applied voltages can be used to deplete areas of the two-dimensional electron gas and create small quasi-zero-dimensional structures, known as gated lateral quantum dots. The voltages can be tuned to make it energetically favorable for a certain number of electrons to occupy the bound states of the quantum dot, thus localizing the bound electrons in space. Equivalent



Figure 1.1: (a) Schematic of an AlGaAs/GaAs gate-defined lateral quantum dot. Confinement along the z direction is obtained by band bending at the heterointerface which occurs, in part, due to the Coulomb interaction with positively charged dopants (represented in orange) located in the AlGaAs layer. Voltages applied to electrostatic gates (shown in blue) are used to deplete the two-dimensional electron gas (labeled 2DEG in green) at the heterointerface (under the dashed circle). By tuning the gate potentials, electrons can be confined to the depleted region. (b) Schematic of the potential, U, experienced by the electron (or hole) along the z direction. Close to the heterointerface, the potential is triangular. The discrete energy levels of the well are shown in orange and the Fermi energy is shown in blue. All states below the Fermi energy will be occupied and are confined (along the z direction) to the heterointerface.

quantum dots have also been fabricated to confine holes (for single-hole spin manipulation).³

Electrons and holes can also be confined to silicon quantum dots [72–74]. Another system studied in the context of spin qubits is an electron (hole) bound to a donor (acceptor) in silicon [75–77]. Group V substitutional impurities can be used to donate an electron to the conduction band of silicon. At low enough temperatures, the extra electron remains bound to the donor to produce an effective hydrogenic system [78]. The electron spin of this system can be used as a qubit [60,75]. Alternatively, group III substitutional impurities can be used to accept an electron and populate the valence band of silicon with a hole. In this case, holes (instead of electrons) remain bound to the acceptors at low enough temperatures. This system has also been studied in the context of a (hole-)spin qubit [79, 80].

Both quantum dots and impurities in silicon can confine particles over a length scale, l, which is small enough for applications in, e. g. quantum information processing, but large

^{3.} Because *p*-doped GaAs samples have shown electrical instability, measurements in these samples are difficult [68–70]. However, recently, there has been success in the experimental study of undoped samples [71]. Conceptually, quantum dots confining holes and electrons are equivalent.

compared to a typical lattice constant of the host material, $a \ (l \gg a)$. A standard approach for investigating these systems analytically is to use $\mathbf{k} \cdot \mathbf{p}$ theory under the envelope function approximation. We discuss this approach in the remainder of this section.

1.2.1 Bloch's theorem

We begin by discussing the problem of solving for the eigenstates of an electron subject to a periodic crystal potential, V_0 , and the associated spin-orbit coupling [Eq. (1.31)], $\propto (\nabla V_0) \times \boldsymbol{p} \cdot \boldsymbol{\sigma}$. The crystal potential, V_0 , is periodic such that $V_0(\boldsymbol{r} + \boldsymbol{R}) = V_0(\boldsymbol{r})$ for any lattice vector, \boldsymbol{R} . Under the Born-Oppenheimer approximation, we assume that the state of the lattice nuclei is decoupled from that of the electron and that the positions of the nuclei are fixed at the positions, $\boldsymbol{R} + \boldsymbol{b}$, where the vectors \boldsymbol{b} (basis for the lattice) locate the nuclei within each unit cell [81]. The Hamiltonian associated with this problem is

$$H_0 = \frac{p^2}{2m} + V_0 + \frac{\hbar}{4m^2c^2}\boldsymbol{p}\cdot\boldsymbol{\sigma} \times (\nabla V_0).$$
(1.33)

According to Bloch's theorem, the eigenstates of this Hamiltonian, $\psi_{\nu k}(\mathbf{r}) = [\psi_{\nu k}^{\uparrow}(\mathbf{r}), \psi_{\nu k}^{\downarrow}(\mathbf{r})]^{T}$, are spinors that can be labeled by a band index ν and a wavevector in the first Brillouin zone of the lattice, \mathbf{k} . These eigenstates (Bloch waves) have spin components

$$\psi^{\sigma}_{\nu \boldsymbol{k}}(\boldsymbol{r}) = \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{N}} u^{\sigma}_{\nu \boldsymbol{k}}(\boldsymbol{r}), \qquad (1.34)$$

where σ is a spin index, N is the number of unit cells in the crystal, and $u_{\nu k}^{\sigma}(\mathbf{r})$ are latticeperiodic Bloch amplitudes, such that $u_{\nu k}^{\sigma}(\mathbf{r} + \mathbf{R}) = u_{\nu k}^{\sigma}(\mathbf{r})$ for any lattice vector, \mathbf{R} [see Fig. 1.2(a)]. The Bloch amplitudes are normalized over the unit cell Ω :

$$\sum_{\sigma} \int_{\Omega} d^3 r \left| u^{\sigma}_{\nu \mathbf{k}}(\mathbf{r}) \right|^2 = 1.$$
(1.35)

For convenience, we introduce a family of complete orthonormal bases. We label each of



Figure 1.2: (a) Schematic of a $\mathbf{k} = \mathbf{0}$ Bloch amplitude, $u_{\nu}(\mathbf{r})$ (shown in blue). This Bloch amplitude is a solution to Eq. (1.41). The black dots represent the positively charged nuclei located at each lattice site that generate a periodic potential, V_0 (shown in black). (b) Eigenstate of the Hamiltonian $H_0 + U$ [see Eq. (1.45)] within the envelope-function approximation. The confinement potential, $U(\mathbf{r})$ (shown in green), is assumed to be slowly-varying on the scale of the lattice constant of the crystal (spacing between the black dots). The eigenstates can be written as slowly-varying envelope functions, $\Psi_{\nu}(\mathbf{r})$ (shown in red), modulating periodic Bloch amplitudes, $u_{\nu}(\mathbf{r})$ (in blue). This figure is an adapted version of a figure that appeared in the author's Master's thesis [83].

these bases with k_0 and write the basis states $|\nu k\rangle_{k_0}$ as [43,82]

$$\langle \boldsymbol{r}\sigma|\nu\boldsymbol{k}\rangle_{\boldsymbol{k}_{0}} = e^{i(\boldsymbol{k}-\boldsymbol{k}_{0})\cdot\boldsymbol{r}}\psi^{\sigma}_{\nu\boldsymbol{k}_{0}}(\boldsymbol{r}) = \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{N}}u^{\sigma}_{\nu\boldsymbol{k}_{0}}.$$
(1.36)

To simplify the derivations presented in the following subsections, we will focus on the $\mathbf{k}_0 = \mathbf{0}$ basis, $|\nu \mathbf{k}\rangle_{\mathbf{0}} := |\nu \mathbf{k}\rangle$, written in terms of the Bloch amplitudes $u_{\nu}(\mathbf{r}) := [u_{\nu \mathbf{0}}^{\uparrow}(\mathbf{r}), u_{\nu \mathbf{0}}^{\downarrow}(\mathbf{r})]^T$ as

$$\langle \boldsymbol{r}\sigma|\nu\boldsymbol{k}\rangle = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\psi^{\sigma}_{\nu\boldsymbol{0}}(\boldsymbol{r}) = \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{N}}u^{\sigma}_{\nu}(\boldsymbol{r}).$$
(1.37)

1.2.2 $k \cdot p$ perturbation theory

The goal of the calculation presented in this subsection is to express a general Bloch amplitude, $u_{\nu k}(\mathbf{r})$, in terms of the $\mathbf{k} = \mathbf{0}$ Bloch amplitudes, $u_{\nu}(\mathbf{r})$.⁴ An equivalent derivation can be used to express arbitrary Bloch amplitudes in terms of any set of fixed $\mathbf{k} = \mathbf{k}_0$ Bloch amplitudes.

^{4.} The derivation presented here is based on the derivation given in Chapter 2 of Ref. [43].

The Schrödinger equation for an electron under the influence of a periodic potential, V_0 , is given by

$$\left[\frac{p^2}{2m} + V_0(\boldsymbol{r}) + \frac{\hbar}{4m^2c^2}\boldsymbol{p}\cdot\boldsymbol{\sigma}\times\nabla V_0(\boldsymbol{r})\right]\psi_{\nu\boldsymbol{k}}(\boldsymbol{r}) = \epsilon_{\nu\boldsymbol{k}}\psi_{\nu\boldsymbol{k}}(\boldsymbol{r}), \quad (1.38)$$

where the $\epsilon_{\nu k}$ are the eigenenergies associated with the eigenstates $\psi_{\nu k}(\mathbf{r})$. Inserting Eq. (1.34) into Eq. (1.38), we can obtain a differential equation for the Bloch amplitudes, $u_{\nu k}(\mathbf{r})$. In Dirac notation this equation becomes [see Eq. (1.36)]

$$\left[\frac{p^2}{2m} + V_0 + \frac{\hbar}{4m^2c^2}\boldsymbol{p}\cdot\boldsymbol{\sigma}\times\nabla V_0 + \frac{\hbar^2k^2}{2m} + \frac{\hbar}{m}\boldsymbol{k}\cdot\boldsymbol{P}\right]|\boldsymbol{\nu}\boldsymbol{0}\rangle_{\boldsymbol{k}} = \epsilon_{\boldsymbol{\nu}\boldsymbol{k}}|\boldsymbol{\nu}\boldsymbol{0}\rangle_{\boldsymbol{k}}, \qquad (1.39)$$

where $\boldsymbol{P} = \boldsymbol{p} + \frac{\hbar}{4mc^2}\boldsymbol{\sigma} \times \nabla V_0$ and we have used $\boldsymbol{p} \to -i\hbar\nabla$:

$$\boldsymbol{p}\psi_{\nu\boldsymbol{k}}(\boldsymbol{r}) = \frac{\hbar\boldsymbol{k}}{\sqrt{N}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\nu\boldsymbol{k}}(\boldsymbol{r}) + \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{N}} \boldsymbol{p} u_{\nu\boldsymbol{k}}(\boldsymbol{r}).$$
(1.40)

At k = 0, Eq. (1.39) reduces to a Schrödinger-like equation for the Bloch amplitudes $|\nu 0\rangle$:

$$\left[\frac{p^2}{2m} + V_0 + \frac{\hbar}{4m^2c^2}\boldsymbol{p}\cdot\boldsymbol{\sigma}\times\nabla V_0\right]|\boldsymbol{\nu}\mathbf{0}\rangle = \epsilon_{\boldsymbol{\nu}\mathbf{0}}|\boldsymbol{\nu}\mathbf{0}\rangle.$$
(1.41)

The states $|\nu \mathbf{0}\rangle$ provide a complete orthonormal basis for the Bloch amplitudes [43]. An arbitrary Bloch function can be expressed in this basis as

$$\left|\nu\mathbf{0}\right\rangle_{\boldsymbol{k}} = \sum_{\nu'} c_{\nu'\nu\boldsymbol{k}} \left|\nu'\mathbf{0}\right\rangle,\tag{1.42}$$

where the coefficients $c_{\nu'\nu k}$ can be determined by inserting Eq. (1.42) into the Schrödinger equation, Eq. (1.39), multiplying on the left by $\langle \nu'' \mathbf{0} |$, and solving the resulting eigenvalue equation:

$$\sum_{\nu'} \left[\left(\epsilon_{\nu' \mathbf{0}} + \frac{\hbar^2 k^2}{2m} \right) \delta_{\nu'' \nu'} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{P}_{\nu'' \nu'} \right] c_{\nu' \nu \mathbf{k}} = \epsilon_{\nu \mathbf{k}} c_{\nu'' \nu \mathbf{k}}, \tag{1.43}$$

with

$$\boldsymbol{P}_{\nu^{\prime\prime}\nu^{\prime}} = \langle \nu^{\prime\prime} \boldsymbol{0} | \boldsymbol{P} | \nu^{\prime} \boldsymbol{0} \rangle.$$
(1.44)

Therefore, using Eqs. (1.42) and (1.43), the Bloch amplitudes, $u_{\nu k}^{\sigma}(\mathbf{r}) = \sqrt{N} \langle \mathbf{r} \sigma | \nu 0 \rangle_{\mathbf{k}}$, for arbitrary \mathbf{k} can be calculated from the $\mathbf{k} = \mathbf{0}$ Bloch amplitudes, $u_{\nu}^{\sigma}(\mathbf{r}) = \sqrt{N} \langle \mathbf{r} \sigma | \nu 0 \rangle_{\mathbf{k}}$, provided the energies $\epsilon_{\nu \mathbf{0}}$ and matrix elements $\mathbf{P}_{\nu''\nu'}$ are known. This technique is sometimes referred to as $\mathbf{k} \cdot \mathbf{p}$ perturbation theory: Solving for the coefficients in Eq. (1.43) is equivalent to performing perturbation theory with an unperturbed Hamiltonian H_0 at k = 0 [see Eq. (1.41)] and perturbation $\frac{\hbar}{m} \mathbf{k} \cdot \mathbf{P}$. This procedure will be useful when we discuss DFT+ $\mathbf{k} \cdot \mathbf{p}$, a method used to calculate hyperfine parameters for materials that have band extrema that are off zone center (see Chapter 2).

We note that here we have presented the double-group formulation of $\mathbf{k} \cdot \mathbf{p}$ theory [84] where the spin-orbit coupling is included in the unperturbed Hamiltonian, H_0 [see Eq. (1.41)]. In this case, the states $|\nu \mathbf{0}\rangle$ transform according to representations of the double group associated with the symmetries of the crystal [85]. A common alternative approach is to treat the spin-orbit coupling as a perturbation in addition to the $\mathbf{k} \cdot \mathbf{p}$ term. Within this alternative approach, the Bloch amplitudes are product states of spin and orbital degrees of freedom (each band is doubly spin degenerate) and the states $|\nu \mathbf{0}\rangle$ transform according to representations of the single group associated with V_0 (see, e.g., Chapter 2 of Ref. [43]).

1.2.3 Envelope function approximation

The previous two subsections dealt with eigenstates of the periodic Hamiltonian, H_0 [Eq. (1.33)]. Here we consider the Hamiltonian $H_0 + U$, where U is an additional potential that varies slowly over the scale of a typical lattice constant of the host material. A common method for determining the eigenstates of this Hamiltonian involves the envelope function approximation [43,82]. As we will show below, the resulting (approximate) eigenstates can be written as slowly-varying envelope functions modulating the periodic Bloch amplitudes [see Fig. 1.2(b)].

The Schrödinger equation for an electron experiencing a periodic lattice potential, V_0 , and a confining potential, U, can be written as:

$$(H_0 + U) |\Psi\rangle = \left[\frac{p^2}{2m} + V_0 + \frac{\hbar}{4m^2c^2}\boldsymbol{p}\cdot\boldsymbol{\sigma} \times (\nabla V_0) + U\right] |\Psi\rangle = \epsilon |\Psi\rangle, \qquad (1.45)$$

where $|\Psi\rangle$ is an eigenstate and ϵ is the associated eigenenergy. We assume that $U(\mathbf{r})$ varies on

a length scale, l, that is much larger than a typical lattice constant of the crystal, $a \ (a \ll l)$. In other words, $U(\mathbf{r})$ has Fourier components at wavevector \mathbf{q} with significant weight only if $q \ll \pi/a$. We expand $|\Psi\rangle$ in terms of the basis $\{|\nu \mathbf{k}\rangle\}$ [Eq. (1.37)]:

$$|\Psi\rangle = \sum_{\nu' \mathbf{k}'} \Psi_{\nu'}(\mathbf{k}') |\nu' \mathbf{k}'\rangle, \qquad (1.46)$$

where the $\Psi_{\nu'}(\mathbf{k}')$ are known as envelope functions. Since $U(\mathbf{r})$ varies slowly on the scale of the lattice constant, we expect $\Psi_{\nu'}(\mathbf{k}')$ to have significant weight only when $k' \ll \pi/a$. Inserting Eq. (1.46) into Eq. (1.45) we obtain:

$$\sum_{\nu' \mathbf{k}'} \Psi_{\nu'}(\mathbf{k}') \left\langle \nu \mathbf{k} \right| (H_0 + U) \left| \nu' \mathbf{k}' \right\rangle = \epsilon \Psi_{\nu}(\mathbf{k}), \qquad (1.47)$$

where H_0 is given by Eq. (1.33) and has matrix elements

$$\langle \nu \boldsymbol{k} | H_0 | \nu' \boldsymbol{k}' \rangle = \left[\left(\epsilon_{\nu \boldsymbol{0}} + \frac{\hbar^2 k^2}{2m} \right) \delta_{\nu \nu'} + \frac{\hbar}{m} \boldsymbol{k} \cdot \boldsymbol{P}_{\nu \nu'} \right] \delta_{\boldsymbol{k} \boldsymbol{k}'}, \qquad (1.48)$$

which contain a $\mathbf{k} \cdot \mathbf{P}$ term, similar to Eq. (1.43). The matrix elements of U are given by

$$\langle \nu \boldsymbol{k} | U | \nu' \boldsymbol{k}' \rangle = \frac{1}{N} \sum_{\boldsymbol{R}\sigma} \int_{\Omega} d\boldsymbol{r} e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{R}+\boldsymbol{r})} u_{\nu}^{\sigma*}(\boldsymbol{r}) U(\boldsymbol{R}+\boldsymbol{r}) u_{\nu'}^{\sigma}(\boldsymbol{r}), \qquad (1.49)$$

where we have divided the integral over the crystal into a sum of integrals over each unit cell and have used the periodicity of the Bloch amplitudes, $u_{\nu}^{\sigma}(\mathbf{R} + \mathbf{r}) = u_{\nu}^{\sigma}(\mathbf{r})$ for any lattice vector \mathbf{R} . We further simplify this integral by making use of the envelope function approximation: Since U varies slowly over the unit cell and the envelope functions only have substantial weight when $k, k' \ll \pi/a$, we can approximate $U(\mathbf{R} + \mathbf{r}) \approx U(\mathbf{R})$ and $e^{i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{R}+\mathbf{r})} \approx e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}}$ in the integrand of Eq. (1.49). The result is

$$\langle \nu \boldsymbol{k} | U | \nu' \boldsymbol{k}' \rangle \simeq \frac{1}{N} \sum_{\boldsymbol{R}} U(\boldsymbol{R}) e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{R}} \delta_{\nu\nu'} \simeq \frac{1}{V} \int d\boldsymbol{r} U(\boldsymbol{r}) e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}} \delta_{\nu\nu'}, \quad (1.50)$$

where V is the total volume of the crystal. As can be seen from Eq. (1.50), the envelope

function approximation neglects interband transitions generated by U (the matrix elements of U are diagonal in the band index ν). This approximation is therefore justified provided the off-diagonal matrix elements of U are negligible compared to the off-diagonal $\mathbf{k} \cdot \mathbf{p}$ matrix elements $\left[\frac{\hbar}{m}\mathbf{k} \cdot \mathbf{P}_{\nu\nu'}\right]$, see Eq. (1.48). Although the envelope function approximation is a standard approach for understanding nanostructure eigenstates, in certain systems, the interband transitions generated by U can lead to important effects. An example of such a system is an asymmetric quantum well where some of these potential-generated transitions are k independent (see Sec. 4.2) and therefore dominate the $\mathbf{k} \cdot \mathbf{p}$ interband contribution in a small k regime. The triangular quantum well and the associated interband transitions are the focus of Chapter 4, below.

Inserting Eqs. (1.48) and (1.50) into Eq. (1.47) we obtain an effective Schrödinger equation for the envelope functions. In position space, this equation becomes

$$\sum_{\nu'} \left[\left(\epsilon_{\nu \mathbf{0}} + \frac{\hbar^2 k^2}{2m} + U(\mathbf{r}) \right) \delta_{\nu\nu'} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{P}_{\nu\nu'} \right] \Psi_{\nu'}(\mathbf{r}) = \epsilon \Psi_{\nu}(\mathbf{r}), \quad (1.51)$$

where $\Psi_{\nu}(\mathbf{r})$ is an envelope function in position space,

$$\Psi_{\nu}(\boldsymbol{k}) = \frac{1}{\sqrt{V}} \int d\boldsymbol{r} \Psi_{\nu}(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}, \qquad (1.52)$$

$$\Psi_{\nu}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \Psi_{\nu}(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \qquad (1.53)$$

and $\mathbf{k} \to -i\nabla$ is a differential operator that acts on $\Psi_{\nu}(\mathbf{r})$. Thus, within the envelope function approximation, the eigenstates of $H_0 + U$ can be written as

$$\langle \boldsymbol{r} | \Psi \rangle = \sum_{\nu} \Psi_{\nu}(\boldsymbol{r}) u_{\nu}(\boldsymbol{r}),$$
 (1.54)

where the envelope functions, $\Psi_{\nu}(\mathbf{r})$, are determined from Eq. (1.51) and the Bloch amplitudes, $u_{\nu}(\mathbf{r})$, are determined from Eq. (1.41). The Bloch amplitudes which vary on the scale of the lattice constant, a, are modulated by the envelope functions which vary on length scale l, such that $a \ll l$, as depicted schematically in Fig. 1.2(b). The procedure described in this section is a standard approach for obtaining eigenstates of Eq. (1.45). The envelope function approximation is valid when the confinement varies slowly compared on the scale of a typical lattice constant of the underlying crystal. The GaAs and silicon lattice constants are ~ 5 Å. Thus, this formalism works well when describing electrons (or holes) confined to e.g. GaAs and silicon quantum wells and quantum dots, where the dimensions are ~ 10 - 100 nm. For donor-/acceptor- impurities with finite nuclear charge in semiconductors, the confining potential diverges as $r \to 0$, $U(r) \sim 1/r$. Therefore, although it may be valid far from the donor/acceptor, the envelope function approximation breaks down as $r \to 0$. Consequently, to solve for the wavefunction close to the impurity [which may be important for determining the impurity hyperfine coupling, $H_{hf} \sim 1/r^2$ as $r \to 0$, see Eq. (1.30)] other techniques are required. We discuss one such technique in Chapter 3.

The goal of this thesis is to calculate matrix elements of the hyperfine and spin-orbit interactions with respect to nanostructure eigenstates [eigenstates of Eq. (1.45)]. Within the envelope function approximation, these eigenstates have two components: (1) the envelope functions, $\Psi_{\nu}(\mathbf{r})$, and (2) the Bloch amplitudes, $u_{\nu}(\mathbf{r})$ [see Eq. (1.54)]. The envelope functions can be determined by solving Eq. (1.51). If the confinement, U, and the $\mathbf{k} \cdot \mathbf{p}$ parameters, $\mathbf{P}_{\nu\nu'}$, are known, Eq. (1.51) is a simple matrix equation. The Bloch amplitudes, $u_{\nu}(\mathbf{r})$, are more difficult to evaluate. These amplitudes depend on the periodic lattice potential, V_0 [see Eq. (1.41)]. In principle, this potential describes the effective potential felt by the electrons in the lattice due to (1) the positively charged nuclei that constitute the lattice and (2) the other electrons in the crystal. Therefore, in general, one must account for many-body interactions when calculating Bloch amplitudes. In this thesis, we account for these manybody interactions through density-functional theory (DFT), which we describe in the next section.

1.3 Density-functional theory

The wavefunction of an electron confined to a nanostructure can be calculated using $\mathbf{k} \cdot \mathbf{p}$ theory under the envelope function approximation, provided the Bloch amplitudes, $u_{\nu}(\mathbf{r})$, are known. In the formalism described above (Sec. 1.2), the Bloch amplitudes are determined by solving Eq. (1.41). In general, electrons (or holes) interact with each other and a many-body wavefunction is required to describe the state of a system. Solving for this many-body wavefunction, including the electron-electron interactions, is a complicated problem. However, using density-functional theory (DFT), this many-body problem can be reduced to solving for a set of single-particle states self-consistently. The goal of this section is to present DFT and explain how it can be used to obtain an approximate description of the Bloch amplitudes.

The non-relativistic many-body (N electron) Schrödinger equation (including the Coulomb interaction) is given by

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_{\text{nuc}}(\boldsymbol{r}_i) + \sum_{i=1}^N \sum_{j < i} U_{ee}(\boldsymbol{r}_i, \boldsymbol{r}_j)\right] \psi(\boldsymbol{\vec{r}}) = \epsilon \psi(\boldsymbol{\vec{r}}), \quad (1.55)$$

where \mathbf{r}_i is the position coordinate of the i^{th} electron, $V_{\text{nuc}}(\mathbf{r}_i)$ is the single-particle potential generated by the atomic nuclei in the lattice, $U_{ee}(\mathbf{r}_i, \mathbf{r}_j)$ is the interaction between the i^{th} and j^{th} electron, $\psi(\mathbf{r}) = \psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N)$ is the many-electron wavefunction (which in principle can depend on the spin, σ_i , of each particle) and ϵ is the energy of the state. For a large number of electrons (such as the number of electrons in a crystal), Eq. (1.55) cannot be solved exactly, in general, because the Hilbert space associated with $\psi(\mathbf{r})$ is exponentially large. Therefore, the full many-body Schrödinger equation can often only be solved approximately. A strategy for obtaining an approximate solution is provided by density-functional theory (DFT).

The starting point for DFT is two theorems proved by Hohenberg and Kohn [86, 87]:⁵

- 1. The total energy of an electron system, ϵ , is a unique functional of the electron density, ρ .
- 2. The energy functional from theorem 1 is minimized by the true ground-state electron density.

These two theorems indicate that if the energy functional, $\epsilon[\rho]$, corresponding to the Schrödinger equation, Eq. (1.55), were known, this functional could be minimized with respect to the density ρ to find the true ground-state density. Because the true energy

^{5.} For an alternative discussion beginning from this starting point, see also the M. Sc. thesis of the author, Ref. [83]

functional is, in general, not known, DFT relies on approximating this functional to obtain an approximate ground-state density.

We begin by writing the energy functional, $\epsilon[\rho]$ as:

$$\epsilon[\rho] = \epsilon_{\text{nuc}}[\rho] + \epsilon_H[\rho] + G[\rho], \qquad (1.56)$$

where the first term on the right-hand side describes the external potential acting on the many-body system,

$$\epsilon_{\rm nuc}[\rho] = \int d\boldsymbol{r} V_{\rm nuc}(\boldsymbol{r})\rho(\boldsymbol{r})$$
(1.57)

and the second term describes the Hartree term,

$$\epsilon_H[\rho] = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},\tag{1.58}$$

where ε_0 is the vacuum permittivity and the factor of 1/2 is included to avoid double counting the contributions. The final term of Eq. (1.56) is a functional of the density which contains all effects not captured by the first two terms. It is not possible to minimize $\epsilon[\rho]$ because a general analytic form of $G[\rho]$ is not known. The crucial step used to simplify this problem is attributed to Kohn and Sham [88, 89]. They wrote

$$G[\rho] = T_s[\rho] + \epsilon_{xc}[\rho], \qquad (1.59)$$

where $T_s[\rho]$ is the kinetic energy of a non-interacting electron system with density $\rho(\mathbf{r})$, and $\epsilon_{xc}[\rho]$ is known as the exchange-correlation energy. While T_s may not be a known functional of the density, we know such a functional exists by the first Hohenberg-Kohn theorem. The benefit of writing $G[\rho]$ as in Eq. (1.59), is that, in terms of single-particle orbitals $\phi_i(\mathbf{r})$, $T_s = -\frac{\hbar^2}{2m} \sum_i \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$ is well understood. The ground-state density [density that minimizes Eq. (1.56)] can thus be determined by solving the following two equations self consistently:

$$H_{KS}\phi_i(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{nuc}}(\boldsymbol{r}) + V_H[\rho(\boldsymbol{r})] + V_{xc}[\rho(\boldsymbol{r})]\right]\phi_i(\boldsymbol{r}) = \epsilon_i\phi_i(\boldsymbol{r})$$
(1.60)

and

$$\rho(\mathbf{r}) = \sum_{i\sigma} \phi_i^{\sigma*}(\mathbf{r}) \phi_i^{\sigma}(\mathbf{r}).$$
(1.61)

Here, the sum over the index i goes over the states with the N lowest eigenenergies, ϵ_i ,

$$V_H[\rho(\boldsymbol{r})] = \frac{\delta\epsilon_H}{\delta\rho(\boldsymbol{r})} = \frac{e^2}{4\pi\epsilon_0} \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r'})}{|\boldsymbol{r} - \boldsymbol{r'}|}$$
(1.62)

is the Hartree potential which includes the Coulomb interaction of the electron with itself, and

$$V_{xc}[\rho(\boldsymbol{r})] := \frac{\delta \epsilon_{xc}}{\delta \rho(\boldsymbol{r})}$$
(1.63)

is the exchange-correlation potential. For completeness we also write

$$V_n(\boldsymbol{r}) = \frac{\delta \epsilon_{\text{nuc}}}{\delta \rho(\boldsymbol{r})}.$$
(1.64)

The exchange-correlation potential contains corrections to the Hartree potential (e.g. V_{xc} cancels the self-energy contribution) and the kinetic energy, as well as other quantummechanical effects (e.g. Pauli exclusion, exchange). If the functional form of $V_{xc}[\rho(\mathbf{r})]$ were known, solving Eqs. (1.60) and (1.61) self-consistently would yield the true ground-state density and energy. However, since it is unknown, many different approximate potentials have been proposed [90–96].

Thus, the problem of minimizing the energy functional of Eq. (1.56) to find the ground-state density has been reduced to solving for the eigenstates, $\phi_i(\mathbf{r})$, of an auxiliary non-interacting system self-consistently [Eqs. (1.60) and (1.61)]. These eigenstates, known as Kohn-Sham orbitals, lead to a many-body state that can be written as a Slater determinant,⁶

$$\psi_{KS} \simeq |\phi_1, \phi_2, \cdots, \phi_N| \,. \tag{1.66}$$

Except in the (rare) cases where the Hartree-Fock approximation becomes exact, ψ_{KS} is not the true many-body ground-state wavefunction of the system under consideration. However, this wavefunction does lead to the true ground-state density [via Eq. (1.61)].

In this section, we have neglected spin-orbit coupling. Otherwise, H_{KS} [Eq. (1.60)] describes the same system as H_0 [Eq. (1.33)]. Therefore, we can approximate the effective single-particle periodic potential, V_0 of Eq. (1.38) by

$$V_0(\boldsymbol{r}) \simeq V_{\text{nuc}}(\boldsymbol{r}) + V_H[\rho(\boldsymbol{r})] + V_{xc}[\rho(\boldsymbol{r})].$$
(1.67)

Under this approximation, we can make the associations

$$\psi_{\nu k}(\boldsymbol{r}) \to \phi_i(\boldsymbol{r}); \quad \epsilon_{\nu k} \to \epsilon_i.$$
 (1.68)

Therefore, we can approximate the Bloch waves, $\psi_{\nu k}(\mathbf{r})$ and the eigenenergies, $\epsilon_{\nu k}$, with the Kohn-Sham orbitals, $\phi_i(\mathbf{r})$, and energies, ϵ_i . We expect this to be a good approximation in the limit (of, e.g., weak correlation) where the true many-body ground-state wavefunction, $\psi(\vec{\mathbf{r}})$, can be well-represented by a single Slater determinant, such that $\psi(\vec{\mathbf{r}}) \simeq \psi_{KS}(\vec{\mathbf{r}})$.

In our analysis above, we have only included the simplest terms that are considered in DFT. One common approach is to include relativistic corrections (such as the Darwin term) to Eq. (1.60), but only include the spin-orbit interaction perturbatively. This approach is known as the scalar-relativistic approximation. Because such calculations are relativistic, it is important to understand that the orbitals ϕ_i will behave like solutions to the Dirac equation

$$\psi_{KS} = |\phi_1, \phi_2, \cdots, \phi_N| \quad \Leftrightarrow \quad \psi_{KS}(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \dots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \dots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \dots & \phi_N(r_N) \end{vmatrix}$$
(1.65)

^{6.} The notation $|\phi_1, \phi_2, \dots, \phi_N|$ indicates a Slater determinant constructed with the single-particle orbitals $\phi_1, \phi_2, \dots, \phi_N$,

and not the Schrödinger equation. This distinction can lead to important consequences. For example, while Schrödinger-like atomic s orbitals have a cusp at the location of the positively charged nucleus [29], Dirac-like s orbitals diverge. This difference can have a significant impact on calculating effects that depend strongly on the electronic density at small radii [28,97–99]. We discuss this impact, in the context of the hyperfine interaction, in greater detail in Chapter 2 below.

As shown in the previous section, the wavefunctions of confined electrons can be written as a product of the $\mathbf{k} = \mathbf{0}$ Bloch waves and slowly-varying envelope functions. While $\mathbf{k} \cdot \mathbf{p}$ theory gives the envelope functions, DFT can give the Bloch waves. Thus, combining these techniques, the electron wavefunction can be calculated. With the wavefunction in hand, we can, in principle, compute matrix elements of general operators. In the remainder of this thesis we focus on understanding the hyperfine and spin-orbit interactions using these wavefunctions.
Preface to Chapter 2

In Chapter 1 we emphasized the importance of understanding spin dynamics in semiconductor nanodevices. An important factor that can influence these dynamics is the hyperfine interaction with the nuclear spins in the underlying lattice. The focus of this chapter is to understand this interaction by computing matrix elements of the hyperfine Hamiltonian.

Under the envelope function approximation, the hyperfine coupling for a spin can be parametrized in terms of a hyperfine tensor. The entries in this tensor are written in terms of material-dependent constants and envelope functions associated with the nanostructure confinement. The hyperfine tensors determine the strength and symmetry of the hyperfine interaction and characterize the magnitude and direction of the Overhauser field.

Here we compute the material-dependent hyperfine parameters using Bloch amplitudes obtained from a density-functional theory calculation (see Sec. 1.3). Using these parameters we theoretically establish the hyperfine tensors for conduction-band electrons and valenceband holes in GaAs and silicon. The calculated electron hyperfine parameters are consistent with Knight-shift measurements in GaAs and silicon. In the case of silicon, hyperfine parameters have previously been evaluated using DFT [100], resulting in values inconsistent with the Knight-shift measurements of Ref. [101]. Here, instead of the DFT approach of Ref. [100] we introduce the DFT+ $k \cdot p$ method which leads to silicon hyperfine parameters consistent with the experimental results. For holes, theoretical work had been limited to approximating the valence-band wavefunctions with hydrogen-like orbitals to compute hyperfine parameters [35,102]. Instead, here we have calculated the valence-band hyperfine parameters using wavefunctions obtained from first principles (DFT). To the best of our knowledge, this is the first time such a calculation has been performed for the purpose of obtaining the GaAs and silicon hole hyperfine parameters.

We note that the focus of this chapter is on the conduction- and valence-band subspaces of GaAs and silicon. However, the procedure we present is general and can be applied to compute hyperfine tensors for other materials and/or bands. For example, this procedure can be applied to understand the hyperfine couplings for holes in germanium. Since the publication of the work presented in this chapter, we have calculated these hyperfine couplings. The results of this calculation are given in an addendum to Chapter 2. We plan to submit the content as part of a future publication.

2 First-principles hyperfine tensors for electrons and holes in GaAs and silicon

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First-principles hyperfine tensors for electrons and holes in GaAs and silicon

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Understanding (and controlling) hyperfine interactions in semiconductor nanostructures is important for fundamental studies of material properties as well as for quantum information processing with electron, hole, and nuclear-spin states. Through a combination of first-principles density-functional theory (DFT) and $k \cdot p$ theory, we have calculated hyperfine tensors for electrons and holes in GaAs and crystalline silicon. Accounting for relativistic effects near the nuclear core, we find contact hyperfine interactions for electrons in GaAs that are consistent with Knight-shift measurements performed on GaAs quantum wells and are roughly consistent with prior estimates extrapolated from measurements on InSb. We find that a combination of DFT and $k \cdot p$ theory (DFT+ $k \cdot p$) is necessary to accurately determine the contact hyperfine interaction for electrons at a conduction-band minimum in silicon that is consistent with bulk Knight-shift measurements. For hole spins in GaAs, the overall magnitude of the hyperfine couplings we find from DFT is consistent with previous theory based on free-atom properties, and with heavy-hole Overhauser shifts measured in GaAs (and InGaAs) quantum dots. In addition, we theoretically predict that the heavy-hole hyperfine coupling to the As nuclear spins is stronger and almost purely Ising, while the (weaker) coupling to the Ga nuclear spins has significant non-Ising corrections. In the case of hole spins in silicon, we find (surprisingly) that the strength of the hyperfine interaction in the valence band is comparable to that in the conduction band and that

the hyperfine tensors are highly anisotropic (Ising) in the heavy-hole subspace. These results suggest that the hyperfine coupling cannot be ruled out as a limiting mechanism for coherence (T_2^*) times recently measured for heavy holes in silicon quantum dots.

2.1 Introduction

Semiconductor nanostructures are essential to confine spin qubits in quantum dots [1, 2] and to implement other spintronic devices [3]. From the perspective of quantum transport and low electronic noise, a near-ideal platform for these devices is provided by high-mobility heterostructures based on GaAs [4,5]. However, every stable isotope of Ga and As has a finite nuclear spin, resulting in a coupling of the electron (or hole) spins to a large reservoir of nuclear spins through the hyperfine interaction [6–8]. If the hyperfine interaction is not fully understood and controlled, this interaction may lead to a randomization of the spins in spintronic or spin-qubit devices. To avoid the effects of the strong hyperfine interactions for electrons in GaAs, there have been many recent studies of alternative devices based on electron spins in silicon, for which the majority isotope has no nuclear spin or based on hole spins in either GaAs or silicon, for which the hyperfine couplings are weak.

A key advantage of hole spins over electron spins in GaAs is that holes have a weaker hyperfine coupling [9–13]. Because the hole hyperfine interaction is anisotropic, it may be possible to further reduce or eliminate the effects of the hole hyperfine coupling through motional-averaging [9,14–16]. An additional benefit of hole spins over electrons is a stronger spin-orbit coupling, leading to robust all-electric hole-spin manipulation [17–21]. This advantage afforded by a stronger spin-orbit coupling does not necessarily come at the cost of significantly shorter spin-relaxation (T_1) times in confined nanostructures [22,23]. Despite these advantages, the electrical instability of p-doped GaAs nanostructures [24–26] has made experimental investigations of these systems difficult. Recent advances in fabricating few-hole quantum dots from undoped samples [27] have now opened up a greater range of possibilities for hole-spin devices. Undoped devices have shown Pauli spin blockade [28,29,53], and measurements have been performed revealing hole-spin relaxation times (T_1) [30], gfactors [29], and spin-orbit couplings [31]. Despite these advances, many details of the hyperfine couplings for holes in GaAs and silicon remain largely unknown.

Electron spins in silicon quantum dots have now reached a level of control and coherence that makes them serious contenders for elements of near-future quantum processors [32–35]. Because of the small abundance (~ 4.7%) of spinful ²⁹Si nuclei in natural silicon, electron (and hole) spins in silicon nanostructures interact more weakly with the nuclear-spin bath. Coherence times for electron spins in natural silicon quantum dots are nevertheless often limited by the hyperfine interaction [36]. Isotopically purified ²⁸Si has been used as an alternative nuclear-spin free host [37–42], but even in these systems, the hyperfine coupling to the few remaining (residual) ²⁹Si nuclear spins can have a measurable effect on a quantumdot-bound electron-spin [43, 44].

Removing the nuclear spins from the host material suppresses decoherence, but it also precludes the potential benefits of a finite hyperfine interaction. These benefits include addressing the nuclear spins and using them as additional qubits for a quantum register [45,46] or a quantum memory [46–48], and using the nuclear spins to apply local effective magnetic fields on the electron or hole spins to locally manipulate them [49,50]. It is therefore important to understand the strength and properties of the hyperfine Hamiltonian for electron and hole spins in semiconductor nanostructures. This knowledge could allow negative effects to be suppressed while maintaining potential advantages of the coupling with the nuclear spins.

Knowing material-specific hyperfine parameters is also important or required to interpret measurements of physical quantities. These quantities include the degree of nuclear polarization from Overhauser shift measurements [51–54], and the nuclear spin polarization in the quantum Hall regime [55–59].

The goal of this work is to accurately calculate the hyperfine parameters for electrons and holes in GaAs and silicon. Earlier attempts at calculating hyperfine constants have relied on estimates of the electronic density (or wave function) based on non-relativistic free-atom properties such as the free-atom orbital radius [9, 60–62]. Instead, here we calculate the hyperfine parameters using all-electron density-functional theory (DFT) accompanied by $\mathbf{k} \cdot \mathbf{p}$ theory (DFT+ $\mathbf{k} \cdot \mathbf{p}$), accounting for relativistic effects, and fully including the anisotropic crystalline environment in our analysis. Typically, DFT procedures are used to calculate electronic densities. If the electronic states under consideration can be approximated as uncorrelated product states of spin and orbital degrees of freedom, the density alone is sufficient to calculate the hyperfine parameters [63]. This approach has been used to calculate hyperfine parameters for electrons in silicon [64]. However, this procedure cannot generally be applied to states (such as the valence-band states of GaAs and silicon) where the spin-orbit coupling is relevant and the states are therefore not necessarily product states. Moreover, the density alone provides no information about the phase of the wave function. Thus, e.g.,

matrix elements of the angular momentum operator cannot generally be calculated from the density alone and the nuclear-orbital interaction [$\sim L \cdot I$, see Eq. (2.5) below] is often neglected [63,65–68]. In contrast, here we apply DFT to evaluate the Kohn-Sham orbitals, which approximate the single-particle wave functions. This provides a description of the full quantum state (accounting for the spin-orbit coupling and phase), so we are able to account for all terms in the hyperfine Hamiltonian.

The hyperfine parameters for the conduction bands of GaAs and silicon have been established experimentally through measurements of the Knight shift. The results found here from DFT for the conduction band of GaAs are consistent with Knight shift measurements in the fractional quantum Hall regime [57, 69]. For silicon, the Knight shift has been measured in n-doped bulk samples [70]. Density functional theory (without $\mathbf{k} \cdot \mathbf{p}$) has been used to calculate the hyperfine constants [64], however the results are inconsistent with the Knight shift measurements of Ref. [70]. In contrast, we find here that a combined DFT+ $k \cdot p$ procedure yields hyperfine constants for electrons in silicon that are consistent with the experiments of Ref. [70]. We further apply this procedure to the valence-band (hole-spin) states of GaAs and silicon where we expect similarly accurate results. There have been fewer experiments focused on the hole hyperfine interaction. Experiments thus far have relied on extracting hole hyperfine couplings in GaAs (and InGaAs) quantum dots through the ratio of the Overhauser shifts for electrons and holes [10-13]. Our theoretical results are roughly consistent with these ratios. Moreover, in silicon, we find hyperfine constants for holes that are consistent with recent T_2^* times measured in silicon quantum dots [19], suggesting those dephasing times may be limited by hyperfine interactions.

The remainder of this paper is organized as follows: In Sec. 2.2 we derive the hyperfine Hamiltonian in the envelope-function approximation accounting for relativistic effects (a finite Thomson radius) and write a projected effective hyperfine Hamiltonian for a nanostructure. In Sec. 2.3 we define the hyperfine parameters for the states at the conduction-band minima and valence-band maxima of GaAs and silicon. In Sec. 2.4 we describe the procedure used to evaluate the hyperfine parameters, with the conclusions given in Sec. 2.5. Technical details are provided in Appendices 2.A-2.F.

2.2 Hyperfine interactions in nanostructures

The goal of this section is to parameterize the hyperfine interactions for a nanostructure in terms of parameters obtained from a bulk calculation. This parameterization can be achieved within the envelope function approximation where the nanostructure confinement potential varies on a length scale that is large compared to the lattice constant of the host material. In nanostructures where the confinement has quickly-varying features on the scale of the lattice constant (e.g. donors or acceptors in silicon with 1/r confining potentials) [71], the formalism developed here cannot be applied and other methods for calculating the hyperfine interactions become necessary [72].

The hyperfine interaction for a many-electron system in contact with nuclear spins I_l at sites l in a nanostructure/molecule/etc. can generally be written (setting $\hbar = 1$) as

$$\mathcal{H}_{\rm hf} = \sum_{l} \gamma_{i_l} \boldsymbol{h}_l \cdot \boldsymbol{I}_l.$$
(2.1)

Here, γ_{i_l} is the gyromagnetic ratio of nuclear isotope i_l at site l and h_l is the hyperfine field operator acting on the many-electron spin/orbital space.

We consider only non-magnetic semiconductors where spin polarization of the core electrons can be neglected. In this case, finite contributions to the hyperfine field arise only from single-particle valence states associated with Bloch waves close to band extrema (valleys). We further assume a nanostructure defined by a slowly-varying potential that modulates a perfectly periodic crystal. This is the regime of validity for the usual envelope-function approximation. In this regime, we rewrite the hyperfine field in terms of a matrix \mathbf{h}^{j} and a multicomponent field operator $\Psi(\mathbf{r})$. The matrix \mathbf{h}^{j} depends only on the properties of the bulk crystal and atom j (e.g. j = Ga, As in GaAs) within the primitive cell, and $\Psi(\mathbf{r})$ accounts for the slowly-varying electronic spin/orbital/valley degrees of freedom, with \mathbf{r} a lattice vector. Further restricting to only short-range¹ contributions to the hyperfine coupling leads to a local (contactlike) form,

$$\boldsymbol{h}_{l} \simeq v_{0} \Psi^{\dagger}(\boldsymbol{r}_{l}) \mathbf{h}^{j_{l}} \Psi(\boldsymbol{r}_{l}), \qquad (2.2)$$

where v_0 is the volume per atom [e.g. $v_0 = \Omega/2$ for a primitive-cell volume Ω containing two atoms, as is the case for diamond (silicon) and zincblende (III-V) lattices considered below]. The matrix \mathbf{h}^{j_l} depends only on the atomic species j_l at site l (and not the isotope i_l) provided we neglect the isotope mass effect [74], consistent with a Born-Oppenheimer approximation. The vector \mathbf{r}_l is the lattice vector that locates the primitive cell containing site l (e.g., if l and l' are in the same primitive cell, then $\mathbf{r}_l = \mathbf{r}_{l'}$). The multicomponent field operator $\Psi(\mathbf{r})$ has elements

$$\Psi_{\nu}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}_{\nu}\cdot\boldsymbol{r}} \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} c_{\boldsymbol{q}\nu}, \qquad (2.3)$$

with crystal volume V and where $c_{q\nu}$ annihilates an electron in an envelope state with band/valley index ν , valley wavevector \mathbf{k}_{ν} , and $|\mathbf{q}|$ is small compared to any reciprocal lattice vector. The matrix \mathbf{h}^{j} describes the short-range contributions to the hyperfine field for atom j at position $\boldsymbol{\delta}_{j}$ within the primitive cell. The associated matrix elements are

$$\mathbf{h}_{\nu\nu\prime}^{j} = \int_{\Omega} d^{3}r \psi_{\nu}^{\dagger}(\boldsymbol{r}) \mathbf{h}(\boldsymbol{r} - \boldsymbol{\delta}_{j}) \psi_{\nu\prime}(\boldsymbol{r}), \qquad (2.4)$$

$$\mathbf{h}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \left(2\mu_B\right) \left(\frac{\boldsymbol{\sigma}}{2} \cdot \overleftarrow{T}(\boldsymbol{r}) + \sigma_0 \frac{1}{r^3} f_{\mathrm{T}}(r) \boldsymbol{L}\right), \qquad (2.5)$$

$$f_{\rm T}(r) = \frac{r}{r + r_{\rm T}/2},$$
 (2.6)

^{1.} In general, the hyperfine field at a nuclear site includes a contribution from electron density within typical atomic dimensions of the nuclear spin (short-range contribution) and a contribution from electron density localized at distant sites (long-range contribution). The long-range contribution is suppressed by a factor $\sim (a_0/a)^3$, where a_0 is the Bohr radius and a is a typical inter-atomic distance. The long-range contribution is thus typically negligible (see Appendix C of Ref. [9]). However, in certain cases with large orbital currents or in materials with large g-factors, the long-range contributions can be significant (see Ref. [73]).

where $\psi_{\nu}(\mathbf{r}) = e^{i\mathbf{k}_{\nu}\cdot\mathbf{r}}u_{\nu}(\mathbf{r})$. Here, the spinor $u_{\nu}(\mathbf{r}) = \left[u_{\nu}^{\uparrow}(\mathbf{r}), u_{\nu}^{\downarrow}(\mathbf{r})\right]^{T}$ describes the latticeperiodic Bloch amplitude for the Bloch wave at wavevector $\mathbf{k} = \mathbf{k}_{\nu}$. We have chosen to normalize the Bloch amplitudes according to the convention:

$$\int_{\Omega} d^3 r u^{\dagger}_{\nu}(\boldsymbol{r}) u_{\nu'}(\boldsymbol{r}) = \frac{\Omega}{v_0} \delta_{\nu\nu'}.$$
(2.7)

In Eq. (2.5), μ_0 is the vacuum permeability, $\mu_{\rm B}$ is the Bohr magneton, we have taken the bare electron g-factor to be $g \simeq 2$, $\boldsymbol{\sigma}$ is the vector of Pauli matrices, and σ_0 is the 2 × 2 identity matrix. The second term in Eq. (2.5) describes coupling of the nuclear magnetic moment to the charge current generated by the electron angular momentum, $\boldsymbol{L} = \boldsymbol{r} \times (-i\boldsymbol{\nabla})$. The factor $f_{\rm T}(r)$ accounts for a cutoff at short distances on the order of the Thomson radius for a nucleus of charge Z|e|, $r_{\rm T} = Z\alpha^2 a_0$ [where $\alpha = (1/4\pi\epsilon_0)e^2/\hbar c \simeq 1/137$ is the fine-structure constant and $a_0 = \hbar/(m_e c\alpha)$ is the Bohr radius]. The tensor $\overrightarrow{T}(\boldsymbol{r})$ accounts for both the Fermi-contact and magnetic dipole-dipole interactions, with tensor elements:

$$T^{\alpha\beta}(\boldsymbol{r}) = \frac{8\pi}{3}\delta_{\mathrm{T}}(\boldsymbol{r})\delta_{\alpha\beta} + \frac{3r_{\alpha}r_{\beta} - r^{2}\delta_{\alpha\beta}}{r^{5}}f_{\mathrm{T}}(r), \qquad (2.8)$$

$$\delta_{\mathrm{T}}(\boldsymbol{r}) = \frac{1}{4\pi r^2} \frac{df_{\mathrm{T}}(r)}{dr}, \qquad (2.9)$$

where $\alpha, \beta \in \{x, y, z\}$. Equation (2.5), with (2.8), includes relativistic effects due to a finite Thomson radius $r_{\rm T} \neq 0$. These relativistic effects can be significant for large-Z atoms [75–78], so they are included here.

Relativistic effects due to $r_{\rm T} \neq 0$ have been neglected in other approaches [63, 64], but we find that these corrections are essential for the present analysis. In particular, our calculations make use of a basis of optimized single-particle states based on the scalar relativistic equation [78, 79]. The *s*-like (l = 0) solutions to the scalar relativistic equation show a weak (integrable) divergence close to a pointlike nucleus, necessitating the cutoff in Eq. (2.9) (see also Fig. 2.1).

An additional common simplification is to neglect the angular-momentum term in Eq. (2.5) (see, e.g., Refs. [63,64]). In this approach, the hyperfine couplings are expressed purely in terms of the electron spin density, without direct reference to the single-particle states and their



Figure 2.1: Electron density near the As site in GaAs. The density is found from the lowest unoccupied Kohn-Sham orbital in the conduction band at $\mathbf{k} = 0$, $\psi_{\text{CB}}^{\sigma}(r)$ (blue solid line, left axis). The weight function $f'_{\text{T}}(r) = 4\pi r^2 \delta_{\text{T}}(\mathbf{r}) = (r_{\text{T}}/2)/(r + r_{\text{T}}/2)^2$ (gray dashed line, right axis) is used to evaluate the contact hyperfine coupling. For As (Z = 33), the Thomson radius is $r_{\text{T}} = Z\alpha^2 a_0 = 1.76 \times 10^{-3} a_0$.

associated phase information. This procedure can be justified when calculating the isotropic Fermi contact term due to s-like states, but for states having a partial-wave expansion with $l \neq 0$ (as we consider below for the valence bands of silicon and GaAs), the angular-momentum term can give a significant contribution to the hyperfine coupling. For example, for a p-like heavy-hole state, $|J = 3/2, l = 1, m_J = 3/2\rangle$ (where J represents the total angular momentum, l gives the orbital angular momentum, and m_J is the angular momentum projected onto the relevant quantization axis), $\frac{|\langle L \rangle|}{|\langle \sigma/2 \rangle|} = 2$, indicating that the nuclear orbital interaction represents a significant portion of the anisotropic hyperfine interaction [see Eq. (2.5)] in this case.

2.2.1 Effective Hamiltonian

We take the hyperfine interaction to be weak compared to other electronic energy scales in a nanostructure, allowing us to consider a projected effective Hamiltonian. When the electronic system can be well-described by a finite-dimensional quasi-degenerate subspace of low-energy states, $\{|n\rangle\}$,² we consider the effective Hamiltonian,

$$H_{\rm hf} = P \mathcal{H}_{\rm hf} P, \tag{2.10}$$

where $P = \sum_{n} |n\rangle \langle n|$ is a projector onto the finite-dimensional subspace $\{|n\rangle\}$. The effect of the hyperfine interaction is then determined by the matrix elements $\langle n| \mathbf{h}_{l} |n'\rangle$.

Equation (2.10) applies to an arbitrary high-dimensional quasi-degenerate space, but a common case is when the ground space is only twofold degenerate. For such a doubly degenerate ground space, $\{|n\rangle\} = \{|+\rangle, |-\rangle\}$, Eq. (2.10) gives

$$H_{\rm hf} = \sum_{l} \left[\boldsymbol{S} \cdot \overleftarrow{\mathbf{A}}_{l} \cdot \boldsymbol{I}_{l} + \gamma_{i_{l}} \mathbf{B}_{l} \cdot \boldsymbol{I}_{l} \right], \qquad (2.11)$$

where the hyperfine tensor $\overleftrightarrow{\mathbf{A}}_l$ and field \mathbf{B}_l are given by:

$$A_l^{\alpha\beta} = 2\gamma_{i_l} \operatorname{Tr}\{S^{\alpha} h_l^{\beta}\}, \qquad (2.12)$$

$$B_l^{\beta} = \frac{1}{2} \text{Tr}\{Ph_l^{\beta}\}, \qquad (2.13)$$

^{2.} Within the envelope function approximation, a general state $|n\rangle$ can be written as $\langle \boldsymbol{r}|n\rangle = \sum_{\nu} F_{\nu}^{n}(\boldsymbol{r})\psi_{\nu}(\boldsymbol{r})$, where the sum, \sum_{ν} is over all spin/orbital/valley states and the $F_{\nu}^{n}(\boldsymbol{r})$ are the slowly-varying (on the scale of the lattice constant) envelope functions. In practice, the sum, \sum_{ν} is restricted to some reasonable set of orbitals and valleys. For example, $|n\rangle$ can be taken to be an eigenstate of the Luttinger Hamiltonian, in which case the sum is restricted to the heavy-hole and light-hole states.

	(electrons)	(holes)		
isotope (i)	$A^i \; (\mu e \mathbf{V})$	$A^i_{\parallel} (\mu e \mathbf{V})$	$A^i_{\perp} \; (\mu e \mathbf{V})$	
⁶⁹ Ga in GaAs	74	1.4	0.35	
⁷¹ Ga in GaAs	94	1.7	0.45	
⁷⁵ As in GaAs	78	11	0.02	
29 Si in silicon	-2.4	-2.5	-0.01	

Table 2.1: Hyperfine parameters calculated for GaAs and crystalline silicon. All parameters have been found from $\mathbf{k} = 0$ Bloch amplitudes approximated by Kohn-Sham orbitals established in DFT using ELK, an all-electron DFT code [79] (see Sec. 2.4 for details). The silicon conduction-band parameter $(A^{^{29}\text{Si}})$ is evaluated using DFT+ $\mathbf{k} \cdot \mathbf{p}$ which accounts for the off-zone-center conduction-band minima in silicon. The valence-band parameters $(A^i_{\parallel} \text{ and } A^i_{\perp})$ are given for a system where the isotope i is located at an 'A' site, with a neighboring ('B' site) atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ (see Sec. 2.3.3 and Fig. 2.3). Numerical convergence has been verified for all parameters to within 2% of the reported values.

and \boldsymbol{S} is the vector of (pseudo)spin-1/2 operators:

$$S^{x} = \frac{1}{2} \left(\left| + \right\rangle \left\langle - \right| + \left| - \right\rangle \left\langle + \right| \right), \qquad (2.14)$$

$$S^{y} = \frac{1}{2i} \left(\left| + \right\rangle \left\langle - \right| - \left| - \right\rangle \left\langle + \right| \right), \qquad (2.15)$$

$$S^{z} = \frac{1}{2} \left(\left| + \right\rangle \left\langle + \right| - \left| - \right\rangle \left\langle - \right| \right).$$

$$(2.16)$$

In the specific case where $\{|+\rangle, |-\rangle\}$ form a Kramers doublet, related by time-reversal $\Theta: \Theta |+\rangle = e^{i\phi_0} |-\rangle$ (where ϕ_0 is a global phase), then we have the further simplification $\mathbf{B}_l = (\langle +| \mathbf{h}_l |+\rangle + \langle -| \mathbf{h}_l |-\rangle)/2 = 0$. This follows directly from the fact that \mathbf{h}_l is odd under time reversal: $\Theta \mathbf{h}_l \Theta^{-1} = -\mathbf{h}_l$. In this (common) scenario (as in the examples given below), the influence of the hyperfine interactions will be well-described by the hyperfine tensor matrix elements, $A_l^{\alpha\beta}$ alone.

2.2.2 Summary of key results

For a conduction-band electron confined to a nanostructure with a spin-independent envelope function, and for a fixed valley: $\Psi_{\sigma}(\mathbf{r}) = F_{\rm e}(\mathbf{r})c_{\sigma}$, we can identify a two-level system $|\pm\rangle = c_{\pm}^{\dagger}|0\rangle$. This allows us to apply Eq. (2.12) with the spin operators given in Eqs. (2.14), (2.15), (2.16). If the electronic state is well-described by an *s*-like band, the isotropic contact interaction dominates, giving the well-known result for an electron spin in a quantum dot [6,7],

$$A_l^{\alpha\beta} = A^{i_l} v_0 \left| F_e(\boldsymbol{r}_l) \right|^2 \delta_{\alpha\beta}, \qquad (2.17)$$

where A^{i_l} is the (bulk) contact hyperfine coupling for isotope i_l at site l (see Table 2.1).

Alternatively, for the valence band of a zincblende III-V semiconductor (GaAs, InAs, InSb, etc.), or for the diamond-lattice form of a group IV element (Si, Ge, etc.), the states at $\mathbf{k} = 0$ transform according to the Γ_8 irreducible representation of the T_d double group. For these states, we can project, for example, onto the two states that transform like states of angular momentum $J_z = m_J = \pm 3/2$: $|\pm\rangle = |m_J = \pm 3/2\rangle$ (the pure heavy-hole states). These are separated in energy from the light-hole states ($|m_J = \pm 1/2\rangle$) under confinement or strain. For these states, the *s*-wave component vanishes identically, and the dominant hyperfine coupling arises from the dipole-dipole and angular-momentum terms. Assuming a pseudospin-independent envelope function for the heavy hole, $\Psi_{m_J}(\mathbf{r}) = F_h(\mathbf{r})c_{m_J}$, Eq. (2.12) gives

$$A_l^{xx} = -A_l^{yy} = A_{\perp}^{i_l} v_0 \left| F_h(\boldsymbol{r}_l) \right|^2, \qquad (2.18)$$

$$A_{l}^{zz} = A_{\parallel}^{i_{l}} v_{0} \left| F_{h}(\boldsymbol{r}_{l}) \right|^{2}, \qquad (2.19)$$

where A_{\parallel}^{i} and A_{\perp}^{i} are valence-band hyperfine parameters (see Table 2.1), and all other hyperfine-tensor elements vanish. Here, the relation $A_{l}^{xx} \neq A_{l}^{yy}$ is a consequence of the fact that the diamond and zincblende lattices do not have a strict fourfold symmetry axis. Equations (2.18) and (2.19) apply in a coordinate system where the site l is located at (0,0,0) with a nearest-neighbor atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in units of the cubic-cell lattice constant (see Sec. 2.3.3). More generally, the influence of the hyperfine coupling can be fully described in the four-dimensional subspace of heavy holes and light holes in terms of the same two coupling constants, A^i_{\perp} and A^i_{\parallel} , given in Table 2.1 (see Sec. 2.3.2).

The parameters A^i , A^i_{\perp} , and A^i_{\parallel} fully characterize the bulk short-range hyperfine coupling for electrons in an *s*-like conduction band and for holes in a valence band that transforms according to the Γ_8 representation of the T_d double group. These parameters depend only on the isotope *i*, through the gyromagnetic ratio γ_i , and on the material-dependent microscopic Bloch functions $\psi_{\nu}(\mathbf{r})$ through the matrix elements given in Eq. (2.4). To approximately determine the relevant Bloch functions in GaAs and silicon, we have performed first-principles DFT calculations. The $\mathbf{k} = 0$ Bloch functions are then approximated directly with optimized Kohn-Sham orbitals (rather than the density alone), providing an accurate representation of the electron/hole states in the vicinity of atoms in the crystal (see Figs. 2.1 and 2.2 for examples in the conduction and valence bands of GaAs, respectively). To find accurate Bloch functions at an off-zone-center band extremum $\mathbf{k} = \mathbf{k}_{\nu} \neq 0$ (as is the case in the conduction band of silicon), we find it is necessary to determine the correct linear combination of $\mathbf{k} = 0$ Kohn-Sham orbitals by diagonalizing an appropriate $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian at $\mathbf{k} = \mathbf{k}_{\nu}$. In each case, the integral in Eq. (2.4) is then evaluated numerically giving the hyperfine parameters. The results are shown in Table 2.1 for GaAs and silicon.

For the conduction bands of GaAs and silicon (electrons), we find contact hyperfine couplings A^i that are consistent with known experimental values (see Table 2.2). There have been fewer experimental studies related to the hyperfine coupling for holes. Moreover, in some cases, experiments on hole spins have led to conflicting interpretations. On one hand, it has been argued that the hyperfine interaction in the heavy-hole subspace is predominantly Ising $(A^i_{\perp} \simeq 0)$ because heavy-hole spin relaxation times have been measured to be consistent with a negligible transverse hyperfine coupling in self-assembled InGaAs quantum dots [80]. In addition, the heavy-hole transverse Overhauser shift has been observed to be small (again, in self-assembled InGaAs quantum dots) [13]. Measurements of tunneling between spin-resolved Landau levels in a two-dimensional hole gas in GaAs are also consistent with a negligible transverse hyperfine coupling [81]. On the other hand, separate experiments measuring the longitudinal Overhauser shift in GaAs/AlGaAs and InGaAs/GaAs quantum dots have been interpreted to indicate a substantial *p-d* hybridization of the valence-band states near the Ga sites, leading to non-negligible transverse hyperfine coupling to the Ga isotopes $(A^i_{\perp} \sim A^i_{\parallel})$ [11]. The results of this experiment, combined with the interpretation of Ref. [11], also suggest

substantial in-plane components of the total heavy-hole Overhauser field. Because the DFT procedure used here gives direct access to the wave function, both the hyperfine couplings and the p-d hybridization can be calculated (see Appendix 2.A). Here, we find an intriguing mix of the two descriptions: For heavy holes, the coupling to the As site is stronger and almost purely Ising (small transverse coupling), while the transverse coupling to the Ga site is a significant fraction of its longitudinal coupling (see Table 2.1 and Appendix 2.A for a possible explanation). However, due to the larger (Ising) hyperfine coupling to the As nuclear spins, the total Overhauser field experienced by a heavy hole in a GaAs quantum dot will be oriented predominantly along the growth direction of the quantum dot, even for a randomly polarized nuclear-spin ensemble. The different behavior at Ga and As sites can be understood as follows: Because As is more electronegative than Ga, the hole is more highly localized around the As site in GaAs (see Fig. 2.2). The potential experienced by the hole in the vicinity of the As site can thus be taken to be more spherically symmetric. Therefore, close to the As site the hole wave function will approximate a pure angular-momentum eigenstate, a p state (see Table 2.3 in Appendix 2.A, below). In contrast, the hole is not sufficiently tightly bound to the Ga atom to fully mask the potential due to neighboring As atoms. In the vicinity of the Ga atom, the hole adapts to the reduced tetrahedral symmetry of the crystal and is therefore not in an angular-momentum eigenstate. Instead, the hole wave function describes a p-d hybridized state (see Fig. 2.2 and Table 2.3). This p-d hybridization leads to non-Ising corrections to the heavy-hole hyperfine Hamiltonian. At the same time, the more delocalized nature of the hole wave function at the Ga sites leads to a significantly smaller hyperfine coupling (due to the larger average distance from the nucleus).

For holes in silicon, we find an Ising hyperfine coupling $(A_{\perp}^{29\text{Si}} \simeq 0)$, see Table 2.1). The strength of the coupling is comparable to the contact interaction $(A^{29\text{Si}})$ for the conduction band of silicon. Typically, the anisotropic hyperfine coupling for (*p*-type valence-band) holes is assumed to be weaker (by a factor of ~ 5-10) than the contact hyperfine coupling for (*s*-type conduction-band) electrons [9]. However, in silicon the states at the conduction-band minima are *s*-*p* hybridized, reducing the effect of the contact interaction for conduction-band states. We find that this reduction leads to a value that is comparable to the (normally smaller) anisotropic hyperfine coupling in the valence band.



Figure 2.2: Calculated density, $\rho = |\phi_{3/2}(\mathbf{r})|^2$, of the $m_J = 3/2$ heavy-hole state in GaAs, resulting from the Kohn-Sham orbital $\phi_{3/2}(\mathbf{r})$. $\rho^{1/5}$ (instead of ρ) is plotted using a color scale (in units of $a_0^{-3/5}$, with a_0 the Bohr radius) so that the features of the density can be visible. The density is shown along a cut in the $(2\bar{1}\bar{1})$ plane. The spheres S_j define regions where the Kohn-Sham orbital $\phi_{3/2}(\mathbf{r})$ has been evaluated to extract the hyperfine tensor for atom j = Ga, As. Regions outside of the spheres S_j are shown in white. The p symmetry can be seen around the As sites (labeled), while the Ga site has a combination of p and d symmetry.

2.3 Bulk hyperfine parameters

Any Bloch wave $\psi_{\nu}^{\sigma}(\mathbf{r})$ can be described near an atomic site j using the partial-wave expansion

$$\psi_{\nu}^{\sigma}(\mathbf{r} + \boldsymbol{\delta}_j) = \sum_{lm} R_{lm\sigma}^{j\nu}(r) Y_{lm}(\theta, \phi), \qquad (2.20)$$

where $R_{lm\sigma}^{j\nu}(r)$ are radial functions and $Y_{lm}(\theta, \phi)$ are the spherical harmonics. States that have a contribution entirely from the l = 0 term to the sum in Eq. (2.20), namely *s*-like states, are isotropic. Therefore, they have a vanishing dipolar and angular-momentum contribution to the hyperfine interaction and contribute only via the contact part of the hyperfine interaction, $\propto \delta_{\rm T}(\mathbf{r})$ [see Eq. (2.8)].

		GaAs		silicon
		η^{Ga}	η^{As}	$\eta^{ m Si}$
(i)	DFT at $\boldsymbol{k} = 0 \ (+\boldsymbol{k} \cdot \boldsymbol{p})$	2500	3800	88
(ii)	Knight shifts (Refs. $[57], [69]$)	2200	3500	—
(iii)	Estimates (Ref. $[60]$)	2600	4400	—
(iv)	Knight shift (Ref. $[70]$)	_	_	100 ± 10
(\mathbf{v})	DFT at $\boldsymbol{k} = \boldsymbol{k}_{\nu}$ (Ref. [64])	—	—	159.4 ± 4.5

Table 2.2: The parameter η^j characterizing the degree of localization of an electron around atom j [see Eq. (2.23)]. This parameter, together with the gyromagnetic ratio γ_i , determines the contact hyperfine coupling for isotope i, A^i [see Eq. (2.25)]. (i): Theoretical results from the present work. (ii): Experimental Knight shifts measured for spin-polarized electronic states in GaAs quantum wells have been used to extract η^j using the procedure described in Appendix 2.B.1. (iii): Theoretical estimates reported in Paget et al. (Ref. [60]), extrapolated from measurements in InSb. (iv): Experimental value of η^j extracted from Knight-shift measurements in bulk silicon (Ref. [70]). The error bar describes the standard deviation of the results of different measurements. (v): Theoretical value calculated by Assali et al., Ref. [64]. The error bar is based on a statistical error from different runs (with different supercell sizes).

2.3.1 Conduction bands with *s*-like Bloch functions

We consider states coming from different equivalent valleys of an *s*-like band, such as the conduction-band states of GaAs (1 valley) and silicon (6 valleys). In the limit of weak spin-orbit coupling, these states can be written as product states of spin and orbit, which means that the index $\nu = (v, \chi)$, where v labels the orbital (valley) and χ labels the spin so that the Bloch amplitudes can be written as $\psi^{\sigma}_{v,\chi}(\mathbf{r}) = \psi^{\sigma}_{v,\sigma}(\mathbf{r})\delta_{\sigma\chi}$. We further assume that the valleys are related by space-group transformations of the crystal so that

$$R_{00\sigma}^{jv\sigma}(r) = R_s^j(r) \quad \forall v, \sigma, \tag{2.21}$$

i.e. the radial function associated with the s part of the Bloch function is identical for all valleys. For these s states, the matrix elements of \mathbf{h}^{j} are given by:

$$\mathbf{h}_{v\chi v'\chi'}^{j} = \frac{2\mu_0}{3}\mu_B \frac{\eta^j}{v_0} \boldsymbol{\sigma}_{\chi\chi'},\tag{2.22}$$

where the dimensionless parameter [70, 82]

$$\eta^{j} = v_0 \left\langle \left| R_s^{j}(r) \right|^2 \right\rangle_{\delta_{\mathrm{T}}}$$
(2.23)

characterizes the degree of localization of the electron at the atom j and is independent of the valley index v because we have assumed that all valleys are equivalent (see Table 2.2). In Eq. (2.23), we have introduced the notation

$$\langle f(r) \rangle_g = \int_0^\infty f(r)g(r)r^2 dr \qquad (2.24)$$

to indicate a weighted average of the function f with respect to the weighting function g. The contact part of the hyperfine Hamiltonian can also be characterized by the parameter

$$A^{i} = \frac{4\mu_{0}}{3}\mu_{B}\gamma_{i}\frac{\eta^{j_{i}}}{v_{0}},$$
(2.25)

where j_i labels the atom associated with isotope *i* (see Table 2.1).

2.3.2 Valence-band holes

We consider here a subspace spanned by states that transform according to the Γ_8 representation of the T_d double group. Examples include the states at the valence-band maxima of silicon and III-V semiconductors such as GaAs.

A simple basis for the Γ_8 representation of the T_d double group is composed of the four states with total angular momentum J = 3/2 and orbital angular momentum l = 1. Without loss of generality, we take the [001] direction (the z-axis) to be a relevant quantization axis. Under this convention, the states that transform like the states with $m_J = \pm 3/2$ units of angular momentum about \hat{z} are the heavy-hole states and those that transform like the $m_J = \pm 1/2$ states are light-hole states. In this four-dimensional subspace, we can therefore label the states with the allowed m_J values, so that $\nu \in \{-3/2, -1/2, 1/2, 3/2\}$. If the expansion from Eq. (2.20) is performed up to l = 2 for each state (see Appendix 2.C.2), the four Bloch amplitudes at the valence-band maximum can be parametrized by three different real radial functions,

$$R_p^j(r) = R_{1,1,\uparrow}^{j,3/2}(r), \qquad (2.26)$$

$$R_d^j(r) = i R_{2,-1,\uparrow}^{j,3/2}(r), \qquad (2.27)$$

$$R_{d'}^{j}(r) = i R_{2,0,\downarrow}^{j,3/2}(r).$$
(2.28)

The remaining radial functions $R_{l,m,\sigma}^{j,m_J}(r)$ either vanish or are linear combinations of these three (see Appendix 2.C.2). Even though the d' orbital is allowed by symmetry, it is often neglected, even in works where d-orbital hybridization for the hole states is taken into account [11]. Because this orbital corresponds to a state with opposite spin [\downarrow , in this case, Eq. (2.28)] relative to the p and d orbitals in the wave function [\uparrow , Eqs. (2.26) and (2.27)], we expect the weight of the d' orbital, or equivalently the magnitude of the $R_{d'}^j(r)$ radial function, to be more significant in materials with large spin-orbit coupling.

In the subspace of heavy holes and light holes, the matrix \mathbf{h}^{j} , given by Eqs. (2.4), (2.5), and (2.6), can be expressed as a linear combination of the angular-momentum matrices for a spin-3/2 particle, \mathbf{J}_{β} , and \mathbf{J}_{β}^{3} , $\beta \in \{x, y, z\}$ [12,83]

$$\mathbf{h}^{j} = \left(\frac{1}{3}h_{\parallel}^{j} - \frac{3}{2}h_{\perp}^{j}\right)\mathbf{J} + \frac{2}{3}h_{\perp}^{j}\mathcal{J},\tag{2.29}$$

where $\mathcal{J} = (J_x^3, J_y^3, J_z^3)$, and where h_{\perp}^j and h_{\parallel}^j are two hyperfine parameters. These two parameters can be written in terms of the matrix elements of $1/r^3$ as

$$h_{\parallel}^{j} = \frac{\mu_{0}}{2\pi} \mu_{B} \left[\frac{8}{5} M_{p,p}^{j} - \frac{12}{7} M_{d,d}^{j} - \frac{4}{7} M_{d',d'}^{j} + \frac{4}{7} \sqrt{\frac{3}{2}} \operatorname{Re} \left(M_{d,d'}^{j} \right) \right], \qquad (2.30)$$
$$h_{\perp}^{j} = \frac{\mu_{0}}{2\pi} \mu_{B} \left[\frac{6}{7} M_{d,d}^{j} + \frac{2}{7} M_{d',d'}^{j} - \frac{30}{7} \sqrt{\frac{3}{2}} \operatorname{Re} \left(M_{d,d'}^{j} \right) \right],$$



Figure 2.3: Cubic unit cell for a zincblende or diamond lattice. The blue and red spheres represent the two inequivalent sites in the zincblende lattice. We have chosen the blue atom to be at the origin, 000 (A site, see main text), and a red atom to be located at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ (B site). An A site can be related to a B site by performing a translation of the coordinate system by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, represented by the blue arrow, followed by a rotation of the coordinate system by $\pi/2$ about the z axis. The red arrow represents the vector $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in the coordinate system with the B site at the origin, 000, and an A site at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

where

$$M_{\lambda\lambda'}^{j} = \left\langle \frac{R_{\lambda}^{j}(r)R_{\lambda'}^{j}(r)}{r^{3}} \right\rangle_{f_{\mathrm{T}}}, \qquad (2.31)$$

for $\lambda, \lambda' \in \{p, d, d'\}$, the numerical factors arise from angular integrals, and $f_{\rm T}$ is the weighting function given by Eq. (2.6). These two parameters can also be expressed in units of energy (see Table 2.1) as

$$A^{i}_{\perp/\parallel} = \gamma_{i} h^{j_{i}}_{\perp/\parallel}.$$
 (2.32)

2.3.3 Choice of coordinate system

Crystals break pure rotational symmetry, therefore their electronic eigenstates cannot in general be written as pure angular-momentum eigenstates. For example, in the valence bands of GaAs and silicon, the eigensates can be approximated by a linear combination of p and d orbitals (see Sec. 2.3.2). The presence of the d orbitals reflects the tetrahedral symmetry of

the crystal and introduces the term proportional to \mathcal{J} in the matrix \mathbf{h}^{j} [Eq. (2.29)] which has consequences on the symmetries of the hyperfine tensor.

In both GaAs and silicon, the coordinate system can be set up so that the cubic unit cell has one nucleus at 000, and another nucleus at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ (Fig. 2.3). Given this specific coordinate system, we can label as A all the sites related to 000 by a lattice vector and all sites related to $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ by a lattice vector are labeled by B, with the understanding that all A sites are equivalent and all B sites are equivalent.

Equations (2.1) and (2.2) for the hyperfine Hamiltonian within the envelope-function approximation can be combined to define a Hamiltonian matrix associated with site l, H^l :

$$\mathcal{H}_{\rm hf} = \sum_{l} v_0 \Psi^{\dagger}(\boldsymbol{r}_l) \mathrm{H}^{l} \Psi(\boldsymbol{r}_l), \qquad (2.33)$$

with

$$\mathbf{H}^{l} = \gamma_{i_{l}} \mathbf{h}^{j_{l}} \cdot \boldsymbol{I}_{l}. \tag{2.34}$$

Here, we recall that i_l indicates the isotope situated at site l and j_l indicates the atom situated at site l. The hyperfine matrix \mathbf{H}^l is simply the hyperfine Hamiltonian matrix expressed in the basis of Bloch states, $\psi_{\nu}(\mathbf{r})$ [see Eq. (2.4)]. In the subspace of valence-band states, this matrix is given by inserting \mathbf{h}^j from Eq. (2.29) into Eq. (2.34). Restricting further to the heavy-hole subspace, and for an isotope i_l located at an A site labeled by l, the matrix is

$$\mathbf{H}_{\rm HH}^{l,A} = \frac{1}{2} \left[A_{\parallel}^{i_l} \sigma_z I_z^{l,A} + A_{\perp}^{i_l} \left(\sigma_x I_x^{l,A} - \sigma_y I_y^{l,A} \right) \right], \tag{2.35}$$

where $I_{\alpha}^{l,A}$ are the nuclear spin operators for the nuclear spin at the A site labeled by l and σ_{α} are Pauli matrices. As can be seen in Fig. 2.3, an A site can be related to a B site by performing a translation of the coordinate system by (1/4, 1/4, 1/4) followed by a rotation of the coordinate system by $\pi/2$ about the z axis. The result of this rotation is that $x \to y$ and $y \to -x$. Under this rotation, $A^{xx} \to A^{yy}$ and $A^{yy} \to A^{xx}$. Therefore, in the same coordinates used to describe $H_{HH}^{l,A}$, the hyperfine coupling for an isotope $i_{l'}$ located at a B site (l') is

$$\mathbf{H}_{\rm HH}^{l',B} = \frac{1}{2} \left[A_{\parallel}^{i_{l'}} \sigma_z I_z^{l',B} - A_{\perp}^{i_{l'}} \left(\sigma_x I_x^{l',B} - \sigma_y I_y^{l',B} \right) \right], \tag{2.36}$$

which has the opposite sign for the term with coefficient A_{\perp} relative to the Hamiltonian for the A sites, $H_{HH}^{l,A}$ [see Eq. (2.35)]. This sign difference for A sites and B sites may lead to non-trivial interference effects in the dynamics of hole spins confined to III-V and group IV nanostructures. We give the valence-band hyperfine couplings for GaAs and silicon in Table 2.1. In each case, the couplings are given assuming a coordinate system where the isotope in question is at an A site. We also present the light-hole hyperfine Hamiltonian matrix in Appendix 2.D.

2.4 First-principles electronic structure

In Eq. (2.2), the multi-component field operator, $\Psi(\mathbf{R})$, acts on the envelope functions, while \mathbf{h}^{j} accounts for the short-range electronic structure, determined by the Bloch waves, $\psi_{\nu}(\mathbf{r})$. The matrix \mathbf{h}^{j} can thus be found from a bulk calculation for the translationally-invariant crystal. Here, we calculate \mathbf{h}^{j} using DFT.

Hyperfine parameters are often evaluated through the density alone [63–68]. Because the matrix elements of orbital angular momentum, $\boldsymbol{L} = \boldsymbol{r} \times (-i\boldsymbol{\nabla})$, depend on the phase of the wave function, the contribution from the nuclear-orbital interaction ($\sim \boldsymbol{L} \cdot \boldsymbol{I}$) to the hyperfine parameters h_{\parallel}^{j} and h_{\perp}^{j} cannot generally be calculated using the density alone. This contribution is therefore often neglected [63,64,68]. Here, we assume the Kohn-Sham orbitals, $\phi_{\nu}(\mathbf{r})$, can approximate the Bloch waves, $\psi_{\nu}(\mathbf{r})$ (as has been done, e.g., in Ref. [84]). This approximation is valid at least when correlations are weak, so that the many-body ground state is well described by a single Slater determinant (Hartree-Fock limit).

All of the DFT calculations presented here are done using the ELK code [79] with the exchange-correlation functional of Perdew, Burke and Ernzerhof (GGA-PBE) [85]. ELK is an all-electron code that avoids potential pitfalls associated with extracting the short-range electronic structure from a pseudopotential [64]. Within ELK, the Kohn-Sham orbitals for the valence electrons are calculated by solving the Dirac equation under the scalar relativistic approximation [86], so it is essential to use the relativistic form of the hyperfine interaction to find accurate results.

To compute the hyperfine parameters we run ELK (with input file set for "very high quality" [vhq parameter] convergence) [79], to compute the Kohn-Sham orbitals at the conduction-

band minima and valence-band maxima of GaAs and silicon. We then treat these Kohn-Sham orbitals as approximations for the Bloch waves, $\psi_{\nu}(\mathbf{r}) \approx \phi_{\nu}(\mathbf{r})$.

2.4.1 Conduction band of GaAs

The Kohn-Sham orbital at the conduction-band minimum of GaAs ($\mathbf{k} = 0$) is found to be almost completely *s*-like (see Appendix 2.E). As explained in Sec. 2.3.1, this symmetry property of the wave function implies that the hyperfine interaction will be dominated by the contact term. The integral for the contact hyperfine interaction has a weighting function, $\delta_{\rm T}(r)$, that weights the points within a distance $r_{\rm T}^{j}$ from the nuclei strongly, where $r_{\rm T}^{j}$ is the Thomson radius for atom *j*. It is therefore important to find an accurate description of the Kohn-Sham orbital at short length scales ($r \leq r_{\rm T}^{j}$). We sample the wave function on an equally spaced one-dimensional (radial) grid of points starting from each atom *j* (Ga or As) within the unit cell out to a distance of $100r_{\rm T}^{j}$. These values represent a numerical description of the conduction-band wavefunction $\psi(\mathbf{r} + \boldsymbol{\delta}_{j})$. Because the *s*-component of the wave function is spherically symmetric, the radial functions are easily determined using $\psi(\mathbf{r} + \boldsymbol{\delta}_{j}) = Y_{0}^{0}(\theta, \phi)R_{s}^{j}(r) = R_{s}^{j}(r)/\sqrt{4\pi}$. Once the radial functions have been obtained, we numerically evaluate the integral from Eq. (2.23) (see Appendix 2.E).

Once the integral $\left\langle |R_s^j(r)|^2 \right\rangle_{\delta_{\mathrm{T}}}$ has been evaluated, it can be used with Eqs. (2.23) and (2.25) to evaluate η^j and the contact hyperfine parameter A^i for the isotopes of Ga and As in GaAs. We have verified that η^j has converged with respect to certain parameters (e.g., the number of basis states and the density of k-points for which the calculation is performed; see Appendix 2.F for the full list) to within 1% of its asymptotic value (see Appendix 2.F for details). The resulting hyperfine constants (given in Table 2.1) are consistent with the accepted values estimated by Paget et al. (Ref. [60]). The accuracy of this estimate may be in question since it is based on measurements in an analogous material (InSb), rather than direct measurements in GaAs. However, the hyperfine constants calculated here are also consistent with Knight-shift measurements made on (fractional and integer) quantum-Hall states in GaAs quantum wells [57, 69] (see Table 2.2, and Appendix 2.B.1 for details).

2.4.2 Conduction band of silicon

In contrast to GaAs, the conduction band of silicon has six minima (valleys). Each minimum is situated at roughly 84% of the way to any of the six equivalent X points from the Γ point. The states at the conduction-band minima of silicon are s-p hybridized. Even though an anisotropic hyperfine interaction is not forbidden by symmetry (due to the s-p hybridization), previous theoretical studies indicate that the contact part of the hyperfine Hamiltonian dominates over the anisotropic piece in bulk silicon [64]. We therefore neglect the anisotropic hyperfine interaction when investigating the hyperfine coupling in the conduction band of silicon. Because only s states have a non-vanishing contact hyperfine interaction, we project onto the s-like component of the states at the conduction-band minima and use the same method described in Sec. 2.4.1 to evaluate the hyperfine constants for these states. The result, $\eta^{\text{Si}} = 160$, is consistent with the theoretical result of Ref. [64], $\eta^{\text{Si}} = 159.4 \pm 4.5$, which was obtained using the WIEN2K [87] all-electron DFT code with the non-relativistic formula for the contact-hyperfine constant [taking the limit as $r_{\rm T}^j \to 0$ in Eq. (2.8)]. Both of these calculations for the density directly at the conduction-band minima are, however, inconsistent with the measured value $\eta^{\rm Si} = 100 \pm 10$, reported in Ref. [70], obtained from Knight-shift and Korringa-relaxation measurements.³ This has led us to a different approach, described below.

In GaAs, where the conduction-band minimum is at the Γ point, we find accurate values of the hyperfine parameters (see Sec. 2.4.1). In contrast, in silicon, where the conduction-band minima are off zone center, we find hyperfine parameters that do not agree with experimental results. Therefore, we have evidence that the DFT procedure used here is more accurate for the Γ -point ($\mathbf{k} = 0$) Bloch functions than for Bloch functions at other points in the Brillouin zone. Because the point-group symmetry at the Γ point is the same as that of the full crystal (as opposed to a subgroup of the crystal point group when $\mathbf{k} \neq 0$), the states at the Γ point have higher symmetry than the states at finite \mathbf{k} . Since the basis set used in the ELK code consists of atomic states, which transform according to representations of the full rotation group, it is plausible to expect that the Γ -point states are more accurate than the states at

^{3.} The authors of Ref. [64] compared their result, $\eta^{\text{Si}} = 159.4 \pm 4.5$, with the result reported in Ref. [82], $\eta^{\text{Si}} = 186 \pm 18$, which was derived from ²⁹Si nuclear-spin relaxation measurements. Although these results seem roughly consistent with each other, there was an error found in the analysis of Ref. [82] which, when accounted for, leads to $\eta^{\text{Si}} = 132 \pm 13$ (see Ch. IX, section III-A of Ref. [88]).

finite \boldsymbol{k} . In contrast to the direct DFT calculations at the band extrema described above, here we now use $\boldsymbol{k} \cdot \boldsymbol{p}$ theory to calculate the wave functions at any finite \boldsymbol{k} , starting from the wave functions calculated with DFT at the Γ point ("DFT+ $\boldsymbol{k} \cdot \boldsymbol{p}$ ").

To implement DFT+ $\mathbf{k} \cdot \mathbf{p}$, we use the experimentally determined values for the $\mathbf{k} \cdot \mathbf{p}$ matrix elements and energy gaps presented first by Cardona and Pollak [89] and then extended by Richard et al. [90] and diagonalize the $\mathbf{k} \cdot \mathbf{p}$ matrix to determine the correct linear combination of $\mathbf{k} = 0$ Bloch amplitudes to describe the states at the conduction-band minima. We then extract the Kohn-Sham orbitals at the Γ point ($\mathbf{k} = 0$) and take the appropriate linear combination and (after projecting onto the *s*-component) follow the procedure outlined in Sec. 2.4.1 for the conduction-band states of GaAs. Although $\mathbf{k} \cdot \mathbf{p}$ theory is perturbative, and improves as $\mathbf{k} \to 0$, in Refs. [89] and [90] the entire band structure is shown to be accurately reproduced using these $\mathbf{k} \cdot \mathbf{p}$ matrix elements and energy gaps. Therefore, using the matrix elements provided in these references should be sufficient for calculations at the conduction-band minima of silicon.

The DFT+ $\mathbf{k} \cdot \mathbf{p}$ procedure yields $\eta^{\text{Si}} = 88$, which is a factor of ~ 2 different from the result $(\eta^{\text{Si}} = 160)$ found above for a calculation of the Bloch functions directly at the conductionband minima. Furthermore, this DFT+ $\mathbf{k} \cdot \mathbf{p}$ result is approximately consistent with the Korringa-relaxation-rate and Knight-shift measurements of Ref. [70], $\eta^{\text{Si}} = 100 \pm 10$ (see Appendix 2.B.1 for a discussion of the Knight shift). This level of consistency suggests that DFT+ $\mathbf{k} \cdot \mathbf{p}$ can be useful to perform accurate calculations in materials where the band extrema are not situated at the Γ point. The agreement with experimental observations is also consistent with the assumption of small anisotropic corrections to the Fermi contact interaction. However, since the reduction of η^{Si} is due to a significant *s-p* hybridization, it would still be interesting to assess the role of anisotropy. A proper account of these effects would require applying the methods discussed here to the full bulk states (instead of their *s* component), but should also take into account the specific nanostructure, e.g., the predominant valley states.⁴

2.4.3 Valence bands of GaAs and silicon

Because the top of the valence band is fourfold degenerate for GaAs and silicon, a general valence-band Kohn-Sham orbital will be a linear combination of all four states. To calculate the anisotropic hyperfine parameters for these valence-band states, we extract the values of a Kohn-Sham orbital at the top of the valence band on a uniform grid of positions, and use group-theoretic arguments to reconstruct $\phi_{3/2}(\mathbf{r})$, the Kohn-Sham orbital that transforms like the state with total angular momentum J = 3/2, orbital angular momentum l = 1 and $m_J = 3/2$ (see Appendix 2.C). We then use the spherical harmonic expansion [Eq. (2.20)] to obtain the radial functions listed in Eqs. (2.26), (2.27), and (2.28). We find that only the radial functions for quantum number l up to l = 2 have significant weight (see Appendix 2.F).

The radial functions are inserted into Eq. (2.31) and the appropriate integrals, $M_{\lambda\lambda'}^{j}$, are computed numerically. The integrals from Eq. (2.31) are estimated by setting a cutoff for the upper bound of integration at $R_{\text{max}} = \sqrt{3}a/8$, where *a* is the cubic lattice constant of the material under consideration and R_{max} is the radius of the largest non-overlapping spheres, S_j , centered at each nuclear site *j* (see Fig. 2.2). Setting the cutoff to R_{max} is equivalent to neglecting long-range contributions to the hyperfine interaction. We make a further approximation, in the case of the anisotropic hyperfine parameters, and set $f_{\rm T}(r) \rightarrow 1$ (or equivalently $r_{\rm T} \rightarrow 0$) when evaluating the matrix elements $M_{\lambda\lambda'}^{j}$ from Eq. (2.31). This is justified because the relativistic radial functions vanish at the origin for all states except *s* states and *p* states with total angular momentum J = 1/2 [76, 78]. The valence-band states can be written as a linear combination of *p* states with J = 3/2 and *d* states [see Eq. (2.46)]. Because the relativistic form is important for $r \leq r_{\rm T}$ and the valence-band states

^{4.} We note that in silicon nanostructures (e.g. quantum dots) the relevant eigenstates are formed by taking linear combinations of the different bulk valley states (and potentially spin states, if spin-orbit coupling is relevant). In these systems, the anisotropic hyperfine coupling may be significant in comparison to the contact piece. If the specific linear combinations making up the eigenstates of a given nanostructure are well understood, the theory presented here can be applied to calculate the appropriate hyperfine tensor. Instead of projecting the bulk states onto the s component, the full bulk states could be used, appropriate linear combinations taken, and hyperfine tensor elements computed using Eq. (2.12)

vanish at the origin and vary on the scale of a Bohr radius, a_B , corrections to the relativistic form are suppressed by $r_T/a_B \lesssim 10^{-3}$. Finally, we verify that the computed values of $M^j_{\lambda\lambda'}$ have converged with respect to the parameters listed in Appendix 2.F to within 2% of their asymptotic values (see Appendix 2.F for details).

In Refs. [10–13], the ratio of the Overhauser shifts of electrons and holes in GaAs quantum dots is measured. From the results of these measurements, the authors conclude $A_{\parallel}/A \sim 10\%$ in GaAs, roughly consistent with the results presented here (see Table 2.1). In Ref. [19], T_2^* times have been measured for a hole-spin qubit defined in a silicon complementary metaloxide-semiconductor (CMOS) quantum dot. It is not clear which mechanism limits T_2^* in these experiments. However, if the coherence times were limited by the hyperfine interaction, the measured T_2^* times would be consistent with the silicon hyperfine constants presented here (see Appendix 2.B.2 for details).

2.5 Conclusions

We have calculated the hyperfine parameters for the conduction and valence bands of GaAs and silicon using the Kohn-Sham orbitals from an all-electron DFT code (ELK), fully accounting for the relativistic form of the hyperfine coupling, and in the case of silicon, we have introduced and employed an expanded DFT+ $\mathbf{k} \cdot \mathbf{p}$ procedure.

For the conduction band of GaAs, our results for η^j are consistent with the accepted values from Paget et al. (Ref. [60]) and with measurements of the Knight shifts in GaAs quantum wells [57,69]. In silicon, our results are roughly consistent with measurements of the Korringa relaxation times and measurements of the Knight shift [70] when we use the DFT+ $\mathbf{k} \cdot \mathbf{p}$ procedure (see Table 2.2).

In the procedure used here, we have accounted for *d*-orbital hybridization in the valenceband states of GaAs. Similar to the analysis presented in Ref. [11], we find that this *d*-orbital hybridization leads to the Ga nuclear spins (and not the As nuclear spins) in GaAs having a substantial transverse hyperfine coupling $(A_{\perp}^i \sim A_{\parallel}^i)$. However, while the results of Ref. [11] (combined with their interpretation) suggest that heavy holes in a GaAs quantum dot may experience a significant in-plane Overhauser field, we find that the total Overhauser field experienced by a heavy hole in a GaAs quantum dot will point predominantly along the

dot growth direction, even for an unpolarized nuclear-spin system. This anisotropy is a consequence of the stronger hyperfine coupling to the As nuclear spins relative to the Ga nuclear spins: $A_{\parallel}^{^{75}\text{As}} \gg A_{\perp}^{^{69}\text{Ga}/^{71}\text{Ga}}$. This finding is consistent with measured heavy-hole spin relaxation times [80], transverse Overhauser-field measurements [13], and measurements of tunneling between spin-resolved Landau levels in a two-dimensional hole gas [81]. Moreover, we find hyperfine constants that are roughly consistent in magnitude with conclusions drawn in Refs. [10-13] from measurements of the ratio of the heavy-hole to electron Overhauser fields. Additionally, if A^i_{\perp} has a significant magnitude only for the Ga nuclear spins, then in nanostructures (quantum dots or quantum wells) with confined heavy holes and a magnetic field along the growth direction, only the Ga nuclear spins can be dynamically polarized (along the growth direction). Alternatively, if light holes are confined to similar nanostructures, all nuclear spins can be dynamically spin polarized (see Appendix 2.D). Therefore, an additional consequence of the hyperfine constants calculated here is that a larger Overhauser field can be generated if light holes are used to dynamically spin polarize the nuclear spins in GaAs instead of heavy holes. For silicon, our results are consistent with T_2^* measurements made in CMOS hole-spin quantum dots [19]. Moreover, in contrast to GaAs, where the hyperfine coupling strength for holes is roughly an order of magnitude smaller than that of electrons $(A_{\parallel}/A \sim 0.1)$, in silicon, we find that the hyperfine coupling strengths for holes and electrons are comparible $(A_{\parallel} \sim A)$.

For holes, experiments (including Overhauser-shift and T_2^* measurements) often only provide indirect measurements of the hyperfine interaction. For example, extracting the hyperfine parameters from Overhauser-shift measurements requires knowledge of the hole envelope functions, the degree of spin polarization of the nuclear spins, and isotopic alloying disorder. Measuring the hole hyperfine coupling directly (e.g., through hole-spin echo envelope modulations (HSEEM) [72]) could instead provide a direct and unambiguous measurement of the hyperfine tensor matrix elements, allowing a direct comparison to the theoretical results presented here.

The method explored here combines DFT, $\mathbf{k} \cdot \mathbf{p}$ theory, and group theory to arrive at an approximate description of the crystal Bloch functions and not only the electronic density. As demonstrated for the conduction band of silicon, $\mathbf{k} \cdot \mathbf{p}$ theory can be crucial in accurately calculating the Bloch functions away from $\mathbf{k} = 0$. The DFT+ $\mathbf{k} \cdot \mathbf{p}$ procedure introduced

here can therefore be important to understand properties of other materials that have band extrema at finite \mathbf{k} . These materials include graphene, nanotubes, Weyl semimetals, and transition metal dichalcogenides. Furthermore, the wave function (including the phase) at all points in the Brillouin zone is required, for example, to evaluate topological invariants (such as Chern numbers). Therefore, DFT+ $\mathbf{k} \cdot \mathbf{p}$ might be important in determining topological invariants and cataloguing different topological phases of materials [91,92]. More generally, this method can be applied to obtain an approximate description of the electronic wave functions for semiconductor systems. These systems include quantum wells, quantum dots, and defect centers in diamond. The electronic wave function can be used to calculate relevant quantities in these systems, including, but not limited to hyperfine interactions, spin-orbit interactions, and transition dipole matrix elements.

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Appendices to Chapter 2

2.A *p*-*d* hybridization of the valence-band states

In the past, calculations of hole hyperfine constants have been performed by approximating the Bloch amplitudes with atomic p functions [9, 61]. Although they are the simplest states that respect the crystal symmetries, p states are not general enough to completely describe the valence-band Bloch functions (see, for example, the discussion in Sec. 2.3.2 or Refs. [11,62,93–95]). The procedure described here allows us to calculate the weight of higher angular momentum states, namely d states, in the valence-band Bloch functions. We can quantify the contribution of the p and d states to the valence-band state around each atom as

$$w_{\lambda}^{j} = \frac{\int_{0}^{R_{\max}} \left| R_{\lambda}^{j}(r) \right|^{2} r^{2} dr}{\sum_{\lambda', j} \int_{0}^{R_{\max}} \left| R_{\lambda'}^{j}(r) \right|^{2} r^{2} dr},$$
(2.37)

for $\lambda \in \{p, d, d'\}$. The results are displayed in Table 2.3. The weight of the *p*-orbital increases with the electronegativity of the nucleus (see Table 2.3). A basic estimate of the electronegativity of the nuclei is given from the effective nuclear charge experienced by the valence electrons of the free atoms calculated from Hartree-Fock theory [96]. In GaAs, the As atom, $Z_{\text{eff}} = 7.4492$ [96], has almost pure *p* symmetry, while the Ga atom, $Z_{\text{eff}} = 6.2216$ [96], has an admixture of *p* and *d* symmetries. As explained in Sec. 2.2.2, the higher electronegativity of the As atom suggests a more spherically symmetric potential, and consequently, a weaker *p*-*d* hybridization (see Fig. 2.2 and Table 2.3). In the case of GaAs, this *p*-*d* hybridization leads to non-Ising corrections to the heavy-hole hyperfine coupling for the Ga nuclear spins.

Additional evidence for this explanation can be found in Ref. [93]. In this reference, the Bloch functions for various zincblende compounds are calculated (using empirical pseudopotentials). From these calculations, the author concludes that, for the studied materials, as the crystals become more ionic, the d-orbitals on the cationic site become more important, and

	present work		Ref. [94]	
atom (j)	w_p^j	w_d^j	w_p^j	w_d^j
Ga	0.13	0.07	0.15	0.20
As	0.79	0.01	0.62	0.03
Si	0.43	0.07	-	-

Table 2.3: Weights, w_{λ}^{j} , of the *p* and *d* contributions for valence-band states for each atom in GaAs and silicon. In Ref. [94] silicon is not studied. The weight $w_{d'}^{j} = 0$ within the accuracy of the present procedure, which is consistent with the results reported in Ref. [94].

the wave function in the vicinity of the anionic site becomes more p-like, consistent with the reasoning provided above. We also note that, although the d' orbital is allowed by symmetry (see Appendix 2.C), its contribution to the valence-band states vanishes within the accuracy of this procedure.

Bogusławski and Gorczyca, Ref. [94], have also projected the GaAs valence-band wave functions onto the spherical harmonics. They used the empirical pseudopotential method to obtain the wave functions. These wave functions are then expanded in terms of p and dspherical harmonics centered at each atom j. They report results for the p and d contributions to the states from each site. The results of Ref. [94] are roughly consistent with our own. They also suggest that the contribution of the d' orbitals is relatively small when compared to the p and d orbitals (see Table 2.3).

Other works using empirical pseudopotentials [93] and tight-binding theory [95] have also found significant p-d hybridization of the Bloch amplitudes near the Ga sites in GaAs. These works have produced results in rough agreement with the results of Ref. [94] presented in Table 2.3.

2.B Comparison with experimental results

2.B.1 Knight shift

The Knight shift, K_l , is the shift in magnetic resonance frequency of an isotope at site l due to the average field $\langle \mathbf{h}_l \rangle$ [88]. Measurements of the Knight shift can be used to characterize

the hyperfine interaction for electrons confined to a given nanostructure.

Measurements of the Knight shift have been made in quantum Hall states of GaAs [57, 69]. For non-interacting *s*-like electrons (such as those in the conduction-bands of GaAs and silicon) in a quantum well with fully spin-polarized electrons, the Knight shift,

$$K_l = \frac{v_0 A^{i_l}}{2h} |F(z_l)|^2 n, \qquad (2.38)$$

is proportional to the hyperfine constant A^{i_l} . In Eq. (2.38), h is Planck's constant, F(z) is the quantum-well envelope function, and n is the sheet density of electrons in the quantum well. In Ref. [57], the Knight shift for nuclei at the center of a GaAs quantum well was measured using optically pumped nuclear magnetic resonance in three different samples in the $\nu = 1/3$ fractional quantum Hall state (having a fully spin-polarized ground state). For a symmetric quantum well with infinite barriers, the largest Knight shift occurs directly in the center of the well, and is proportional to $|F(z = L/2)|^2 = 2/L$, where L is the well width. Using this value for the envelope function, the hyperfine coupling was extracted from the Knight-shift measurement and a value of $A_c^{^{71}\text{Ga}} = v_0 A^{^{71}\text{Ga}}/h = (4.5 \pm 0.2) \times 10^{-13} \text{ cm}^3/\text{s}^3$ was reported. This value can be converted into a value for η^{j_l} (for atom j_l at site l) using Eq. (2.25), and is presented in Table 2.2. More recently, Knight-shift measurements have been made in GaAs in the quantum Hall regime, close to a filling factor $\nu = 1$ [69]. The results for the Knight shifts for ⁶⁹Ga and ⁷⁵As relative to that of ⁷¹Ga (plotted in Fig. 1 of Ref. [69]) can be combined with the Knight-shift measurement of Ref. [57] and Eq. (2.38) to obtain values for the hyperfine constants for 69 Ga and 75 As. The values of η^{j_l} obtained from these measurements are consistent with our calculated values (see Table 2.2).

The Knight shift has also been measured in *n*-doped bulk silicon samples [70]. The extracted hyperfine parameter is $\eta^{\text{Si}} = 100 \pm 10$, approximately consistent with our calculated value of $\eta^{\text{Si}} = 88 \pm 1$ (see Table 2.2).

2.B.2 Hole-spin coherence times

The hyperfine field can limit coherence times for electrons or holes [19] trapped in nanostructures. Recently, Maurand et al. [19], measured the coherence time, $T_2^* = (59 \pm 1)$ ns, of a hole-spin qubit confined to a CMOS silicon quantum dot. Under the assumption that there are enough nuclear spins interacting with the hole spin that the hyperfine-field value will be Gaussian distributed, we can estimate the coherence time for the heavy-hole spin using [9]

$$\frac{1}{2(T_2^*)^2} \approx \frac{1}{4N} \sum_i g_i I_i (I_i + 1) (A^i_{\parallel})^2, \qquad (2.39)$$

where g_i is the abundance of isotope *i* having nuclear spin I_i , and *N* is the number of nuclear spins in the nanostructure. From the quantum dot level-spacing from Maurand et al. [19], we estimate $N \sim 10^3$, assuming a spherical quantum dot. Calculating T_2^* from Eq. (2.39) using our result for $A_{\parallel}^{\text{Si}}$, $I_i = 1/2$, and the natural abundance of ²⁹Si ($g_{29}_{\text{Si}} = 4.7\%$), we find T_2^* to be on the order of 100 ns. Our estimate of T_2^* is therefore of the same order as the measured value.

2.C Group theory and projection operators

To reconstruct the heavy-hole and light-hole states from an arbitrary linear combination of these four states, we use the projection operator technique [97] from group theory.

The states at the top of the valence band of group IV and III-V semiconductors transform according to the Γ_8 representation of the tetrahedral double group, T_d (or equivalently the Γ_8^+ representation of the O_h double group) [97]. We start by constructing the Γ_8 representation and then show how it can be used along with the projection operators to determine states that will contribute to the partial-wave expansion of the heavy-hole and light-hole states.

2.C.1 Construction of the Γ_8 representation

A known basis for the Γ_8 representation of the tetrahedral double group, T_d , is the set of four J = 3/2 angular momentum eigenstates with l = 1 (see Table D.1. p. 522 in Ref. [97]). In the $|J, l, m_J\rangle$ basis, where J represents the total angular momentum, l gives the orbital angular momentum, and m_J is the angular momentum projected onto the relevant quantization axis (the z-axis, e.g. [001]), these states are $|3/2, 1, \pm 3/2\rangle$, which transform like the heavy-hole states, and $|3/2, 1, \pm 1/2\rangle$, which transform like the light-hole states. According to the

definition of basis vectors [97],

$$\mathcal{O}_i |3/2, 1, m_J\rangle = \sum_{m'_J = -3/2}^{3/2} [D^{(\Gamma_8)}(\mathcal{O}_i)]_{m_J m'_J} |3/2, 1, m'_J\rangle, \qquad (2.40)$$

where $\mathcal{O}_i \in T_d$ is a symmetry operation and $D^{(\Gamma_8)}(\mathcal{O}_i)$ is the Γ_8 representation of the \mathcal{O}_i symmetry.

Using the orthonormality of the basis states, we can construct the Γ_8 representation matrices as

$$[D^{(\Gamma_8)}(\mathcal{O}_i)]_{m_J m'_J} = \langle 3/2, 1, m'_J | \mathcal{O}_i | 3/2, 1, m_J \rangle, \qquad (2.41)$$

for all symmetry operations $\mathcal{O}_i \in T_d$. Furthermore, we have

$$\langle 3/2, 1, m'_J | \mathcal{O}_i | 3/2, 1, m_J \rangle = \sigma(\mathcal{O}_i) W^{3/2}_{m_J m'_J}(a_i, b_i, c_i), \qquad (2.42)$$

where $\sigma(\mathcal{O}_i) = 1$ if the operation is a pure rotation, $\sigma(\mathcal{O}_i) = (-1)^l$ if the operation involves an inversion, and $W^J(a, b, c)$ is the J^{th} Wigner D matrix. The angles a_i , b_i and c_i are the symmetry-dependent Euler angles, where a_i is an initial rotation around the z-axis, b_i a subsequent rotation around a perpendicular axis, labeled y ([010]) and c_i is the final rotation around the z-axis (these angles can be found for the different symmetry operations $\mathcal{O}_i \in$ T_d in Table I of Ref. [98]). Inserting Eq. (2.42) into Eq. (2.41), we can construct the Γ_8 representation of the T_d double group, { $D^{(\Gamma_8)}(\mathcal{O}_i)$ }.

2.C.2 Projection operators

Since each valence-band state transforms like one of the four $|3/2, 1, m_J\rangle$ states, we label each state by m_J . This labeling is consistent with the notation developed above. We now define the projection operators and show how to use them to construct the heavy-hole and light-hole states. For the Γ_8 basis states, the projection operators $\hat{P}_{m_J m'_J}$, are defined by the equation

$$\hat{P}_{m_J m'_J} \left| m'_J \right\rangle = \left| m_J \right\rangle, \tag{2.43}$$

where m_J and m'_J run over the four basis states of the Γ_8 representation. Under the Γ_8 representation, the projection operators are written as [97]

$$\hat{P}_{m_J m'_J} = \frac{1}{12} \sum_i \{ [D^{(\Gamma_8)}(\mathcal{O}_i)]^{-1} \}^*_{m_J m'_J} \mathcal{O}_i, \qquad (2.44)$$

where the numerical prefactor comes from the ratio of the order of the Γ_8 representation to the order of the double group T_d .

Because the projection operators are linear, $\hat{P}_{3/2,3/2}$ can retrieve the component of any state that transforms like $|3/2\rangle$ under the symmetry operations of the double group T_d . Therefore, by systematically applying the $\hat{P}_{3/2,3/2}$ projection operator to the 6 *p*-states (l = 1) and the 10 *d*-states (l = 2), we can calculate the *d*-orbital hybridized heavy-hole state $|3/2\rangle$. The result is

$$\langle r|3/2 \rangle = R_p(r) |1,1\rangle |+\rangle - iR_d(r) |2,-1\rangle |+\rangle$$

$$-iR_{d'}(r) |2,0\rangle |-\rangle , \qquad (2.45)$$

where r is a radial coordinate, $R_{\lambda}(r)$ are real radial functions and we have used the basis of states $|l, m\rangle |\sigma\rangle$. The basis vectors $|l, m\rangle |\sigma\rangle$ are related to $|J, l, m_J\rangle$ basis vectors by the Clebsch-Gordon coefficients. We then construct the other three states by applying the projection operators $\hat{P}_{m_J,3/2}$ to the state from Eq. (2.45)
$$\langle r| - 3/2 \rangle = R_p(r) |1, -1\rangle |-\rangle + iR_d(r) |2, 1\rangle |-\rangle + iR_{d'}(r) |2, 0\rangle |+\rangle , \langle r| + 1/2 \rangle = R_p(r) \left(\sqrt{\frac{2}{3}} |1, 0\rangle |+\rangle + \sqrt{\frac{1}{3}} |1, 1\rangle |-\rangle \right) - i\tilde{R}_1(r) |2, 2\rangle |+\rangle - i\tilde{R}_2(r) |2, -2\rangle |+\rangle - i\frac{R_d(r)}{\sqrt{3}} |2, -1\rangle |-\rangle ,$$

$$\langle r| - 1/2 \rangle = R_p(r) \left(\sqrt{\frac{2}{3}} |1, 0\rangle |-\rangle + \sqrt{\frac{1}{3}} |1, -1\rangle |+\rangle \right) + i\tilde{R}_1(r) |2, -2\rangle |-\rangle + i\tilde{R}_2(r) |2, 2\rangle |-\rangle + i\frac{R_d(r)}{\sqrt{3}} |2, 1\rangle |+\rangle ,$$

$$(2.46)$$

where $\tilde{R}_1(r) = \sqrt{1/3}R_d(r) + \sqrt{1/2}R_{d'}(r)$ and $\tilde{R}_2(r) = \sqrt{1/2}R_{d'}(r) - \sqrt{1/3}R_d(r)$. Finally, we note that we also enforce

$$\Theta \langle r|3/2 \rangle = e^{i\phi_0} \langle r| - 3/2 \rangle \tag{2.47}$$

where Θ is the time-reversal operator and ϕ_0 is a global phase. This equation restricts the relative phases of the p and d parts of the wave functions to be as shown in Eqs. (2.45) and (2.46). We also note that we have omitted the \mathbf{k}_{ν} quantum number for the valence-band states since the valence-band maximum for group IV and III-V semiconductors is situated at the Γ point, where $\mathbf{k} = 0$.

The advantage of applying the projection operators to atomic orbitals is that the symmetry of the states can be easily identified. For example, in the case of the valence-band states of GaAs and silicon, the deviation from pure p symmetry (and the *d*-orbital hybridization) can be easily understood by using the projection operators (as described above) to write the states as in Eqs. (2.45) and (2.46). We note that the group theory projection operators can also be applied directly to wave functions defined numerically on a grid of points by applying the symmetry operators \mathcal{O}_i [see Eq. (2.44)] directly to the coordinates (for an implementation, see Ref. [99]).

2.D Light-hole hyperfine Hamiltonian

Projecting the hyperfine matrix [Eq. (2.34)] onto the light-hole subspace results in

$$\mathbf{H}_{\rm LH}^{l,A} = \frac{1}{2} \left[\left(\frac{1}{3} A_{\parallel}^{i_l} - 4 A_{\perp}^{i_l} \right) \sigma_z I_z^{l,A} \right]$$
(2.48)

$$+\left(\frac{2}{3}A_{\parallel}^{i_l}+A_{\perp}^{i_l}\right)\left(\sigma_x I_x^{l,A}+\sigma_y I_y^{l,A}\right)\bigg],\tag{2.49}$$

where the Pauli matrices, σ_{α} , act in the light-hole subspace. This hyperfine matrix is given for an isotope i_l located at an A site labeled by l (see Sec. 2.3.3). In contrast to the heavyhole hyperfine matrix, the light-hole hyperfine matrix is invariant under $A^{xx} \to A^{yy}$ and $A^{yy} \to A^{xx}$. Therefore the hyperfine matrix for A sites is equivalent to the hyperfine matrix for B sites. In addition, the logitudinal and transverse light-hole hyperfine couplings depend on both A_{\parallel} and A_{\perp} [see Eqs. (2.48) and (2.49)]. Therefore, in contrast to heavy holes, even when $A_{\perp} \ll A_{\parallel}$ (e.g. for the As site in GaAs), the transverse light-hole hyperfine coupling is of the same order as the longitudinal hyperfine coupling [see Eqs. (2.48) and (2.49)].

2.E s-like Kohn-Sham orbitals

The *s*-like states that contribute to the conduction-band minimum of GaAs are 'almost purely s-like,' which we take to mean

$$\frac{\sum_{l>0} N_l^{\nu}}{N_0^{\nu}} < 10^{-3}, \tag{2.50}$$

where

$$N_{l}^{\nu} = \sum_{m=-l}^{l} \sum_{\sigma,j} \int_{0}^{R_{\max}} \left| R_{lm\sigma}^{j\nu} \right|^{2} r^{2} dr.$$
(2.51)

In Eq. (2.51) $R_{\text{max}} = \sqrt{3}a/8$, where *a* is the lattice constant. R_{max} is half the distance between nearest-neighbor atoms in the crystal.

For s-like orbitals the contact hyperfine interaction dominates. Since the contact hyperfine constants are determined by the integral $\langle |R_s^j(r)|^2 \rangle_{\delta_{\rm T}}$, we present here the procedure used to evaluate this integral. Since the relativistic s-like radial function has a power-law divergence at the origin [76,78], we fit the points that are within a distance of $10r_{\rm T}^j$ from each atom with a power law and evaluate the integral

$$\left\langle \left| R_s^j(r) \right|^2 \right\rangle_{\delta_{\mathrm{T}}}^{\mathrm{in}} = \int_0^{10r_{\mathrm{T}}^j} \left| R_{\mathrm{fit},s}^j(r) \right|^2 \delta_{\mathrm{T}}(r) r^2 dr, \qquad (2.52)$$

where $R_{\text{fit},s}^{j}(r) = \Lambda r^{-\xi}$ is the best fit function to the radial part of the Kohn-Sham orbital, with Λ and ξ being fit parameters. We then use a Riemann sum to evaluate the integral for all points $10r_{\text{T}}^{j} < r_{n} < 100r_{\text{T}}^{j}$,

$$\left\langle \left| R_s^j(r) \right|^2 \right\rangle_{\delta_{\mathrm{T}}}^{\mathrm{out}} = \sum_{r_n = 10r_{\mathrm{T}}^j}^{100r_{\mathrm{T}}^j} \left| R_n^j \right|^2 \delta_{\mathrm{T}}(r_n) r_n^2 \Delta, \qquad (2.53)$$

where r_n is the set of points where the radial function $R_s^j(r)$ is sampled, $R_n^j = R_s^j(r_n)$, and $\Delta = r_{n+1} - r_n$. We then approximate

$$\left\langle \left| R_s^j(r) \right|^2 \right\rangle_{\delta_{\mathrm{T}}} \approx \left\langle \left| R_s^j(r) \right|^2 \right\rangle_{\delta_{\mathrm{T}}}^{\mathrm{in}} + \left\langle \left| R_s^j(r) \right|^2 \right\rangle_{\delta_{\mathrm{T}}}^{\mathrm{out}}.$$
 (2.54)

In Eq. (2.54) we have taken contributions to the integral [Eq. (2.24)] to be negligible for $r > 100r_{\rm T}$. This approximation is justified because the scale at which the weighting function in the integral [$\delta_{\rm T}(r)$] decays is given by $r_{\rm T}$ [see Eq. (2.9)].

2.F Convergence criteria

For each parameter p (e.g. p can be the density of k states at which the DFT calculation is performed), we construct $\alpha^{j}(p)$, $\alpha \in \{\eta, h_{\perp}, h_{\parallel}\}$. In other words, we evaluate α^{j} for a range of values of the parameter p. Once α^{j} has been evaluated for multiple values of p, we fit $\alpha^{j}(p)$ to a power law of the form

$$\alpha^j(p) = \Lambda p^{-\xi} + \alpha_0^j, \qquad (2.55)$$

where Λ , ξ and α_0^j are fit parameters and, in particular, α_0^j is the asymptotic value of α^j as a function of p. In all cases, we find that

$$\frac{\left|\alpha^{j}(p_{\rm vhq}) - \alpha_{0}^{j}\right|}{\alpha_{0}^{j}} < e, \tag{2.56}$$

where $p_{\rm vhq}$ is the 'very high quality' value of the parameter p, determined by ELK [79], and e = 0.01 for $\alpha = \eta$ and e = 0.02 for $\alpha \in \{h_{\perp}, h_{\parallel}\}$. This procedure was carried out for the parameters gmaxvr, lmaxvr, nempty, rgkmax, chgexs, swidth [79], as well as the number of k points in the first Brillouin zone at which the Kohn-Sham orbitals were found, and the number of points in the unit cell at which the wave functions were extracted.

In addition, we have verified the smallness of the error made in expanding the valence-band states only up to l = 2 in the spherical harmonic expansion [see Eq. (2.20)]. Specifically, if we define

$$\mathcal{M}_{j}(l_{\max}) = \sum_{\sigma} \int_{\mathcal{S}_{j}} dr d\Omega \frac{\left| \sum_{l=0}^{l=l_{\max}} \sum_{m=0}^{l} R_{lm\sigma}^{j\nu}(r) Y_{lm}(\theta, \phi) \right|^{2}}{r}, \qquad (2.57)$$

where the integral is over the sphere S_j surrounding atom j (see Fig. 2.2), we have verified that

$$\frac{\mathcal{M}_j(3) - \mathcal{M}_j(2)}{\mathcal{M}_j(3)} < 0.001 \tag{2.58}$$

for all atoms j in GaAs and silicon. Since the hyperfine parameters are calculated from matrix elements of $\mathbf{h}(\mathbf{r}) \sim 1/r^3$ [see Eq. (2.5)] and $\mathcal{M}_j(l_{\text{max}})$ is a (diagonal) matrix element of $1/r^3$, Eq. (2.58) should be a good measure of the error made in neglecting terms with l > 2when calculating hyperfine constants.

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Addendum to Chapter 2 - Hyperfine interaction for hole spins in germanium

Since the writing of the published portion of Chapter 2, hole spins in strained germanium quantum dots have shown promise as qubit candidates. Like silicon, germanium possesses a low abundance ($\sim 7.8\%$) of spinful nuclei, which results in a weaker interaction with the nuclear-spin bath via the hyperfine interaction (in comparison to e.g. GaAs). However, hole spins in strained germanium possess an additional advantage: the small effective mass weakens the engineering constraints required to build precise devices [1–3].

Recently, few-hole planar germanium quantum dots have been fabricated and studied. In Ref. [4], a quantum dot in the single-hole regime was demonstrated. Relaxation times (T_1) , and coherence times (T_2^*) have been measured in these devices and Pauli spin blockade has been demonstrated [4,5]. Furthermore, the strong spin-orbit coupling has been used for fast all-electrical qubit manipulation [2]. These advances have laid the foundation for future hole-spin germanium devices. However, the germanium hole hyperfine coupling has yet to be established.

There is evidence suggesting that charge noise limits the phase coherence time, T_2^* in current germanium quantum-dot devices [4]. As germanium devices are engineered with a decreasing amount of charge noise, it becomes increasingly likely that coherence times will be limited by a different mechanism. The hyperfine interaction has been shown to be the dominant decoherence mechanism in other host materials (e.g. GaAs, silicon). Even when isotopically purifying silicon to remove the spinful nuclei (²⁹Si), the hyperfine coupling to the remaining residual nuclear spins has been shown to limit coherence times [6, 7]. It is likely that the hyperfine interaction will also eventually limit the coherence times for hole spins in germanium quantum dots. Therefore, quantifying the strength of this interaction for germanium hole spins may be important to understand the decoherence in future germanium devices.



Figure 2.4: Calculated density, $\rho = |\phi_{3/2}(\mathbf{r})|^2$, of the $m_J = +3/2$ heavy-hole state in germanium, resulting from the Kohn-Sham orbital $\phi_{3/2}(\mathbf{r})$. $\rho^{1/5}$ is plotted (rather than ρ) using a color scale (in units of $a_0^{-3/5}$, with a_0 the Bohr radius) so that the features of the density can be visible. The two germanium nuclei within a primitive unit cell are each at the center of one of the circles. ρ is shown along a cut in the $(2\bar{1}\bar{1})$ plane. We neglect the long-range dipolar (hyperfine) coupling between the nuclear spin and hole-spin density outside the sphere S_{Ge} .

Germanium hole hyperfine interaction

In the four-dimensional valence-band subspace of germanium (and silicon and III-V materials) spanned by the heavy and light holes, the hyperfine interaction between a hole and a nuclear spin I takes the following form [see Eq. (2.29)]

$$\mathbf{H}_{\mathrm{VB}}^{i} = \left(\frac{1}{3}A_{\parallel}^{i} - \frac{3}{2}A_{\perp}^{i}\right)\mathbf{J}\cdot\mathbf{I} + \frac{2}{3}A_{\perp}^{i}\mathcal{J}\cdot\mathbf{I}, \qquad (2.59)$$

where *i* labels the nuclear isotope under consideration, **J** is the vector of spin-3/2 matrices (where the heavy holes are labeled by $m_J = \pm 3/2$ and the light holes are labeled by $m_J = \pm 1/2$), $\mathcal{J} = (J_x^3, J_y^3, J_z^3)$, and where A_{\perp}^i and A_{\parallel}^i are two hyperfine parameters. This Hamiltonian can be projected onto the heavy-hole subspace to obtain the heavy-hole hyperfine Hamiltonian

$$\mathbf{H}_{\rm HH}^{i} = A_{\parallel}^{i} s_{z} I_{z} + A_{\perp}^{i} \left(s_{x} I_{x} - s_{y} I_{y} \right), \qquad (2.60)$$

	(electrons)	(holes)	
isotope (i)	$A^i \; (\mu e \mathbf{V})$	$A^i_{\parallel} \; (\mu e \mathrm{V})$	$A^i_{\perp} \; (\mu e \mathbf{V})$
⁶⁹ Ga in GaAs	74	1.4	0.35
⁷¹ Ga in GaAs	94	1.7	0.45
⁷⁵ As in GaAs	78	11	0.02
²⁹ Si in silicon	-2.4	-2.5	-0.01
⁷³ Ge in germanium	-	-1.1	0.02

Table 2.4: Hyperfine parameters calculated for GaAs and crystalline germanium and silicon. All parameters have been found from $\mathbf{k} = 0$ Bloch amplitudes approximated by Kohn-Sham orbitals established in DFT using ELK, an all-electron DFT code. The silicon conduction-band parameter $(A^{2^{9}\text{Si}})$ is evaluated using DFT+ $\mathbf{k} \cdot \mathbf{p}$ which accounts for the off-zone-center conduction-band minima in silicon (see Sec. 2.4.2). These hyperfine couplings imply that the heavy-hole hyperfine Hamiltonian is almost entirely Ising-like in germanium, silicon, and for the arsenic nuclear spins in GaAs [see Eq. (2.60)]. Numerical convergence has been verified for all parameters to within 2% of the reported values (see Appendix 2.F).

where s is a pseudospin-1/2 operator in the heavy-hole subspace. In Eq. (2.60), A^i_{\parallel} parameterizes the strength of the Ising part of the hyperfine coupling and A^i_{\perp} parameterizes the strength of the transverse hyperfine coupling. In the light-hole subspace, the hyperfine Hamiltonian has the form

$$\mathbf{H}_{\rm LH}^{i} = \left(\frac{1}{3}A_{\parallel}^{i} - 4A_{\perp}^{i}\right)s_{z}I_{z} + \left(\frac{2}{3}A_{\parallel}^{i} + A_{\perp}^{i}\right)\left(s_{x}I_{x} + s_{y}I_{y}\right),\tag{2.61}$$

where now s is a pseudospin-1/2 operator in the light-hole subspace. Using the Kohn-Sham orbitals and the procedure outlined in Sec. 2.4.3, we can calculate the hyperfine parameters for the valence band of germanium (again neglecting long-range contributions, see Fig. 2.4). We obtain $A_{\parallel}^{^{73}\text{Ge}} = -1.1 \,\mu\text{eV}$ and $A_{\perp}^{^{73}\text{Ge}} = 0.02 \,\mu\text{eV}$ (see Table 2.4). These values imply that the germanium heavy-hole hyperfine coupling is almost purely Ising-like [see Eq. (2.60)].

Contribution to T_2^* from the hyperfine interaction

The hyperfine interaction can limit coherence times for electrons or holes trapped in quantum dots. We consider a quantum dot defined in a quantum well of width, w, with parabolic

in-plane confinement. The envelope function for such a dot can be written as [8],

$$F(\mathbf{r}) = F_z(z)F_{\boldsymbol{\rho}}(\boldsymbol{\rho}), \qquad (2.62)$$

with

$$F_z(z) = \sqrt{\frac{2}{w}} \sin\left(\frac{\pi z}{w}\right), \quad z \in [0, w]$$
(2.63)

and

$$F_{\boldsymbol{\rho}}(\boldsymbol{\rho}) = \frac{1}{\sqrt{\pi}a_B^*} \exp\left(-\frac{\rho^2}{2a_B^{*2}}\right),\tag{2.64}$$

where z is the direction of the quantum-well confinement, $\rho = (x, y)$ is the in-plane (perpendicular to the z-axis) position vector, and a_B^* is the effective Bohr radius of the quantum dot. For an out-of-plane magnetic field (along z), if (1) the nuclear spin bath is in an infinite temperature state so that the nuclear spins sample all possible spin configurations and (2) there are enough nuclear spins interacting with the hole spin that the hyperfine-field value will be Gaussian distributed, then we can estimate the coherence time for a quantum-dot-confined heavy-hole spin [with envelope function given by Eq. (2.62)] using [8; see also Appendix 2.B.2]

$$\frac{1}{2(T_2^*)^2} \approx \frac{1}{4N} \sum_i g_i I_i (I_i + 1) (A^i_{\parallel})^2.$$
(2.65)

In Eq. (2.65) g_i is the abundance of isotope *i* having nuclear spin I_i , and $N = \pi a_B^{*2} w/v_0$ is the number of nuclear spins in the quantum dot (v_0 is the atomic volume of the host material). Planar germanium quantum dots have recently been fabricated in germanium quantum wells with w = 18 nm [2]. If, for example, we assume that the effective Bohr radius for these dots is $a_B^* \simeq 50 \text{ nm}$ (estimated from the dashed circle in Fig. 2a of Ref. [2]), then we expect $T_2^* \simeq 1 \,\mu\text{s}$ for a germanium heavy hole due to the hyperfine interaction (see Fig. 2.5). This value of T_2^* is slightly larger than the values measured in Ref. [4], $T_2^* = 140 \text{ ns}$ and $T_2^* = 380 \text{ ns}$ in two different quantum dots (see Fig. 4b of Ref. [4]). There is evidence suggesting that the measured coherence times are limited by charge noise. It is reasonable to expect the hyperfine interaction to limit coherence times in future devices where charge noise is suppressed. It is therefore important to understand the germanium valence-band hyperfine interaction if germanium quantum dots are to host hole-spin qubits with long coherence times.



Figure 2.5: T_2^* as a function of effective Bohr radius a_B^* of a lateral germanium quantum dot (in blue), assuming an out-of-plane magnetic field, a well width w = 18 nm and an abundance of 73 Ge ($I_{7^3\text{Ge}} = 9/2$), $g_{7^3\text{Ge}} = 7.76\%$ (natural germanium). The top axis indicates how many nuclei are under the hole wavefunction ($N = \pi a_B^{*2} w/v_0$). The dashed lines represent the experimentally measured values of T_2^* from Ref. [4].

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Preface to Chapter 3

In the previous chapter, we used DFT to compute hyperfine parameters for electrons and holes. Although there is experimental evidence that the values we calculated are accurate for electrons, direct measurements of the hole hyperfine parameters are not yet available. In this chapter, we calculate the coherence of the hole spin after a spin-echo pulse sequence as a function of the hole hyperfine constants. We show how measurements of spin-echo envelope modulations can be used to determine the hole hyperfine constants experimentally.

The system of interest in this chapter is a light hole bound to a boron acceptor in silicon. While this system has been proposed as an interesting spin qubit, the hyperfine coupling to the boron nuclear spin remains an open question. We estimate this hyperfine coupling and demonstrate that our estimated value, which is on the order of 1% of the phosphorus donor hyperfine coupling, would still be measurable via hole spin echo envelope modulations. Because the confining potential ($\sim 1/r$) of a boron acceptor diverges at the boron site, the envelope function approximation breaks down. Therefore, we base the estimate on empirical observations instead of the theory presented in Chapter 2. However, the DFT method presented in Chapter 2 can, in principle, be applied to a boron acceptor to more firmly establish the hyperfine coupling. Due to the lack of translational symmetry, application of the DFT method would involve a large supercell calculation. This (computationally intensive) supercell calculation is beyond the scope of this thesis and is left for future work.

Hole spin echo envelope modulations provide a direct measurement of hole hyperfine couplings. While we focus on the boron acceptor hyperfine coupling in this chapter, the theory can be extended to other systems. If applied to systems where the envelope function approximation is valid (e.g. quantum dots, quantum wells), this method could be used to verify the hole hyperfine constants calculated in Chapter 2.

We note that at the time of publication of the manuscript presented in Chapter 3, Ref. [23] of this chapter (see References for Chapter 3, below) was 'in preparation'. Since, this reference has been published and is reproduced as Chapter 2 of this thesis.

3 Hole spin echo envelope modulations

This chapter is the integral text (including references) from:

Hole spin echo envelope modulations

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Hole spins in semiconductor quantum dots or bound to acceptor impurities show promise as potential qubits, partly because of their weak and anisotropic hyperfine couplings to proximal nuclear spins. Since the hyperfine coupling is weak, it can be difficult to measure. However, an anisotropic hyperfine coupling can give rise to a substantial spin-echo envelope modulation that can be Fourier-analyzed to accurately reveal the hyperfine tensor. Here, we give a general theoretical analysis for hole-spinecho envelope modulation (HSEEM), and apply this analysis to the specific case of a boron-acceptor hole spin in silicon. For boron acceptor spins in unstrained silicon, both the hyperfine and Zeeman Hamiltonians are approximately isotropic leading to negligible envelope modulations. In contrast, in strained silicon, where light-hole spin qubits can be energetically isolated, we find the hyperfine Hamiltonian and q-tensor are sufficiently anisotropic to give spin-echo-envelope modulations. We show that there is an optimal magnetic-field orientation that maximizes the visibility of envelope modulations in this case. Based on microscopic estimates of the hyperfine coupling, we find that the maximum modulation depth can be substantial, reaching $\sim 10\%$, at a moderate laboratory magnetic field, $B \lesssim 200 \,\mathrm{mT}$.

3.1 Introduction

Recent theoretical [1,2] and experimental [3,4] work has shown that hole spins bound to boron acceptors in silicon may be viable qubits. In this system, a strong spin-orbit coupling can be used to manipulate the spins with electric fields while the influence of electrical noise is suppressed [1]. This type of all-electrical control is more difficult in electron-spin systems, where the spin-orbit interaction is weaker. A further possible advantage of hole spins is a weak and anisotropic hyperfine coupling that can be controlled to extend spin coherence times [5]. A hole spin bound to an acceptor in silicon therefore offers certain important advantages over other spin qubits.

Hyperfine interactions can have a significant influence on the spin dynamics of both electrons and holes in semiconductor nanostructures. To accurately control these spins, it is important to first experimentally extract details of the relevant hyperfine parameters. Spectroscopic techniques (e.g., paramagnetic spin resonance) can be used to resolve the large hyperfine splittings for electrons bound to donor impurities [6, 7]. However, these methods applied to, e.g., boron acceptors in silicon have not yet resolved the much smaller hyperfine couplings expected for *p*-like orbitals composing the valence band, for which the dominant contact interaction vanishes. For example, in Ref. [8] it has been estimated that the hyperfine field for boron acceptors must be less than ~ 0.7 mT to be consistent with recent spin-resonance measurements. This is in contrast with the larger hyperfine field of $A/g\mu_{\rm B} \simeq 3.6 \,\mathrm{mT}$ experienced by a phosphorus-donor-bound electron in Si ($g \simeq 2$) due to the hyperfine coupling to a ³¹P nuclear spin ($A/h \simeq 100 \,\mathrm{MHz}$). Spectral hole-burning experiments showing the transfer of spin polarization from boron acceptors to surrounding ²⁹Si nuclear spins indicate that the hyperfine coupling must be finite, but of undetermined strength [9].

Although the hyperfine coupling has not yet been experimentally resolved for boron acceptors in pure silicon, electron-nuclear double resonance (ENDOR) experiments have established the hyperfine coupling and quadrupolar splittings for boron acceptors at several lattice sites and in several polymorphs of SiC (specifically, 3C-, 4H- and 6H-SiC). These experiments give hyperfine fields on the order of $A/g\mu_{\rm B} \sim 0.1 \,\mathrm{mT}$ [10, 11]. If the hyperfine coupling is similarly weak for boron acceptors in pure silicon, it may not have been visible in Ref. [8], but it would nevertheless have important implications for hole-spin dynamics.

As an alternative to ENDOR, direct measurements of electron-spin-echo envelope modulation (ESEEM) [12, 13] can be a sensitive probe of the hyperfine coupling when that coupling is anisotropic. This technique has been successfully applied, for example, to understand the anisotropic hyperfine coupling for weakly coupled ²⁹Si nuclear spins surrounding a phosphorus donor impurity in isotopically enriched ²⁹Si [14] and for ¹³C nuclear spins weakly coupled to nitrogen-vacancy- (NV-) center spins in diamond [15]. The influence of echo envelope modulation on decoherence/dynamics for donor-bound electrons and NV-center spins has also been analyzed in detail theoretically [16–18].

Here, we theoretically establish conditions (e.g., strain, magnetic field) for an experiment to extract hyperfine parameters from *hole*-spin-echo envelope modulations (HSEEM), applicable to an acceptor impurity or quantum-dot-bound hole spin. In particular, we find that envelope modulations will be negligible for hole spins in unstrained silicon, but by introducing biaxial tensile strain, a light-hole spin qubit can show substantial modulations. For concrete calculations, we focus on the case of a light hole bound to a boron acceptor in silicon, where we expect the effect of envelope modulations to be significant. However, much of the analysis presented here translates naturally to hole spins at other acceptor sites or in semiconductor quantum dots in group IV or III-V materials having a valence band with states that transform according to the Γ_8 representation of the T_d group at the band extremum. The HSEEM effect studied here has the same basic origin as ESEEM, introduced by Rowan, Hahn, and Mims (Refs. [12, 13]). This effect is distinct from modulations arising from non-secular hyperfine couplings for heavy-hole spin qubits [19, 20], or from measurement feedback effects [21].

There are several issues that distinguish the case of HSEEM from the more conventional ESEEM. For example, in contrast with the case of a donor-bound electron, acceptor-bound hole spins have a highly anisotropic g-tensor. This anisotropy, along with the anisotropy of the hyperfine interaction, result in a visibility (modulation depth) of envelope modulations that has a non-trivial dependence on the applied magnetic-field orientation (Fig. 3.1, below). The modulation depth also depends on the strength of the hyperfine interaction, relative to the nuclear-spin Larmor frequency. To establish the maximum experimentally achievable modulation depth, we have determined the optimal magnetic-field orientation for a boron acceptor in silicon. In addition, we have estimated the form and typical energy scale determining the acceptor hyperfine tensor from a semiempirical microscopic analysis.

From the estimated hyperfine tensor for a boron acceptor, we evaluate the echo envelope function for a light-hole spin qubit [Fig. 3.1(a), below]. We find substantial modulation amplitude ($\geq 10\%$) in a moderately weak magnetic field ($B \leq 200 \,\mathrm{mT}$). The maximum modulation depth can be achieved only when the magnetic-field orientation has been optimized [see Fig. 3.1(b)]. This suggests that (under reasonable, but carefully designed experimental conditions), the hyperfine tensor can be extracted for a boron acceptor spin.

The rest of this article is organized as follows: in Sec. 3.2 we review HSEEM and explain how it can be used to measure hyperfine couplings. In Sec. 3.3 we estimate the hyperfine tensor for a boron acceptor in silicon. In Sec. 3.4, we describe how the hyperfine tensor from Sec. 3.3 can be combined with the general analysis of Sec. 3.2 to predict envelope modulations for a light-hole spin qubit. In Sec. 3.5 we present our conclusions.

3.2 Hole-spin-echo envelope modulations (HSEEM)

3.2.1 Spin Hamiltonians

The hyperfine interaction for a hole-spin qubit in contact with a nuclear spin I can generally be written (with $\hbar = 1$) as [22]

$$H_{\rm hf} = \boldsymbol{S} \cdot \overleftarrow{\mathbf{A}} \cdot \mathbf{I} + \boldsymbol{\mathcal{B}} \cdot \boldsymbol{I}, \qquad (3.1)$$

where S is a pseudospin-1/2 operator acting in the two-dimensional qubit Hilbert space, $\overleftarrow{\mathbf{A}}$ is the hyperfine tensor, and \mathcal{B} gives rise to a chemical shift that may depend on the hole wavefunction, but is generally independent of the value of the pseudospin. If the qubit under consideration is composed of a Kramers doublet (two states related by time reversal), \mathcal{B} vanishes identically [23]. In an applied magnetic field B, the full Hamiltonian is

$$H = \mu_{\rm B} \boldsymbol{B} \cdot \overleftarrow{\mathbf{g}} \cdot \boldsymbol{S} - \gamma \boldsymbol{B} \cdot \boldsymbol{I} + H_{\rm hf}, \qquad (3.2)$$

where $\overleftarrow{\mathbf{g}}$ is the hole-spin *g*-tensor, $\mu_{\rm B}$ is the Bohr magneton, and γ is the nuclear-spin gyromagnetic ratio. For simplicity, we take the direction of the magnetic field, \boldsymbol{B} , to define the *z*-axis ($\hat{\mathbf{z}} = \hat{\boldsymbol{B}} = \boldsymbol{B}/|\boldsymbol{B}|$). We neglect the quadrupolar interaction between the

nuclear spin and an electric-field gradient (this becomes exact for a nuclear spin I = 1/2 with a vanishing quadrupole moment or for a local cubic symmetry, leading to a vanishing electric-field gradient [24]). The Hamiltonian, Eq. (3.2), can be rewritten in terms of the nuclear-spin Zeeman splitting and the hole pseudospin splitting due to an effective magnetic field, $B_{\text{eff}} = \mathbf{B} \cdot \overleftarrow{\mathbf{g}}$ as

$$H = \Omega_S S_c - \omega_I I_z + H_{\rm hf}, \tag{3.3}$$

where $\Omega_S = \mu_B | \boldsymbol{B} \cdot \overleftrightarrow{\mathbf{g}} | = \mu_B | \boldsymbol{B}_{\text{eff}} |$ is the pseudospin splitting due to $\boldsymbol{B}_{\text{eff}}, \omega_I = \gamma B$ is the nuclear-spin Zeeman splitting, and $S_c = \hat{\mathbf{c}} \cdot \boldsymbol{S}$, where $\hat{\mathbf{c}} := \hat{\boldsymbol{B}}_{\text{eff}} = \boldsymbol{B}_{\text{eff}} / B_{\text{eff}}$.

When $\Omega_S \gg |A_{\alpha\beta}|$, we retain only the secular contributions (those that commute with S_c), giving

$$H \simeq H_0 = \Omega_S S_c - \omega_I I_z + H_{\rm hf}^0, \qquad (3.4)$$

$$H_{\rm hf}^0 = A_{cx} S_c I_x + A_{cy} S_c I_y + A_{cz} S_c I_z, \qquad (3.5)$$

where we restrict to the case $\mathcal{B} \to 0$. Terms that do not commute with the nuclear-spin Zeeman term, $\sim I_z$, are included since the nuclear-spin Zeeman energy may be comparable to the hyperfine parameters, $\omega_I \sim A_{\alpha\beta}$. Equations (3.4) and (3.5) are the standard starting point for studies of electron-spin-echo envelope modulation [12, 16, 17].

3.2.2 Hahn echo envelope

In a hole-spin Hahn echo experiment, the hole pseudospin is initially aligned with the effective magnetic field (i.e., along $\hat{\mathbf{c}}$). A $\pi/2$ -pulse is then applied, resulting in an equal superposition of Zeeman eigenstates. After some time τ , a π -pulse is performed to invert the spin, followed by a free evolution and detection after a further time τ .

The time-evolution operator describing the dynamics of this Hahn echo pulse sequence is given by [12]

$$U(2\tau) = U_0(\tau) R_{\pi} U_0(\tau) R_{\pi/2}, \qquad (3.6)$$

where

$$U_0(t) = e^{-iH_0 t} (3.7)$$

is the time-evolution operator under the Hamiltonian H_0 [Eq. (3.4)] and

$$R_{\theta} = e^{-iS_{b}\theta} \tag{3.8}$$

represents a rotation by angle θ around the $\hat{\mathbf{b}}$ axis, with $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$, and $\hat{\mathbf{c}}$ forming a right-handed triad: $\hat{\mathbf{a}} = \hat{\mathbf{b}} \times \hat{\mathbf{c}}$. We take π - and $\pi/2$ -pulses to be instantaneous relative to the time scale of envelope modulations.

The echo envelope, $V(\tau)$, describes the coherence of this hole spin at the end of a Hahn echo sequence and is defined as

$$V(\tau) = 2\text{Tr}\{\rho(2\tau)\sigma_+\} = 2\left\langle\sigma_+(2\tau)\right\rangle,\tag{3.9}$$

where

$$\sigma_+ = S_a + iS_b, \tag{3.10}$$

and the density operator at the end of the sequence is given by

$$\rho(2\tau) = U(2\tau)\rho(0)U^{\dagger}(2\tau), \qquad (3.11)$$

with $\rho(0)$ describing the initial state.

For explicit calculations, we now specialize to the case where the hole spin is prepared in the Zeeman ground state, $|\Downarrow\rangle \langle \Downarrow|$, and the nuclear spin is described by a maximally mixed (infinite-temperature) state, so that

$$\rho(0) = \frac{1}{2I+1} \mathbb{I} \otimes \left| \Downarrow \right\rangle \left\langle \Downarrow \right|, \qquad (3.12)$$

where $|\Uparrow\rangle$ ($|\Downarrow\rangle\rangle$) is an eigenstate of S_c with eigenvalue +1/2(-1/2). The echo envelope, $V(\tau)$, results from a sum over rotations of the hole pseudospin arising from each nuclear-spin Zeeman eigenstate, labeled by m_I , the eigenvalue of I_z . A consequence of the choice of (infinitetemperature) initial conditions [Eq. (3.12)] is that the average $\langle S_b(2\tau)\rangle = 0$ is preserved throughout the evolution and $V(\tau) = 2 \langle S_a(2\tau) \rangle$ (a real quantity). For a non-equilibrium (or low-temperature thermal) state of the nuclear-spin system, $V(\tau)$ may generally become complex and the specific expressions given below will not be realized. The echo envelope $V(\tau)$ would, however, be constructed from the same Fourier components, realized from the eigenvalues of H_0 . In an ensemble, a finite-temperature pseudo-pure hole-spin initial state will result in the same dynamics described here, but with a reduction in $V(\tau)$ by a factor $\epsilon \simeq \Omega_S/k_{\rm B}T$ at high spin temperature (for $\Omega_S/k_{\rm B}T \ll 1$).

3.2.3 Extracting hyperfine parameters

The full Hamiltonian (in the secular approximation and in a rotating frame at the hole Zeeman frequency with corresponding unitary $U_Z(t) = e^{i\Omega_S S_c t}$) is given, from Eqs. (3.4) and (3.5), by

$$\tilde{H} = \sum_{\beta} S_c A_{c\beta} I_{\beta} - \omega_I I_z, \qquad (3.13)$$

where $\beta \in \{x, y, z\}$.

Because $H_{\rm hf}^0$ contains anisotropic terms $(A_{cx}S_cI_x, A_{cy}S_cI_y)$, the nuclear-spin quantization axis depends on the state of the hole spin. Inverting the hole-spin orientation with a π -pulse during the Hahn echo sequence [Eq. (3.6)] then results in an interference effect. This produces a beating (modulations) in the echo envelope function [12]. This signal can be used to extract information about the hyperfine constants $A_{c\beta}$. There are well-known ways to do this extraction (see, e.g., Ref. [14] where the envelope-modulation frequencies were measured as a function of the magnetic-field orientation). Here, for completeness, we illustrate how these parameters can be found in the present context and with a fixed magnetic-field orientation. For the Hamiltonian, \tilde{H} , and for the initial conditions given by Eq. (3.12), the echo envelope can be approximated by [13, 25]

$$V(\tau) \approx 1 - \frac{V_0}{2} [1 - \cos(\omega_+ \tau)] [1 - \cos(\omega_- \tau)], \qquad (3.14)$$

where

$$\omega_{\pm} = \sqrt{\left(\pm \frac{A_{cz}}{2} - \omega_I\right)^2 + \left(\frac{A_{\rm nc}}{2}\right)^2} \tag{3.15}$$



Figure 3.1: (a) Spin-echo envelope function, $V(\tau)$, for a light hole bound to a ¹¹B acceptor in silicon. The exact numerical result from Eq. (3.9) (blue solid line) is compared to the approximate form from Eq. (3.14) (red dashed line). The magnetic field is taken to have magnitude B = 200 mT and is oriented to maximize the modulation depth, $\theta = \theta_{\text{max}} \simeq 0.2 \pi$ [see Fig. 3.1(b)]. (b) Modulation depth V_0 as a function of the magnetic field orientation angle θ (see inset) at a magnetic field strength of B = 200 mT. The light holes transform like states of angular momentum $J_3 = \pm 1/2$ about the x_3 axis. For example, for biaxial tensile strain along [100] and [010], the ground-state doublet will be composed of $J_3 = \pm 1/2$ light-hole states where x_3 corresponds to the [001] direction. The effective magnetic field, B_{eff} , is defined above Eq. (3.3) in the main text. The modulation depth is independent of the azimuthal angle since both the Zeeman Hamiltonian [Eqs. (3.38) and (3.39)] and the hyperfine Hamiltonian, Eq. (3.26), are cylindrically symmetric in this case.

are the nuclear-spin precession frequencies, and where

$$A_{\rm nc} = \sqrt{A_{cx}^2 + A_{cy}^2}$$
(3.16)

is the non-collinear part of the hyperfine interaction. In addition, the modulation depth V_0 is given by

$$V_0 = \frac{4}{3}I(I+1)k; \quad k = \frac{(\omega_I A_{\rm nc})^2}{(\omega_+ \omega_-)^2}, \tag{3.17}$$

and k is a parameter introduced in Ref. [13] that gives the spin-echo modulation depth for a nuclear spin I = 1/2. Equation (3.14) applies in the limit of a small modulation depth, with corrections of order ~ $\mathcal{O}(k^2)$ [25]. The parameter k depends on both the orientation and the magnitude of the magnetic field, **B**. The orientation of **B** determines the $\hat{\mathbf{c}}$ axis and k depends on $\hat{\mathbf{c}}$ through $A_{\rm nc}$ [see Eqs. (3.16) and (3.17)]. We can therefore maximize k with an appropriate choice for the magnetic-field orientation [Fig. 3.1(b)]. Furthermore, since $\omega_I \propto B$, if $\omega_I \gg A_{\rm nc}$, then $k \propto 1/B^2$ [see Eq. (3.17)]. Thus, k (and V_0) are strongly suppressed in a strong magnetic field.

From measurements of $V(\tau)$, the hyperfine parameters, A_{cz} and A_{nc} , can be determined independently via Fourier analysis, provided the nuclear-spin Larmor frequency, ω_I , is known. If the qubit under consideration were not composed of a Kramers doublet, the nuclear-spin Larmor frequency may generally be affected by a finite chemical shift $\mathcal{B} \neq 0$, introduced in Eq. (3.1) (this could be the case, e.g., for a mixed heavy-hole/light-hole qubit system). In such a situation, ω_I should be measured independently to establish the hyperfine parameters. The analysis presented here has so far neglected a finite Hahn-echo decay time (T_2). To extract the hyperfine coupling $\sim A_{cz}$ from envelope modulations, it is important that the envelope decay time be sufficiently long. A minimal condition to resolve the coupling constant A_{cz} is $T_2 > \hbar/A_{cz}$. We discuss this condition in the context of a light-hole qubit at a boron acceptor impurity in silicon in Sec. 3.4.1, below.

3.3 Hyperfine tensor for a boron acceptor in silicon

Both the form and typical size of the hyperfine tensor can have an important influence on the visibility of envelope modulations. To accurately estimate the hyperfine tensor, it is important to have a precise description of the electronic state in the immediate vicinity of the nucleus. In general, this requires careful consideration of central-cell corrections, since the envelope-function approximation breaks down due to the $\sim 1/r$ singularity in the impurity potential [26–28]. If we are willing to forgo a high degree of accuracy, a reasonable procedure is to start from the states evaluated within the envelope-function approximation and to adjust these states appropriately to account for short-ranged corrections. A similar approach was followed by Kohn and Luttinger (Ref. [29]) in early work on the hyperfine coupling for a phosphorus donor impurity in silicon.

Two corrections to the wavefunctions are required in the Kohn-Luttinger approach. First, the bulk silicon Bloch functions should be replaced by atomic-like functions of appropriate symmetry and extent to characterize the wavefunction near the impurity nucleus. Second, the electronic density should be rescaled to account for short-ranged corrections in the 'central-cell' (this is equivalent to rescaling the envelope function very close to the impurity nucleus). This central-cell correction is indicated by the fact that the binding energy calculated in the envelope-function approximation underestimates the true binding energy, suggesting a higher density near the impurity is required to account for the short-ranged potential. To calculate the hyperfine coupling for a phosphorus donor, Kohn and Luttinger estimated a rescaling parameter based directly on the experimentally measured binding energy and the solution to an envelope-function equation in an exterior region (outside a specified cutoff radius). This procedure has the disadvantage that the result depends on the choice of cutoff radius. Here, we take a slightly different approach. To estimate the rescaling parameter for a boron acceptor in silicon, we take advantage of the experimentally well-established hyperfine coupling for a phosphorus donor. The phosphorus donor and boron acceptor in silicon have similar binding energies (see Table 3.1, below), suggesting the two problems may have similar

electrostatics.¹ Based on this observation, we can extract the rescaling parameter from the known hyperfine coupling for a phosphorus donor and use it as an approximate proxy for the rescaling parameter of the boron acceptor. This procedure avoids potential ambiguity in the choice of cutoff radius. Based on the results obtained by Kohn and Luttinger for a donor impurity, we expect this procedure should give the strength of the hyperfine tensor for a boron acceptor to within a factor of 2-3, sufficient to establish whether the tensor can be measured experimentally under reasonable conditions.

For a donor or acceptor impurity, the wavefunction associated with spin $\sigma = \uparrow, \downarrow$ for a ground-state doublet labeled by pseudospin σ' can be approximated (far from the impurity nucleus) with the envelope-function approximation assuming N_v degenerate valleys related by symmetry (e.g., $N_v = 6$ for the conduction band of silicon and $N_v = 1$ for the valence band of silicon) [30]:

$$\langle \boldsymbol{r}\sigma | \sigma' \rangle = \Psi^{\sigma}_{\sigma'}(\boldsymbol{r}) = \frac{1}{\sqrt{N_v}} \sum_{\nu \in \mathcal{S}_{\sigma'}} F_{\nu}(\boldsymbol{r}) \psi^{\sigma}_{\nu \boldsymbol{k}_{\nu}}(\boldsymbol{r}).$$
 (3.18)

Here, $F_{\nu}(\mathbf{r})$ is an envelope function that solves the Schrödinger equation for a slowly varying impurity potential and with an effective-mass tensor associated with band/valley index ν at wavevector $\mathbf{k} = \mathbf{k}_{\nu}$. The symbol $S_{\sigma'}$ indicates the subset of symmetry-related band/valley states associated with pseudospin σ' . We have neglected spin-orbit coupling in the envelope equation, leading to a spin-independent envelope function $F_{\nu}(\mathbf{r})$. However, the Bloch functions $\psi^{\sigma}_{\nu \mathbf{k}}(\mathbf{r})$ solve the Schrödinger equation for the perfectly periodic bulk crystal potential including the short-ranged spin-orbit coupling:

$$\psi_{\nu \boldsymbol{k}}^{\sigma}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\nu \boldsymbol{k}}^{\sigma}(\boldsymbol{r}).$$
(3.19)

^{1.} Here, we use the term 'electrostatics' to describe the problem of finding the full wavefunction of the impurity-bound hole. This includes the long-range properties (band properties like the effective mass) and short-range properties (such as the core electronic structure of the impurity atom). If the electrostatics of the phosphorus donor and the boron acceptor are similar, then the rescaling parameter (central-cell corrections) should also be similar. While the similarity in binding energies is fully consistent with the two impurities having similar electrostatics, we cannot rule out the possibility of an accidental coincidence in binding energy. Ultimately, the true value of the hyperfine coupling (and central-cell correction) should be established experimentally, as proposed here.

The lattice-periodic Bloch amplitudes $u_{\nu k}^{\sigma}(\mathbf{r})$ are normalized over the primitive-cell volume, Ω , and the envelope functions are normalized over all space:

$$\sum_{\sigma} \int_{\Omega} d^3 r \left| u_{\nu k}^{\sigma}(\boldsymbol{r}) \right|^2 = 1; \quad \frac{1}{\Omega} \int d^3 r \left| F_{\nu}(\boldsymbol{r}) \right|^2 = 1.$$
(3.20)

To separate the isotropic and anisotropic hyperfine interactions, it is useful to expand the Bloch functions around the impurity site at $\mathbf{r} = 0$ in terms of spherical harmonics,

$$\psi^{\sigma}_{\nu \boldsymbol{k}_{\nu}}(\boldsymbol{r}) = \sum_{lm} R^{\sigma \nu}_{lm}(r) Y_{lm}(\theta, \phi), \qquad (3.21)$$

where $R_{lm}^{\sigma\nu}(r)$ are radial functions.

We first restrict to the case of donor states, where the dominant contribution to the hyperfine interaction arises from the l = 0 (s-like) term in the expansion given in Eq. (3.21). From the transformation properties of the valley states under crystalline and time-reversal symmetries, all l = 0 contributions can be related to a common radial function $R_s(r)$, independent of $\sigma \nu$:

$$R_{00}^{\sigma\nu}(r) = \alpha_s R_s(r), \quad \nu \in \mathcal{S}_{\sigma}, \quad (\sigma = \sigma'), \tag{3.22}$$

where α_s is a parameter controlling the degree of s-hybridization, and $R_s(r)$ describes the radial function in the immediate vicinity of the impurity, normalized to an atomic volume $(\frac{4}{3}\pi r_0^3 = \Omega/2)$:

$$\int_{0}^{r_{0}} dr r^{2} \left| R_{s}(r) \right|^{2} = 1.$$
(3.23)

For the l = 0 (s-like) contribution, only the isotropic Fermi contact interaction contributes, yielding the effective spin Hamiltonian for the conduction-band states [29, 31]:

$$H_{\rm hf}^C = A^i \boldsymbol{S} \cdot \boldsymbol{I}, \tag{3.24}$$

where A^i is the contact hyperfine interaction, proportional to the on-site electronic density, and *i* labels the nuclear isotope. Within the envelope-function approximation, we take $F_{\nu}(\mathbf{r}) \simeq F_{\nu}(0)$ to be approximately constant in the vicinity of the nucleus. Consistent with this limit, applying Eq. (3.18), and the expansion, Eq. (3.21), gives the hyperfine coupling to a phosphorus-donor nuclear spin $(i = {}^{31}P)$ in silicon [23, 29]:

$$A^{^{31}\mathrm{P}} = \frac{\mu_0}{3\pi} \mu_B \gamma_{^{31}\mathrm{P}} N_v \left| \alpha_s \right|^2 \left| F_{\mathrm{P}}(0) \right|^2 \left| R_s(0) \right|^2.$$
(3.25)

Here, μ_0 is the vacuum permeability and $N_v = 6$ for the conduction band of silicon. We have approximated the envelope function for a phosphorus donor with the form for an isotropic effective mass, $F_{\nu}(\mathbf{r}) \simeq F_P(\mathbf{r})$, independent of the band/valley index ν (consistent with Kohn and Luttinger, Ref. [29]). The weight factor, $|\alpha_s|^2$, has been estimated in Ref. [32] for a Pdonor (by diagonalizing the $\mathbf{k} \cdot \mathbf{p}$ matrix presented in Ref. [33]), giving $|\alpha_s|^2 \approx 0.38$.

We now consider states relevant to acceptor impurities, with pure p symmetry (states that only have an l = 1 contribution to their spherical harmonic expansion). The top of the valence band in bulk silicon is fourfold degenerate. This degeneracy is generally broken into two Kramers doublets (at zero magnetic field) due to confinement and strain in the vicinity of an acceptor impurity. Here, we consider the pair of states $\nu = \sigma'$ that transform like the $J_3 = \pm 1/2$ (light-hole) states of the Γ_8 representation of the T_d double group (which we label with $\nu = \sigma' = \uparrow$ and $\nu = \sigma' = \Downarrow$), where J_3 characterizes angular momentum about the x_3 axis. The effective hyperfine Hamiltonian then takes the anisotropic form [found by projecting Eq. (3.41) in Appendix 3.B onto the light-hole subspace] [23, 34]

$$H_{\rm hf}^{\rm LH} = \frac{1}{3} A^{i}_{\parallel} \left[S_3 I_3 + 2 \left(S_1 I_1 + S_2 I_2 \right) \right], \qquad (3.26)$$

where A_{\parallel}^{i} is the hyperfine parameter for isotope *i* and S_{j} and I_{j} , with $j \in \{1, 2, 3\}$, are (pseudo)spin operators obeying the usual commutation relations: $[S_{j}, S_{k}] = i\epsilon_{jkl}S_{l}$, $[I_{j}, I_{k}] = i\epsilon_{jkl}I_{l}$. The coordinate system defined by x_{j} (j = 1, 2, 3) is generally determined by strain/confinement in the vicinity of the acceptor,² independent of the orientation of the applied magnetic field \boldsymbol{B} ($\propto \hat{\mathbf{z}}$) and the effective field acting on the hole spin due to an anisotropic *g*-tensor, $\boldsymbol{B}_{\text{eff}}$ ($\propto \hat{\mathbf{c}}$). The relationship between these quantities is indicated in the inset of Fig. 3.1(b).

^{2.} In the case of a flat (quasi-2D) unstrained quantum dot, the effective mass results in a heavy-hole $(J_3 = \pm 3/2)$ ground state. For an acceptor impurity or quantum dot under biaxial in-plane tensile strain along [100] and [010], the light-hole $(J_3 = \pm 1/2)$ states may describe the ground state. The x_3 axis is the out-of-plane direction (e.g., the growth axis for a quantum dot defined in a 2D hole gas at a heterostructure interface). For example, for a growth axis along [001], we could take $x_3 = [001]$, $x_1 = [100]$, and $x_2 = [010]$.
Averaging the hyperfine Hamiltonian as in the case of a phosphorus donor, described above, but now for states describing a boron acceptor impurity in silicon, gives [23]

$$A^{i}_{\parallel} = \frac{4\mu_{0}}{5\pi} \mu_{B} \gamma_{i} |F_{\rm B}(0)|^{2} \int_{0}^{r_{0}} dr |R_{p}(r)|^{2} / r, \qquad (3.27)$$

where $F_{\nu}(\mathbf{r}) = F_{\rm B}(\mathbf{r})$ is the boron-acceptor envelope function and $R_p(r)$ is the radial part of the Bloch function at the valence-band maximum in silicon ($\mathbf{k} = 0$), normalized over an atomic volume. As described above, we have assumed pure *p*-like states, $\alpha_p = 1$. Accounting for *p*-*d* hybridization of the acceptor state would, in general, modify the anisotropy of the hyperfine tensor [23, 34]. In writing Eq. (3.27), we have furthermore neglected long-ranged contributions to the hyperfine interaction between a nuclear spin and electron/hole spin density in a distant unit cell [5,35]. The radial function $R_p(r)$ is related to the radial functions from Eq. (3.21) through

$$R_{10}^{\uparrow\uparrow}(r) = R_{10}^{\downarrow\downarrow}(r) = \sqrt{\frac{2}{3}}R_p(r),$$
 (3.28)

$$R_{11}^{\downarrow\uparrow}(r) = R_{1-1}^{\uparrow\downarrow}(r) = \sqrt{\frac{1}{3}}R_p(r),$$
 (3.29)

where all other $R_{lm}^{\sigma\nu}(r)$ vanish and the numerical factors are determined by Clebsch-Gordan coefficients [23].

To account for deviations in the wavefunctions in the central-cell region, we now make two adjustments to the usual envelope-function approximation, as described above. First, the radial functions $R_{s(p)}(r)$ associated with the silicon Bloch functions are replaced with hydrogenic orbitals having an effective core charge determined by Hartree-Fock theory for free boron and phosphorus atoms (taken from Ref. [36]). Specifically, we replace $R_s(r)$ with a 3s radial function with effective charge $Z_P = 5.64$ for the phosphorus donor and $R_p(r)$ is replaced with a 2p hydrogenic radial function with effective charge $Z_B = 2.42$ for the boron acceptor. Second, the scaling parameters $|F_{P(B)}(0)|^2$ should be determined to account for the central-cell correction. With the normalization given in Eq. (3.20), $|F_{P(B)}(0)|^2$ corresponds to the probability to find the electron/hole in the central-cell region. For a phosphorus donor impurity, Eq. (3.25) can be used to extract $|F_P(0)|^2$ from the known value of the hyperfine coupling [6], $A^{^{31}{\rm P}}/2\pi = 117\,{\rm MHz}$:

$$|F_P(0)|^2 = 0.014. \tag{3.30}$$

Equation (3.30) should be contrasted with the result from a direct application of the Kohn-Luttinger envelope function, $|F_P^{\text{KL}}(0)|^2 = \Omega/\pi a_l a_t^2 = 0.0019$ with $a_j = a_0 \kappa m_0/m_j$; j = l, t. Here, a_0 is the Bohr radius, m_0 is a free-electron mass, $\kappa = 11.7$ is the dielectric constant for bulk silicon, and the longitudinal/transverse effective masses are $m_l = 0.98$, $m_t = 0.19$. Empirically, the hyperfine coupling is therefore enhanced by a factor of $\simeq 7$ relative to the value expected within the envelope-function approximation. Based on density functional calculations for bulk silicon [23], we find that replacing the silicon Bloch functions with a 3s hydrogenic function for phosphorus leads to a further enhancement of the hyperfine coupling by a factor of $\simeq 3$. The combination of these two effects, due to central-cell corrections and strain in the vicinity of the donor, lead to more than an order-of-magnitude increase in the hyperfine coupling relative to what would be expected from a naïve application of the envelope-function approximation.

To approximate the hyperfine coupling for a boron acceptor from Eq. (3.27), we take

$$|F_{\rm B}(0)|^2 \approx |F_{\rm P}(0)|^2$$
, (3.31)

with $|F_P(0)|^2$ established empirically from Eq. (3.30). Equation (3.31) is justified by the observation that the binding energies of phosphorus donors and boron acceptors are similar (see Table 3.1), and hence that the electrostatics and resulting central-cell corrections may therefore be similar. Note that effective mass theory fails in the vicinity of the impurity potential, so it is not clear what (if any) further corrections could be made to Eq. (3.31) to account for the different effective masses in the conduction and valence bands. The ultimate accuracy of Eq. (3.31) should be determined experimentally through direct measurements of the hyperfine coupling constants. Here, we use this relation only to establish the plausibility of measuring envelope modulations for a boron-acceptor-bound light-hole spin qubit under realizable experimental conditions. Using the assumption given in Eq. (3.31) gives

$$A_{\parallel}^{^{11}\mathrm{B}}/2\pi \approx 1\,\mathrm{MHz}.\tag{3.32}$$

i	Ι	δ_i	$E \ (meV)$	$\gamma_i/2\pi \left(\frac{\mathrm{MHz}}{\mathrm{T}}\right)$	Hyperfine (MHz)
$^{31}\mathrm{P}$	1/2	100%	44 [37]	17	$A^i/h = 117$ [6]
$^{10}\mathrm{B}$	3	20%	45 [37]	0.46	$A^i_{\parallel}/h pprox 0.3$
$^{11}\mathrm{B}$	3/2	80%	45 [37]	1.4	$\ddot{A}^i_{\parallel}/h pprox 1$

Table 3.1: The isotope (i), nuclear spin (I), natural isotopic abundance (δ_i) , measured binding energy (E) from Ref. [37], gyromagnetic ratio (γ_i) , and hyperfine parameters for a phosphorus donor and a boron acceptor in silicon. The value for $A^{^{31}P}$ was measured in Ref. [6] and A^i_{\parallel} for boron acceptors [see Eq. (3.26)] was estimated, as described in the main text.

This result is also displayed in Table 3.1. This hyperfine coupling is sufficiently small that it may not have been resolved in the experiments of Ref. [8], but should be observable in the HSEEM experiments described above. Although it is not clear that the values should be the same (or even comparable), the estimate given in Eq. (3.32) for a boron acceptor in silicon is within a factor of ~ 3 of the hyperfine coupling for boron acceptors in SiC measured with ENDOR [10,11]. While the hyperfine coupling for boron acceptors in SiC may not be a good measure of the hyperfine coupling for boron acceptors in silicon, the ENDOR experiments described in Refs. [10,11] provide evidence that even the weak (relative to electrons) hyperfine interaction for holes can have a measurable effect.

The estimated value given in Eq. (3.32) has been used to generate the plots in Fig. 3.1, where we have considered the case of ¹¹B as an example. The hyperfine coupling for a boron acceptor in silicon (as estimated here) is roughly two orders of magnitude smaller than the coupling for a phosphorus donor. Nevertheless, an HSEEM experiment would show echo envelope modulations with reasonable visibility $V_0 \gtrsim 0.1$ at sufficiently low magnetic fields $B \lesssim 200 \,\mathrm{mT}$.

3.4 HSEEM for a hole-spin qubit

A boron-acceptor-bound hole spin will generally couple to the nuclear spin associated with either of the stable isotopes, ¹⁰B (I = 3) or ¹¹B (I = 3/2). In addition, the hole spin may also couple to proximal ²⁹Si (I = 1/2, natural abundance 4.7%). In what follows,

we will neglect coupling to nearby ²⁹Si. This is justified either by the weaker overlap of the hole envelope function with nuclear spins far from the central boron potential, or by considering acceptors in isotopically purified ²⁸Si/³⁰Si (both isotopes having nuclear spin I = 0). Furthermore, since both boron isotopes have a nuclear spin I > 1/2 and the boron acceptor in silicon has tetrahedral (T_d) symmetry, the nuclear quadrupolar interaction does not generally vanish. However, when the quadrupolar spitting is much smaller than the anisotropic part of the hyperfine interaction, the quadrupolar interaction can be neglected in calculating echo-envelope modulations [10]. We are unaware of direct measurements for the quadrupolar splittings or hyperfine couplings for boron acceptors in silicon. However, ENDOR measurements on several polymorphs of SiC give quadrupolar splittings that are ~ 10% of the measured value of $A_{\rm nc}$ [10, 11]. The crystalline and electronic structure of SiC differs from that of silicon and may generally lead to distinct values of the hyperfine coupling and quadrupolar splitting. Nevertheless, our estimated value of the hyperfine coupling for a boron acceptor in silicon is comparable to the measured values for boron acceptors in SiC (see Sec. 3.3). Provided the quadrupolar splittings in both materials are also similar, ignoring the quadrupolar interaction is well justified here.

In Ref. [4], hole-spin-echo experiments have been carried out for both strained and unstrained samples. Without externally applied strain, the ground space of a boron acceptor in silicon is fourfold degenerate, spanned by the heavy-hole $(J_3 = \pm 3/2)$ and light-hole states $(J_3 = \pm 1/2)$. We neglect the small anisotropy term, $[q \simeq 0 \text{ in Eq. } (3.37)]$ resulting in a valence-band Zeeman Hamiltonian $\propto \mathbf{J} \cdot \mathbf{B}$ under an applied magnetic field \mathbf{B} . We further consider pure *p*-like states $(\alpha_p = 1)$, giving $A_{\perp}^i = 0$ in Eq. (3.40), resulting in a hyperfine coupling $\propto \mathbf{J} \cdot \mathbf{I}$ [Eq. (3.41)]. Under these conditions, the secular hyperfine coupling (the part that commutes with the valence-band Zeeman Hamiltonian) will commute with the nuclear Zeeman term for any orientation of the applied magnetic field, \mathbf{B} . The result is that the nuclear-spin quantization axis will be independent of the hole-spin state, and there will be no echo envelope modulations under these conditions. In contrast, under biaxial tensile strain, the ground space is spanned by only the light-hole ($J_3 = \pm 1/2$) states [see, for example, Ref. [38] or Eq. (1) in the supplemental material of Ref. [4]]. For light-hole states, both the effective Zeeman Hamiltonian [Eq. (3.38) in Appendix 3.A] and the hyperfine Hamiltonian [Eq. (3.26)] show strong anisotropy. In this case, we expect substantial envelope modulations for the appropriate orientation of B. Up to small corrections, the dynamics of the acceptor-bound light-hole spin coupled to a boron nuclear spin will therefore be well described by the analysis presented in Sec. 3.2.3.

For a light-hole spin bound to a boron acceptor (boron isotope i) in silicon, A_{cz}^i and A_{nc}^i can be determined using the light-hole hyperfine tensor [Eq. (3.26)] and the *g*-tensor described in Appendix 3.A, following the procedure outlined in Sec. 3.2.1. This procedure gives

$$A_{cz}^{i} = \frac{\sqrt{5 - 3\cos(2\theta)}}{3\sqrt{2}} A_{\parallel}^{i}, \qquad (3.33)$$

$$A_{\rm nc}^{i} = \frac{1}{2} \sqrt{\frac{1 - \cos(4\theta)}{5 - 3\cos(2\theta)}} A_{\parallel}^{i}.$$
(3.34)

Inserting Eqs. (3.33) and (3.34) into Eq. (3.17) gives the orientation (θ) dependence of the modulation depth, V_0 . In Fig. 3.1(a), we show the echo envelope, $V(\tau)$, for a light-hole spin bound to a ¹¹B acceptor. The magnetic field orientation θ has been chosen to maximize the modulation depth, V_0 [Fig. 3.1(b)]. The plots have been obtained using the estimate for A_{\parallel}^{11B} discussed in Sec. 3.3. Recent spin-echo experiments have been performed on an ensemble of boron acceptors in strained silicon, where the light-hole spin can be energetically isolated [4]. In these experiments, the applied magnetic field was oriented in-plane [corresponding to $\theta = \pi/2$ in Fig. 3.1(b)] to maintain a high quality factor for a superconducting resonator used for inductive detection. Since we predict $V_0 \simeq 0$ for $\theta = \pi/2$, we do not expect envelope modulations to be visible under the specific conditions of Ref. [4]. However, our analysis predicts significant modulations for a similar experiment with an out-of-plane component of magnetic field.

For illustrative purposes, we have focused here on the case of a single boron acceptor in silicon, and have considered the example of ¹¹B. The same analysis gives the envelope modulation for a ¹⁰B acceptor if we account for the difference in nuclear spin I and gyromagnetic ratio γ_i for the two isotopes i (see Table 3.1). In particular, we can relate the two signals noting that both the nuclear Larmor frequencies and the hyperfine couplings are related by the gyromagnetic ratios: $\omega_I^i/\omega_I^{i'} = A_{\parallel}^i/A_{\parallel}^{i'} = \gamma_i/\gamma_{i'}$. This relationship assumes two isotopes of the same chemical species and neglects small corrections to the electronic structure due to

the difference in nuclear mass. The echo envelope signal arising from an ensemble of many boron acceptors including both isotopes will be given by a weighted average:

$$V(\tau) = \delta_{^{10}\text{B}}V_{^{10}\text{B}}(\tau) + \delta_{^{11}\text{B}}V_{^{11}\text{B}}(\tau), \qquad (3.35)$$

where $V_i(\tau)$ is the echo envelope for isotope *i* [displayed in Eq. (3.14)], and δ_i is the isotopic abundance of isotope *i*. When the Larmor frequency of each isotope is much larger than the hyperfine coupling, $\omega_I^i \gg A_{\parallel}^i$, the modulation depth and frequencies determining $V_{10B}(\tau)$ are simply related to those for $V_{11B}(\tau)$ [see Eqs. (3.15) and (3.17)]:

$$\omega_{\pm}^{^{11}\mathrm{B}} = \frac{\gamma_{^{11}\mathrm{B}}}{\gamma_{^{10}\mathrm{B}}} \omega_{\pm}^{^{10}\mathrm{B}}; \quad V_0^{^{11}\mathrm{B}} \simeq \frac{I(I+1)|_{I=\frac{3}{2}}}{I(I+1)|_{I=3}} V_0^{^{10}\mathrm{B}}, \tag{3.36}$$

where ω_{\pm}^{i} and V_{0}^{i} are the frequencies and modulation depth parametrizing the echo envelope $V_{i}(\tau)$. If the isotopes in the sample are distributed according to the natural isotopic abundances (see Table 3.1), Eq. (3.36) results in modulation frequencies $\omega_{\pm}^{^{11}\text{B}} \approx 3\omega_{\pm}^{^{10}\text{B}}$ and a relative amplitude $\delta_{^{11}\text{B}}V_{0}^{^{11}\text{B}}/(\delta_{^{10}\text{B}}V_{0}^{^{10}\text{B}}) \simeq \frac{5}{4}$. Thus, for a natural isotopic abundance, we expect the envelope modulations arising from the two isotopes to have comparable amplitudes and the modulation frequencies are simply related by the gyromagnetic ratios of the two isotopes.

3.4.1 Model limitations

Several limitations of the model have alredy been discussed. Here, we collect and discuss the most significant limitations to be considered if an experiment is to accurately extract the hyperfine parameters.

Finite coherence time—To extract the hyperfine couplings experimentally from envelope modulations, the Hahn-echo decay time, T_2 , should exceed the typical inverse hyperfine coupling strengths. From our estimate of the hyperfine coupling $(A_{\rm nc}/h \sim A_{cz}/h \sim A_{\parallel}/h \simeq$ 1 MHz for ¹¹B as given in Table 3.1), this gives the requirement $T_2 \gg \hbar/A_{\parallel} \simeq 0.2 \,\mu$ s. Recent experiments (Ref. [4]) have demonstrated significantly longer Hahn-echo decay times, $T_2 = 0.9 \,\mathrm{ms}$, at $B \simeq 200 \,\mathrm{mT}$ for light-hole spins at boron acceptors in isotopically purified ²⁸Si. This suggests that recently measured coherence times are long enough to extract the hyperfine parameters from envelope modulations.

Non-uniform strain distribution—For an ensemble of acceptor impurities, a non-uniform strain distribution will generally lead to damped envelope modulations, on a time scale t_{damp} . This effect is commonly observed for phosphorus donor impurities in silicon, even without intentionally introducing additional strain [17]. For an experiment in which biaxial tensile strain is induced, as in Ref. [4], we estimate the variation in the hyperfine parameters $\delta A_{\alpha\beta}$ across the sample from the degree of heavy-hole/light-hole mixing generated by the Bir-Pikus Hamiltonian [38, 39]. This gives a variation $\delta A_{\alpha\beta}/A_{\parallel} \sim \delta \epsilon/\epsilon$, where ϵ is the average strain along x_1 and x_2 and $\delta \epsilon$ describes the variation in strain accross the sample. To resolve the modulation frequencies with a resolution $\lesssim A_{\parallel}$, we therefore require a sufficiently long damping time $t_{\text{damp}} \sim \hbar/\delta A_{\alpha\beta} \gg \hbar/A_{\parallel}$. In terms of strain, this condition requires a variation that is small compared to the average, $\delta \epsilon/\epsilon \ll 1$.

3.5 Conclusions

Understanding the hyperfine coupling of valence-band (hole) spin states is an important step to predicting and controlling spin qubits derived from these states. Boron-acceptorspin qubits show potential for rapid local electric-field control, with relative immunity to electric-field noise [1, 2, 4], but the hyperfine couplings for these qubits are still relatively poorly understood. This hyperfine coupling may be small enough that it is difficult to resolve with certain spectroscopic techniques [8], but, as we have shown, it may lead to a significant echo envelope modulation at moderate magnetic fields.

As a concrete example, we have calculated the echo envelope function for a hole spin confined to a boron acceptor in silicon. Without induced strain, the hole spin will show virtually no envelope modulations. In contrast, a qubit defined in, e.g., the two-dimensional light-hole subspace will show substantial modulations. This qubit can be energetically isolated through biaxial tensile strain. The form of the hyperfine tensor in this case is given by the symmetry of the underlying electronic states. By accounting for semiempirical corrections to the envelope-function approximation, we have estimated the typical size of the hyperfine parameter. With this knowledge, we have shown that it is possible to maximize the visibility of envelope modulations with an appropriate orientation of the applied magnetic field. Similarly, an experiment with the 'incorrect' magnetic-field orientation $[\theta = 0, \pi/2 \text{ in Fig. 3.1(b)}]$ would show no modulation at all.

When the envelope modulations are visible, they can be used to accurately quantitatively determine the hyperfine tensor for a hole-spin qubit at an acceptor impurity, allowing for better control of hole-spin qubits and the nuclear spins that couple to them.

There will be small corrections to the analysis presented here due, e.g., to the electric quadrupolar interaction with a nuclear spin I > 1/2, p-d hybridization of the microscopic electronic states, and further central-cell corrections that are not captured in our simple semiempirical approach. Many of these effects (beyond the scope of the present work) could potentially be captured using *ab initio* methods that have previously been applied to phosphorus donors in silicon [40]. An especially intriguing future question is whether the hyperfine tensor for an acceptor-spin qubit can be efficiently tuned or modulated through local strain or electric fields. The strong anisotropy present in hole-spin hyperfine coupling may also provide an advantage in directly controlling the nuclear spin for a quantum memory or ancilla qubit [41].

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Appendices to Chapter 3

3.A g-tensor for light holes

To obtain the g-tensor for light holes, we consider the Luttinger Hamiltonian [42]. The Zeeman term in the valence-band subspace of silicon can be written as $[42, 43]^3$

$$H_z = 2\mu_B \kappa \boldsymbol{B} \cdot \mathbf{J} + 2\mu_B q \boldsymbol{B} \cdot \boldsymbol{\mathcal{J}}, \qquad (3.37)$$

where $\mathcal{J} = (J_x^3, J_y^3, J_z^3)$. In the case of silicon, $\kappa = -0.42$ and q = 0.01 [43]. Since $|q| \ll |\kappa|$, we neglect the term proportional to q for simplicity. Neglecting mixing with heavy-hole states, we project H_z onto the light-hole subspace, and write the resulting matrix as

$$H_z^{\rm LH} = \mu_B \boldsymbol{B} \cdot \overleftarrow{\mathbf{g}} \cdot \boldsymbol{S}, \qquad (3.38)$$

where

$$\overleftarrow{\mathbf{g}} = 2 \begin{bmatrix} 2\kappa & 0 & 0\\ 0 & 2\kappa & 0\\ 0 & 0 & \kappa \end{bmatrix}$$
(3.39)

is the g-tensor for light holes in silicon. We note that the g-tensor is written in a basis (x_1, x_2, x_3) , where x_3 is the hole-spin quantization axis.

^{3.} The convention used here is that the pseudo-angular-momentum **J** measures the pseudo-angular-momentum of the crystal. Therefore, a hole in state $J_3 = m$ indicates that an electron with $J_3 = -m$ has been anihilated from the filled valence band, and the remaining member of the Kramers doublet has $J_3 = m$.

3.B Hyperfine Hamiltonian in the valence band of silicon

The hyperfine Hamiltonian projected onto the four-dimensional subspace spanned by the valence-band states at the Γ point of silicon can be written as [23]

$$H_{\rm hf}^{\rm VB} = \left(\frac{1}{3}A^i_{\parallel} - \frac{3}{2}A^i_{\perp}\right)\mathbf{J}\cdot\mathbf{I} + \frac{2}{3}A^i_{\perp}\mathcal{J}\cdot\mathbf{I},\tag{3.40}$$

where A^i_{\parallel} and A^i_{\perp} are hyperfine parameters. We neglect A^i_{\perp} in our calculations, consistent with valence-band states that are pure *p*-states ($\alpha_p = 1$) leaving

$$H_{\rm hf}^{\rm VB} \approx \frac{1}{3} A^i_{\parallel} \mathbf{J} \cdot \mathbf{I}.$$
 (3.41)

Thus, in the limit of pure *p*-states, the hyperfine interaction is invariant under simultaneous rotations of the pseudospin-3/2, **J**, and the nuclear spin, **I**.

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Preface to Chapter 4

As explained in Sec. 1.2.3, under the envelope function approximation, the confinement potential is assumed to generate no interband transitions. In this chapter, we go beyond the envelope function approximation and include these transitions in our analysis of heavy holes in an asymmetric quantum well. We consider a triangular quantum well generated by a constant electric field and the associated electric-dipole coupling of the valence-band states. In the valence-band subspace, this coupling can be viewed as a pseudospin-electric coupling for hole spins. Similar to the approach described in Chapter 2, we use the Kohn-Sham orbitals to compute the valence-band electric-dipole matrix elements. A consequence of these non-vanishing matrix elements is a new dipolar spin-orbit coupling which had previously been neglected. We demonstrate that the dipolar spin-orbit coupling may be important when trying to understand certain system properties (e.g. heavy-hole spin splitting) quantitatively.

In addition to the electric-dipole matrix elements described above, we also use the Kohn-Sham orbitals to calculate other material parameters. In particular, we compute momentum and Zeeman-Hamiltonian matrix elements. The level of accuracy of the results varies, but in all cases said results are of the same order of magnitude as the accepted values. Thus, we demonstrate the versatility of the approach outlined in Chapter 2 by calculating material parameters other than hyperfine couplings. These parameters include: electric-dipole matrix elements, $\mathbf{k} \cdot \mathbf{p}$ parameters, g-tensors, and spin-orbit couplings.

Because the valence band of GaAs is fourfold degenerate at the Γ point, a general Kohn-Sham orbital, evaluated using DFT, will be a linear combination of all four states. Since the material parameters mentioned above are defined with respect to particular matrix elements of the corresponding operators, specific Kohn-Sham orbitals must be extracted from the general linear combination. To perform this extraction, we have written a freely-available code implementing group-theoretic projection operators (see Chapter 4 of Ref. [85] or Appendix 2.C.2) available on Github, Ref. [103]. This code can project any function defined on a grid of points onto an arbitrary basis function of a (single or double) group representation, provided the associated matrix representation of the group is known. We note that while this chapter has not been published, it has been submitted for consideration in Physical Review B. A preprint of the paper is available on the arXiv [104].

4 Pseudospin-electric coupling for holes beyond the envelope-function approximation

This chapter is the integral text (including references) from:

Pseudospin-electric coupling for holes beyond the envelope-function approximation

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In the envelope-function approximation, interband transitions produced by electric fields are neglected. However, electric fields may lead to a spatially local (k-independent) coupling of band (internal, pseudospin) degrees of freedom. Such a coupling exists between heavy-hole and light-hole (pseudo-)spin states for holes in III-V semiconductors, such as GaAs, or in group IV semiconductors (germanium, silicon, ...) with broken inversion symmetry. Here, we calculate the electric-dipole (pseudospin-electric) coupling for holes in GaAs from first principles. We find a transition dipole of 0.5 debye, a significant fraction of that for the hydrogen-atom $1s \rightarrow 2p$ transition. In addition, we derive the Dresselhaus spin-orbit coupling that is generated by this transition dipole for heavy holes in a triangular quantum well. A quantitative microscopic description of this pseudospin-electric coupling may be important for understanding the origin of spin splitting in quantum wells, spin coherence/relaxation (T_2^*/T_1) times, spin-electric coupling for cavity-QED, electric-dipole spin resonance, and spin non-conserving tunnelling in double quantum dot systems.

4.1 Introduction

A standard theoretical tool for studying electrons (or holes) confined to nanostructures is $\mathbf{k} \cdot \mathbf{p}$ theory under the envelope function approximation [1,2]. Within this formalism, one ignores interband coupling due to an electric field ($\propto \nabla U$) arising from the slowly-varying part of the potential, U. This established procedure has been used to understand two distinct forms of spin-orbit coupling for semiconductors [1]: Rashba spin-orbit coupling [3] (arising from inversion asymmetry in U, structure inversion asymmetry) and Dresselhaus spin-orbit coupling [4] (arising from inversion asymmetry in the underlying crystal, bulk inversion asymmetry).

Beyond the envelope function approximation, an electric field can lead to interband coupling. For states that transform like the Γ_8 representation of the tetrahedral double group (T_d) , this coupling can be parameterized by a single constant, χ [5]. The unit cell of, e.g., bulk silicon or germanium has a center of inversion symmetry,¹ which precludes any interband electric-dipole coupling in the valence-band subspace, leading to $\chi = 0$. However, in the presence of an acceptor (or any other impurity), inversion symmetry is broken and the point-group symmetry is reduced to T_d . This reduction in symmetry gives rise to a finite electric-dipole matrix element between the heavy-hole and light-hole states (which transform like the Γ_8 representation of T_d) [5]. The interband coupling influences the spectrum of acceptors in silicon in the presence of an electric field [6] and could allow for better control of acceptor spin qubits in silicon [7].

In contrast to silicon or germanium, III-V semiconductors do not have a center of inversion symmetry and the valence-band states transform according to the Γ_8 representation of T_d . Therefore, the electric field can couple valence-band states, even in the absence of an acceptor. Specifically, this interband coupling allows for an AC electric field to generate Rabi oscillations between heavy-hole and light-hole pseudospin states, even without heavy-hole/light-hole mixing. In the case of III-V semiconductors, the interband coupling parameter χ is a material

^{1.} Strictly speaking, silicon is not inversion symmetric. It has a diamond crystalline structure and is therefore symmetric under the (non-symmorphic) symmetry operation which can be described by an inversion of the crystal about a lattice site followed by a translation of the crystal by (1/4, 1/4, 1/4). Although it is not a proper inversion, this symmetry still precludes interband electric-dipole coupling in the valence-band subspace.

parameter that can be evaluated given the crystal eigenstates (Bloch functions). Recently, the Bloch amplitudes for the valence band of GaAs have been approximated using the Kohn-Sham orbitals from an all-electron density-functional theory calculation [8]. Here, we evaluate the $\mathbf{k} \cdot \mathbf{p}$ parameters and band gaps in GaAs using the technique described in Ref. [8]. The resulting calculated parameters are in reasonable agreement with empirically established $\mathbf{k} \cdot \mathbf{p}$ parameters (with some exceptions, discussed below). We apply the same technique to calculate χ .

A nonzero transition dipole ($\chi \neq 0$) in III-V semiconductors modifies the heavy-hole spin-orbit interactions for a two-dimensional hole gas in an asymmetric quantum well. Here, we study the heavy-hole spin-orbit couplings for a simple (single-subband) valence-band model. We find a spin-orbit coupling term in the heavy-hole subspace that is linear in the wavevector (k_{\parallel}), with Dresselhaus symmetry, and that is proportional to χ . Because it originates from the finite interband transition dipole matrix element, we call this term dipolar spin-orbit coupling. From this analysis, we find the dipolar spin-orbit coupling is of the same order as other known contributions.

Including the dipolar spin-orbit coupling in our analysis, we are able to characterize the heavy-hole spin splitting in a triangular GaAs quantum well. The dipolar spin-orbit coupling can affect the interpretation of experiments sensitive to the Dresselhaus spin-orbit coupling. In recent experiments, the leakage current passing through a double quantum dot containing holes in the Pauli-spin-blockade regime was measured as a function of the direction of an applied magnetic field (angle relative to the current) [9]. The angular dependence of the observed current was consistent with spin-orbit coupling that is almost entirely Dresselhaus-like. In other recent experiments, the relaxation time, T_1 , for a heavy-hole spin in a GaAs quantum dot was measured as a function of the strength of an applied magnetic field, B [10]. The measured relaxation times are consistent with $T_1 \propto B^{-5}$, which is a signature of Dresselhaus spin-orbit coupling, provided the k_{\parallel} -linear Rashba contribution is negligible [11]. These two experiments indicate that characterizing the Dresselhaus spin-orbit coupling is crucial to understanding heavy-hole-spin dynamics in these systems. Therefore, the dipolar spin-orbit coupling can play an important role in understanding heavy-hole spin dynamics.

The rest of this article is organized as follows: In Sec. 4.2 we introduce the interband electric dipole coupling into the $\mathbf{k} \cdot \mathbf{p}$ formalism going beyond the enevelope-function approximation.

In Sec. 4.3 we discuss the first-principles calculation of material parameters (e. g. $\mathbf{k} \cdot \mathbf{p}$ parameters) for GaAs. In Sec. 4.4 we derive the spin-orbit couplings for heavy holes in a triangular quantum well. Conclusions are given in Sec. 4.5.

4.2 Electric-dipole coupling within the $k \cdot p$ formalism

The goal of this section is to rederive the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, extending beyond the envelopefunction approximation. In this extension, in addition to intraband terms generated within the usual envelope-function approximation, we also include interband coupling generated by the confining potential.

We begin from the Hamiltonian $H = H_0 + U$, where H_0 describes a perfectly periodic crystal (including the spin-orbit coupling) and $U = e\mathbf{E} \cdot \mathbf{r}$, where -e is the electron charge and \mathbf{E} is a uniform electric field. The term U models the potential experienced by electrons or holes in an asymmetric quantum well at a heterointerface.

The eigenstates of H_0 are Bloch waves. These states can be represented by spinors, $\psi_{\nu k}(\boldsymbol{r}) = \left[\psi_{\nu k}^{\uparrow}(\boldsymbol{r}), \psi_{\nu k}^{\downarrow}(\boldsymbol{r})\right]^T$, with components

$$\psi^{\sigma}_{\nu \boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u^{\sigma}_{\nu \boldsymbol{k}}(\boldsymbol{r}), \qquad (4.1)$$

where ν is a band index, \mathbf{k} is a wavevector restricted to the first Brillouin zone, σ is a spin index, N is the number of unit cells in the crystal and $u_{\nu \mathbf{k}}^{\sigma}(\mathbf{r})$ are lattice-periodic Bloch amplitudes, which are normalized over the primitive-cell volume, Ω :

$$\sum_{\sigma} \int_{\Omega} d^3 r \, |u_{\nu \boldsymbol{k}}^{\sigma}(\boldsymbol{r})|^2 = 1.$$
(4.2)

The eigenenergies associated with the states $\psi_{\nu k}(\boldsymbol{r})$ are labeled $\epsilon_{\nu k}$. A convenient complete orthonormal basis can be written in terms of the $\boldsymbol{k} = \boldsymbol{0}$ Bloch amplitudes, and is given by a set of spinors $\phi_{\nu k}(\boldsymbol{r}) = \left[\phi_{\nu k}^{\uparrow}(\boldsymbol{r}), \phi_{\nu k}^{\downarrow}(\boldsymbol{r})\right]^{T}$, with components [1, 12],

$$\phi^{\sigma}_{\nu \boldsymbol{k}}(\boldsymbol{r}) = \langle \boldsymbol{r}\sigma | \nu \boldsymbol{k} \rangle = \frac{1}{\sqrt{N}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u^{\sigma}_{\nu}(\boldsymbol{r}), \qquad (4.3)$$

where $u_{\nu}^{\sigma}(\boldsymbol{r}) := u_{\nu \boldsymbol{0}}^{\sigma}(\boldsymbol{r}).$

Any eigenstate $|\Psi\rangle$ of the Hamiltonian H can be expressed in terms of the states $|\nu' \mathbf{k}'\rangle$ as

$$|\Psi\rangle = \sum_{\nu' \boldsymbol{k}'} \Psi_{\nu'}(\boldsymbol{k}') |\nu' \boldsymbol{k}'\rangle, \qquad (4.4)$$

where $\Psi_{\nu'}(\mathbf{k}')$ are coefficients that describe the envelope functions in \mathbf{k} -space for a slowly-varying potential.

We insert Eq. (4.4) into the Schrödinger equation to obtain:

$$\sum_{\nu' \mathbf{k}'} \Psi_{\nu'}(\mathbf{k}') \langle \nu \mathbf{k} | (H_0 + U) | \nu' \mathbf{k}' \rangle = \epsilon \Psi_{\nu}(\mathbf{k}), \qquad (4.5)$$

where ϵ is the eigenenergy of $|\Psi\rangle$. We now evaluate the matrix elements $\langle \nu \mathbf{k} | (H_0 + U) | \nu' \mathbf{k}' \rangle$ from Eq. (4.5) to obtain a matrix equation for the envelope functions. Within the double-group formulation of $\mathbf{k} \cdot \mathbf{p}$ theory [13], we write

$$\langle \nu \boldsymbol{k} | H_0 | \nu' \boldsymbol{k}' \rangle = \delta_{\boldsymbol{k}\boldsymbol{k}'} \left[\left(\epsilon_{\nu \boldsymbol{0}} + \frac{\hbar^2 k^2}{2m} \right) \delta_{\nu\nu'} + \frac{\hbar}{m} \boldsymbol{k} \cdot \boldsymbol{\pi}_{\nu\nu'} \right], \qquad (4.6)$$

with

$$\boldsymbol{\pi}_{\nu\nu'} = \sum_{\sigma} \int_{\Omega} d\boldsymbol{r} u_{\nu}^{\sigma*}(\boldsymbol{r}) \left[\boldsymbol{p} + \frac{\hbar}{2mc^2} \boldsymbol{S} \times \nabla V_0(\boldsymbol{r}) \right] u_{\nu'}^{\sigma}(\boldsymbol{r}), \qquad (4.7)$$

where V_0 is the periodic potential and \boldsymbol{S} is the electron spin-1/2 operator. The term $\frac{\hbar}{m} \boldsymbol{k} \cdot \boldsymbol{\pi}_{\nu\nu'}$ in Eq. (4.6) is taken as a perturbation in $\boldsymbol{k} \cdot \boldsymbol{p}$ theory. In contrast to the single-group formulation of $\boldsymbol{k} \cdot \boldsymbol{p}$ theory, where the spin-orbit coupling is also a perturbation [1], here we include the spin-orbit coupling in the unperturbed portion of the $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian, so that $\epsilon_{\nu 0}$ is defined by [13]

$$\left[\frac{p^2}{2m} + V_0 + \frac{\hbar}{2m^2c^2}\boldsymbol{p}\cdot\boldsymbol{S}\times(\nabla V_0)\right]|\boldsymbol{\nu}\boldsymbol{0}\rangle = \epsilon_{\boldsymbol{\nu}\boldsymbol{0}}|\boldsymbol{\nu}\boldsymbol{0}\rangle.$$
(4.8)

We write the matrix elements of U using standard manipulations as

$$\langle \nu \boldsymbol{k} | U | \nu' \boldsymbol{k}' \rangle \simeq \frac{e}{V} \delta_{\nu\nu'} \int d\boldsymbol{r} e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}} \boldsymbol{E} \cdot \boldsymbol{r} + \frac{e}{N} \boldsymbol{E} \cdot \sum_{\boldsymbol{K}\sigma} \delta_{\boldsymbol{k}-\boldsymbol{k}',\boldsymbol{K}} \int_{\Omega} d\boldsymbol{r} e^{i\boldsymbol{K}\cdot\boldsymbol{r}} u_{\nu}^{\sigma*}(\boldsymbol{r}) \boldsymbol{r} u_{\nu'}^{\sigma}(\boldsymbol{r}), \quad (4.9)$$

where $V = N\Omega$ is the crystal volume and where the first term gives the usual envelopefunction approximation [1]. This term results after assuming that the slowly varying envelope functions have substantial Fourier components only for $k, k' \ll \pi/a$. In the same limit, only the $\mathbf{K} = 0$ contribution to the second term is relevant, giving

$$\langle \nu \boldsymbol{k} | U | \nu' \boldsymbol{k}' \rangle \simeq \frac{e}{V} \delta_{\nu\nu'} \int d\boldsymbol{r} e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}} \boldsymbol{E} \cdot \boldsymbol{r} + e a_B \boldsymbol{E} \cdot \boldsymbol{d}_{\nu\nu'} \delta_{\boldsymbol{k}\boldsymbol{k}'},$$
 (4.10)

where $-ea_B \boldsymbol{d}_{\nu\nu\prime}$ is the dipole matrix element,² with

$$\boldsymbol{d}_{\nu\nu\nu'} = \sum_{\sigma} \int_{\Omega} d\boldsymbol{r} u_{\nu}^{\sigma*}(\boldsymbol{r}) \boldsymbol{r} u_{\nu'}^{\sigma}(\boldsymbol{r}) / a_B, \qquad (4.11)$$

and $ea_B \simeq 2.5 \,\mathrm{D}$ (a_B is the Bohr radius and D is a debye). We note that both terms in Eq. (4.10) arise at leading (zeroth) order in the same small parameter, $|\mathbf{k} - \mathbf{k}'| a \ll 1$.

To derive an effective Schrödinger equation for the envelope functions, we insert Eqs. (4.6) and (4.10) into Eq. (4.5). We then write the envelope functions in position space using

$$\Psi_{\nu}(\boldsymbol{k}) = \frac{1}{\sqrt{V}} \int d\boldsymbol{r} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \Psi_{\nu}(\boldsymbol{r}).$$
(4.12)

^{2.} If the electric field, \boldsymbol{E} , and the corresponding magnetic vector potential, \boldsymbol{A} , are time dependent, the electric dipole operator, $-e\boldsymbol{E}\cdot\boldsymbol{r}$, can be reexpressed as $-\frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{p}$, using a gauge transformation. However, in the zero-frequency limit, the $-\frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{p}$ operator can exhibit singular behaviour (see e.g. Chapter 5 of Ref. [14]). To avoid such complications, we focus here only on the $\boldsymbol{E}\cdot\boldsymbol{r}$ form of the electric dipole operator.

The resulting Schrödinger equation is

$$\sum_{\nu'} \left[H_{\boldsymbol{k}\cdot\boldsymbol{p}}^{\nu\nu'} + H_E^{\nu\nu'} \right] \Psi_{\nu'}(\boldsymbol{r}) = \epsilon \Psi_{\nu}(\boldsymbol{r}), \qquad (4.13)$$

where

$$H^{\nu\nu'}_{\boldsymbol{k}\cdot\boldsymbol{p}} = \left[\epsilon_{\nu\boldsymbol{0}} + \frac{\hbar^2 k^2}{2m} + e\boldsymbol{E}\cdot\boldsymbol{r}\right]\delta_{\nu\nu'} + \frac{\hbar}{m}\boldsymbol{k}\cdot\boldsymbol{\pi}_{\nu\nu'},\qquad(4.14)$$

with $\mathbf{k} \to -i\nabla$, and

$$H_E^{\nu\nu'} = ea_B \boldsymbol{E} \cdot \boldsymbol{d}_{\nu\nu'}. \tag{4.15}$$

Eq. (4.13) acts as a Schrödinger equation for the long-range degrees of freedom, described by the envelope functions, $\Psi_{\nu}(\mathbf{r})$. While the standard envelope-function approximation neglects interband transitions generated by the potential U, here they are included via $H_E^{\nu\nu'}$.

In the rest of this paper, we determine the size of the electric-dipole term [Eq. (4.15)] for the heavy-hole and light-hole bands of GaAs from first principles, and analyze some consequences of this term for an asymmetric quantum well. The general methods described in this section can, however, be applied to a wide range of other materials and bands, whenever the matrix elements $d_{\nu\nu'}$ are nonzero.

4.3 First-principles material parameters for GaAs

To find general material parameters (e. g. $\pi_{\nu\nu'}, d_{\nu\nu'}$), we need an accurate description of the Bloch amplitudes, $u_{\nu}(r)$ [see Eqs. (4.7) and (4.11)]. These parameters have been calculated for GaAs using various techniques, including tight-binding methods [15] and density functional theory (DFT) with empirical pseudopotentials [16, 17] (or a combination of both, where the tight-binding parameters are calculated within DFT [18]). In pseudopotential methods, the core electrons around each nucleus are 'frozen'. Interactions between valence-shell and core-shell electrons are then included at the level of an effective potential. In contrast, all-electron DFT techniques solve for the (Kohn-Sham) orbitals of all electrons (including the core electrons). An all-electron approach may be important to describe the electronic states at short length scales, close to the nuclei. All-electron DFT can be performed using, e.g., the open-source ELK code [19, 20]. The Kohn-Sham orbitals resulting from ELK have been used

to accurately calculate hyperfine parameters for electrons and holes in GaAs and silicon [8]. In this paper, we use an equivalent procedure to evaluate other GaAs material parameters $(\mathbf{k} \cdot \mathbf{p})$ parameters and the matrix elements $\mathbf{d}_{\nu\nu'}$).

From ELK, we have extracted optimized Kohn-Sham orbitals for GaAs at the Γ point $(\mathbf{k} = \mathbf{0})$. From these orbitals, we have evaluated matrix elements of the momentum operator, giving $\mathbf{k} \cdot \mathbf{p}$ parameters P, P', and Q (see Appendix 2.F for details). The calculated band structure is shown in Fig. 4.1, resulting in a first-principles estimate for the band gaps. In Table 4.1, we compare the $\mathbf{k} \cdot \mathbf{p}$ parameters and energy gaps found from this procedure with accepted values (tabulated in the book by Winkler, Ref. [1]). We comment on agreement/disagreement of these parameters with the accepted values in Sec. 4.3.1, below.

In addition to the $\mathbf{k} \cdot \mathbf{p}$ parameters, there are two parameters (κ, q) that characterize the strength and symmetry of the Zeeman interaction. These parameters are derived as follows. In the presence of a magnetic field \mathbf{B} , the electron Zeeman Hamiltonian is

$$H_Z = -\boldsymbol{\mu} \cdot \boldsymbol{B},\tag{4.16}$$

where $\boldsymbol{\mu}$ is the magnetic moment,

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar} \left(g_L \boldsymbol{L} + g_s \boldsymbol{S} \right). \tag{4.17}$$

In Eq. (4.17), μ_B is the Bohr magneton, $g_L = 1$ and $g_s = 2$ are g-factors, \boldsymbol{L} is the electron orbital angular momentum operator and \boldsymbol{S} is the electron spin operator. In the valence band of GaAs, where ν and ν' span the heavy-hole and light-hole states (Γ_8 representation of the T_d double group), the effective Zeeman Hamiltonian matrix is [1,21]:

$$\mathcal{H}_Z = 2\kappa\mu_B \boldsymbol{B} \cdot \mathbf{J} + 2q\mu_B \boldsymbol{B} \cdot \boldsymbol{\mathcal{J}},\tag{4.18}$$

where $\mathbf{J} = (J_x, J_y, J_z)$ is the vector of spin-3/2 matrices, $\mathcal{J} = (J_x^3, J_y^3, J_z^3)$, and the parameters κ and q are determined through matrix elements of the magnetic moment operator $\boldsymbol{\mu}$.³ The

$$-\langle J_z = 3/2 | \, \mu_z \, | J_z = 3/2 \rangle = 3\kappa + \frac{27}{4}q \tag{4.19}$$

^{3.} For example, κ and q can be calculated by solving the following two equations:



Figure 4.1: GaAs band structure generated using the ELK code [19, 20]. The band structure is given between high-symmetry points $L \to \Gamma \to X$. The labels $\Gamma_{j_1j_2}$, $j_1 \in \{6, 7, 8\}$, $j_2 \in \{c, v\}$ for each band at the Γ point indicate the representation of the basis states with the subscript $j_2 = c$ (v) indicating conduction- (valence-) band states. See Sec. 3.3 of Ref. [1] for more details. Inset: schematic showing detail of the topmost valence bands and lowest conduction band. The labels CB, HH, LH, SO indicate the conduction band, heavy-hole band, light-hole band, and split-off band, respectively.

Parameter	Present Work	Winkler (Ref. $[1]$)
P	$7.9\mathrm{eV}\mathrm{\AA}$	$10.493\mathrm{eV}\mathrm{\AA}$
Q	$7.4\mathrm{eV}\mathrm{\AA}$	$8.165\mathrm{eV}\mathrm{\AA}$
P'	$1.7i\mathrm{eV}\mathrm{\AA}$	$4.780i\mathrm{eV}\mathrm{\AA}$
E_0	$0.41\mathrm{eV}$	$1.519\mathrm{eV}$
Δ_0	$0.33\mathrm{eV}$	$0.341\mathrm{eV}$
E'_0	$3.5\mathrm{eV}$	$4.488\mathrm{eV}$
Δ_0'	$0.18\mathrm{eV}$	$0.171\mathrm{eV}$
κ	0.61	1.20
q	0.01	0.01
χ	0.2	-

Table 4.1: Material parameters found from density functional theory (present work) and the accepted values from Table D.1 of Ref. [1]. The $\mathbf{k} \cdot \mathbf{p}$ parameters P, Q, and P' are defined in Eq. (3.3) of Ref. [1]. For a discussion of the convergence of the calculation, see Appendix 4.A.

parameters κ and q, calculated from first principles, are compared with the accepted values in Table 4.1.

As described above, matrix elements of the momentum operator ($\propto P, P', Q$), band gaps $(E_0, E'_0, \Delta_0, \Delta'_0)$, and matrix elements of the magnetic moment operator ($\propto \kappa, q$) are sufficient to parametrize $\mathbf{k} \cdot \mathbf{p}$ theory within the envelope-function approximation. However, as described in Sec. 4.2, in certain circumstances, matrix elements of the electric-dipole operator ($\propto d_{\nu\nu'}$) may also be relevant. In a subspace spanned by states that transform according to the Γ_8 representation of the tetrahedral double group (e.g., the heavy-hole and light-hole states), the effective projected electric-dipole Hamiltonian matrix derived from $H_E^{\nu\nu'}$ is [5]:

$$\mathcal{H}_E = \frac{1}{\sqrt{3}} e a_B \chi \left[E_x \{ J_y, J_z \} + E_y \{ J_z, J_x \} + E_z \{ J_x, J_y \} \right], \tag{4.21}$$

and

$$-\langle J_z = 1/2 | \, \mu_z \, | J_z = 1/2 \rangle = \kappa + \frac{1}{4}q, \qquad (4.20)$$

where the states $|J_z\rangle$ are the valence-band orbitals that transform like states with total angular momentum J_z along \hat{z} .

where χ is a parameter that controls the strength of the electric-dipole matrix elements. We have numerically evaluated the matrix elements $d_{\nu\nu'}$ [see Eq. (4.15)] giving $\chi = 0.2$ (listed in Table 4.1). While \mathcal{H}_E arises physically from the electric-dipole operator, this term can be written as an effective pseudospin J = 3/2 quadrupole term (similar to that analyzed in Refs. [22, 23]).⁴

The electric-dipole term given by Eq. (4.21) may lead to important measurable effects. For example, when this term is included, an oscillating electric field can drive electric-dipole transitions between heavy-hole and light-hole states. For crystals with a center of inversion symmetry, $\chi = 0$ identically and these transitions vanish. However, in GaAs we find (within DFT) that the heavy-hole/light-hole transition dipole is $ea_B\chi \simeq 0.5$ D, a substantial fraction ($\simeq 40\%$) of that for a $1s \rightarrow 2p$ hydrogen atom transition.⁵ In Sec. 4.4 below, we explore further consequences of this term for an asymmetric quantum well.

4.3.1 Accuracy of first-principles parameters

The results given in Table 4.1 show a broad range of agreement between the parameters calculated here within DFT and the accepted values listed in Ref. [1]. The spin-orbit gaps, Δ_0, Δ'_0 , and parameter q are well-reproduced in DFT (within 5% of the accepted values). However, P, Q, and E'_0 deviate by 20%-30%, and the calculated P', E_0 , and κ differ from the accepted values by as much as a factor of 4. We note that the spin-orbit gaps Δ_0, Δ'_0 depend on short-range properties of the wavefunctions near the nuclear cores (where the spin-orbit coupling diverges $\propto \nabla V(r) \propto 1/r^2$). This level of agreement is consistent with the agreement found previously for short-range hyperfine parameters [8]. In contrast, the other parameters

^{4.} Specifically, we can rewrite Eq. (4.21) as $\mathcal{H}_E = ea_B\chi\left(E_x\tilde{Q}_{yz} + c.p.\right)$. Here, "c.p." indicates cyclic permutations and $\tilde{Q}_{ij} = \{J_i, J_j\}$ is proportional to the usual quadrupole matrix up to an additive constant [24]: $Q_{ij} = eQ\left[\frac{3}{2}\tilde{Q}_{ij} - \delta_{ij}J(J+1)\right] / [6J(2J-1)]$, with quadrupole moment Q. Thus, although this term is generated through an electric dipole coupling, the usual dipole selection rules do not apply (with respect to the pseudospin). In particular, \mathcal{H}_E allows for "double-quantum" transitions having $|\Delta J_z| = 2$ (e.g. $|J_z = +3/2\rangle \leftrightarrow |J_z = -1/2\rangle$).

^{5.} The electric-dipole matrix element describing this hydrogenic transition is given by $e \langle 1 0 0 | x | 21 \pm 1 \rangle = p\chi_{1s\to 2p}$, where $\chi_{1s\to 2p} \approx 0.5 (\chi/\chi_{1s\to 2p} \approx 0.4)$ and the states, $|n l m\rangle$ are the hydrogen-atom eigenstates (*n* is the principal quantum number, *l* is the orbital angular momentum, and *m* is the orbital angular momentum along the axis of quantization).

listed above depend on the electronic structure far from the nuclear cores. For example, in a tight-binding theory, the band gaps E_0 and E'_0 depend on overlaps of atomic wavefunctions localized at different sites.

The discussion above indicates a strong degree of confidence in the accuracy of the DFT procedure in calculating short-range quantities. For longer-range quantities, the results are mixed but nevertheless produce the correct order of magnitude: the calculated quantities are all within a factor of ~ 4 of their accepted value. We therefore expect the true value of the parameter χ to be within a factor of ~ 4 of the value reported here. To unambiguously establish the accuracy of the calculated value of χ , a direct comparison to experiment is required. As discussed above, observation of electrically driven heavy-hole light-hole Rabi oscillations would provide a direct measurement of χ . Another possible experiment that could quantitatively establish χ would be measurements of the heavy-hole spin splitting and spin-orbit coupling, which we discuss in the next two sections.

4.4 Spin-orbit interactions for a triangular quantum well

The goal of this section is to explore the influence of \mathcal{H}_E [Eq. (4.21)] on heavy-hole spinorbit coupling for an asymmetric quantum well. We consider a quantum well formed at a heterointerface where the confinement can be described by a triangular potential due to an electric field $\boldsymbol{E} = E_z \hat{\boldsymbol{z}}$,

$$U(z) = \begin{cases} \infty & z \le 0, \\ eE_z z & z > 0. \end{cases}$$
(4.22)

For the valence band of a III-V semiconductor, where ν and ν' are restricted to the heavy-hole (HH) and light-hole (LH) states, we write the Hamiltonian matrix

$$\mathcal{H} = \mathcal{H}_L + U(z)I_4 + \mathcal{H}_1 + \mathcal{H}_3 + \mathcal{H}_E, \qquad (4.23)$$

where I_4 is the 4×4 identity matrix and

$$\mathcal{H}_L = \frac{\hbar^2}{2m} \left[\left(\gamma_1 + \frac{5}{2} \gamma_2 \right) k^2 I_4 - 2\gamma_2 (\mathbf{k} \cdot \mathbf{J})^2 \right]$$
(4.24)

γ_1	γ_2	C_k	b_{41}	b_{42}	b_{51}	b_{52}	r_{41}
		(eVÅ)	$(eV \text{\AA}^3)$	$(eV \text{\AA}^3)$	$(eV \text{\AA}^3)$	$(eV \text{\AA}^3)$	$(e\text{\AA}^2)$
6.85	2.10	-0.0034	-81.93	1.47	0.49	-0.98	-14.62

Table 4.2: GaAs valence-band parameters. The parameters γ_1 and γ_2 are taken from Table D.1 of Ref. [1]; C_k , b_{41} , b_{42} , b_{51} , and b_{52} are taken from Table 6.3 of Ref. [1]. The parameter r_{41} is taken from Table 6.6 of Ref. [1].

is the Luttinger Hamiltonian within the spherical approximation, with parameters γ_1 and γ_2 (see Table 4.2 for values in GaAs). The term \mathcal{H}_1 is linear in k [25]:

$$\mathcal{H}_{1} = -\frac{2C_{k}}{\sqrt{3}} \left[k_{x} \{ J_{x}, J_{y}^{2} - J_{z}^{2} \} + \text{c.p.} \right], \qquad (4.25)$$

while \mathcal{H}_3 is cubic in k:

$$\mathcal{H}_{3} = -b_{41} \left[\{k_{x}, k_{y}^{2} - k_{z}^{2}\} J_{x} + \text{c.p.} \right] - b_{42} \left[\{k_{x}, k_{y}^{2} - k_{z}^{2}\} J_{x}^{3} + \text{c.p.} \right] - b_{51} \left[\{k_{x}, k_{y}^{2} + k_{z}^{2}\} \{J_{x}, J_{y}^{2} - J_{z}^{2}\} + \text{c.p.} \right] - b_{52} \left[k_{x}^{3} \{J_{x}, J_{y}^{2} - J_{z}^{2}\} + \text{c.p.} \right], \qquad (4.26)$$

where C_k , b_{41} , b_{42} , b_{51} , and b_{52} are material parameters (see Table 4.2 for values in GaAs). In Eqs. (4.24), (4.25), and (4.26), \mathbf{k} is a differential operator, $\mathbf{k} = -i\nabla$. In contrast to \mathcal{H}_1 and \mathcal{H}_3 , \mathcal{H}_E depends on the strength of the electric field, E_z [see Eq. (4.21)]. However, \mathcal{H}_E , \mathcal{H}_1 , and \mathcal{H}_3 share a common origin: they all stem from bulk-inversion asymmetry. Therefore, a general theory accounting for bulk-inversion asymmetry should include \mathcal{H}_E .

To derive the effective heavy-hole spin-orbit Hamiltonian, we rewrite \mathcal{H} as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}',\tag{4.27}$$

where \mathcal{H}_0 contains the potential energy, U, and the diagonal part of the Luttinger Hamiltonian,

 \mathcal{H}_L , giving matrix elements

$$\mathcal{H}_0^{\nu\nu'} = \left[(\mathcal{H}_L)_{\nu\nu} + U(z) \right] \delta_{\nu\nu'}. \tag{4.28}$$

The eigenfunctions of $\mathcal{H}_0^{\nu\nu}$ are $\Psi_{\nu}^{k_x,k_y,n}(\mathbf{r}) = F^{k_x}(x)F^{k_y}(y)F_{\nu}^n(z)$, where $F^{k_x}(x)$ and $F^{k_y}(y)$ are plane waves, while the envelope function $F_{\nu}^n(z)$ solves the differential equation:

$$\left[-\frac{\hbar^2}{2m_{\nu}}\frac{d^2}{dz^2} + U(z)\right]F_{\nu}^n(z) = \epsilon_{\nu}^n F_{\nu}^n(z).$$
(4.29)

Here, m_{ν} is the effective mass $(m_{\rm HH} = \frac{m}{\gamma_1 - 2\gamma_2}$ for heavy holes and $m_{\rm LH} = \frac{m}{\gamma_1 + 2\gamma_2}$ for light holes), and ϵ_{ν}^n is the energy for subband n. The envelopes, $F_{\nu}^n(z)$, are given by Airy functions (see Appendix 4.B).

We project the Hamiltonian matrix \mathcal{H} onto the lowest subband (n = 1) to obtain a 4×4 Hamiltonian matrix, \hat{H} (see Appendix 4.C for a discussion of the influence of higher subbands, n > 1). The 'hat' on \hat{H} indicates that the matrix describes only the lowest subband, n = 1. The matrix elements of \hat{H} can be written in terms of diagonal matrix elements of k_z^2 , e.g.,

$$\langle k_z^2 \rangle = -\int_0^\infty dz F_{\rm HH}^1(z) \frac{d^2}{dz^2} F_{\rm HH}^1(z),$$
 (4.30)

together with the following parameters:

$$l = -\frac{\sqrt{3}\hbar^2}{2m}\xi\gamma_2\tag{4.31}$$

and

$$\lambda = \frac{\sqrt{3}\hbar^2}{m}\gamma_2\eta_1,\tag{4.32}$$

where

$$\xi = \int_0^\infty dz F_{\rm HH}^1(z) F_{\rm LH}^1(z), \tag{4.33}$$

and

$$\eta_i = \int_0^\infty dz F_{\rm HH}^1(z) \frac{d^i}{dz^i} F_{\rm LH}^1(z), \qquad (4.34)$$

where $\frac{d^i}{dz^i}$ is the *i*th derivative with respect to *z*.

Using second-order degenerate perturbation theory (an approximate Schrieffer-Wolff transformation [26]), we project the Hamiltonian matrix, \hat{H} , onto the heavy-hole subspace. This gives the effective 2 × 2 heavy-hole Hamiltonian:

$$\hat{H}_{\rm HH} = \epsilon(k_{\parallel}) + \hat{H}_c + \hat{H}_D, \qquad (4.35)$$

where $\mathbf{k}_{\parallel} = k_x \hat{\mathbf{x}} + k_y \hat{\mathbf{y}}$, $\epsilon(k_{\parallel}) = \epsilon_{\text{HH}}^1 + (\gamma_1 + \gamma_2) \frac{\hbar^2 k_{\parallel}^2}{2m}$, \hat{H}_c represents cubic (in k_{\parallel}) spin-orbit coupling and \hat{H}_D represents the linear (in k_{\parallel}) Dresselhaus spin-orbit coupling. The model studied here also leads to a linear Rashba spin-orbit coupling (see Appendix 4.D). However, for the range of electric fields considered, we find the linear Rashba spin-orbit coupling to be at most ~ 10% of the linear Dresselhaus spin-orbit coupling (see Fig. 4.7 below). Therefore, for simplicity, we neglect the linear Rashba spin-orbit coupling in the main text and restrict the discussion of this term to Appendix 4.D.

4.4.1 Cubic spin-orbit coupling

The cubic spin-orbit coupling term is

$$\hat{H}_{c} = i\gamma^{R} \left(k_{+}^{3} \sigma_{-} - k_{-}^{3} \sigma_{+} \right) + \gamma^{D} \left(k_{+} k_{-} k_{+} \sigma_{-} + k_{-} k_{+} k_{-} \sigma_{+} \right),$$
(4.36)

where γ^R and γ^D are the cubic Rashba and Dresselhaus spin-orbit couplings, respectively, $k_{\pm} = k_x \pm i k_y$, and $\sigma_{\pm} = (\sigma_x \pm i \sigma_y)/2$ are Pauli matrices. For the triangular potential chosen here, $\gamma^R \simeq \gamma_1^R$ (see Appendix 4.E), where

$$\gamma_1^R = -\frac{2\lambda l}{\Delta_{\rm HL}} \tag{4.37}$$

and $\gamma^D \simeq \gamma^D_1 + \gamma^D_2$, where

$$\gamma_1^D = \frac{lC_k \xi^2}{\Delta_{\rm HL}},\tag{4.38}$$

and

$$\gamma_2^D = \frac{3\hbar^2 \gamma_2}{8m\Delta_{\rm HL}} \left[(4b_{41} + 7b_{42} + 2b_{51}) \xi \eta_2 - 8b_{51}\eta_1^2 \right].$$
(4.39)



Figure 4.2: Magnitude of the cubic spin-orbit coupling coefficients γ_1^R [in blue, see Eq. (4.37)], γ_2^D [in green, see Eq. (4.39)], and γ_1^D [in yellow, see Eq. (4.38)] as a function of electric field, E_z . The material parameters used (for GaAs) are given in Table 4.2.

In Eqs. (4.37), (4.38), and (4.39) $\Delta_{\rm HL} = \epsilon_{\rm HH}^1 - \epsilon_{\rm LH}^1$ is the heavy-hole/light-hole splitting in the lowest subband. As can be seen from Fig. 4.2, for electric field strengths $E_z \gtrsim 10^6 \,\rm V/m$, we have $|\gamma^R| \gg |\gamma^D| \simeq |\gamma_1^D + \gamma_2^D|$. We thus find that the cubic spin-orbit coupling is predominantly Rashba-like (consistent with, e.g., Ref. [27]).

4.4.2 Linear spin-orbit coupling

Spin-dependent transport and spin-relaxation measurements performed on heavy-holes in GaAs quantum dots are consistent with a spin-orbit coupling that is substantially Dresselhauslike [9, 10]. As demonstrated in Sec. 4.4.1, when the cubic spin-orbit coupling dominates over the linear spin-orbit coupling (large k_{\parallel} regime), we find a Rashba-like heavy-hole spin-orbit coupling. However, the linear spin-orbit coupling that dominates for small k_{\parallel} is predominantly Dresselhaus-like [as described above following Eq. (4.35)]. This observation may suggest that the experiments conducted in Refs. [9, 10] are sensitive to the small- k_{\parallel} spin-orbit coupling analyzed here.

The linear Dresselhaus spin-orbit coupling is

$$\hat{H}_D = \beta \left(k_- \sigma_+ + k_+ \sigma_- \right).$$
 (4.40)

The coefficient β can be written as a sum of five terms:

$$\beta = \beta_{C_k} + \beta_{\chi} + \beta_0 + \beta_{b1} + \beta_{b2}, \qquad (4.41)$$

where

$$\beta_{C_k} = \frac{\sqrt{3}C_k}{2},\tag{4.42}$$

$$\beta_{\chi} = \frac{2\lambda e a_B E_z \chi \xi}{\Delta_{\rm HL}},\tag{4.43}$$

$$\beta_0 = -\frac{2\lambda C_k \eta_1}{\Delta_{\rm HL}},\tag{4.44}$$

$$\beta_{b1} = \frac{3}{4} \left(b_{42} + b_{51} \right) \left\langle k_z^2 \right\rangle, \tag{4.45}$$

and

$$\beta_{b2} = \frac{\sqrt{3b_{52}\lambda\eta_3}}{\Delta_{\rm HL}}.\tag{4.46}$$

The dipolar spin-orbit coupling term (the term with coefficient β_{χ}) arises from non-vanishing electric-dipole matrix elements (\mathcal{H}_E with $\chi \neq 0$). Therefore, it vanishes identically within the envelope-function approximation. However, β_{χ} is of the same order as the other linear Dresselhaus spin-orbit coefficients for $E_z \gtrsim 10^6 \text{ V/m}$ (see Fig. 4.4). As can be seen in Fig. 4.4, β_{χ} , β_{b1} , and β_{b2} vary as a function of electric field. In fact, there is a value of the electric field where β_{b1} exactly cancels β_{C_k} (see gray line in Fig. 4.4). For an electric field, $E_z \sim 9 \times 10^6 \text{ V/m}$, the dipolar spin-orbit coupling ($\propto \beta_{\chi}$) contributes approximately half



Figure 4.3: Spin splitting, Δ , in GaAs from eigenvalues of Eq. (4.35) (in blue) as a function of $k_{\parallel} = k_x$ ($\mathbf{k}_{\parallel} = k_{\parallel} \hat{\mathbf{x}}$) for an electric field $E_z = 10^6 \text{ V/m}$. The top horizontal axis indicates the hole sheet density, $n_p = k_{\parallel}^2/(2\pi)$, associated with a Fermi wavevector, $k_F = k_{\parallel}$. The splitting is linear in k_{\parallel} for $k_{\parallel} \leq 0.02 \text{ nm}^{-1}$, meaning the linear Dresselhaus spin-orbit coupling dominates in this region. The splitting due to the spin-orbit coupling term with coefficient γ_1^R (in yellow) dominates at large k_{\parallel} . The material parameters used (for GaAs) are given in Table 4.2.



Figure 4.4: Magnitude of the linear Dresselhaus spin-orbit coupling coefficient, β (black solid line) as a function of electric field, E_z . The dotted lines give the different contributions to β : β_{C_k} [in green, see Eq. (4.42)], β_{b1} [in red, see Eq. (4.45)], β_{χ} [in blue, see Eq. (4.43)], β_0 [in yellow, see Eq. (4.44)], and β_{b2} [in purple, see Eq. (4.46)]. The material parameters used (for GaAs) are listed in Table 4.2. The gray line indicates the value of E_z for which $\beta_{C_k} + \beta_{b1} = 0$.
of the total spin splitting at small k_{\parallel} , where the linear Dresselhaus term dominates (see Fig. 4.5). The dipolar spin-orbit coupling is therefore necessary for a quantitative theory of spin-orbit couplings for heavy holes in asymmetric GaAs quantum wells. Specifically, this term may be relevant in interpreting the experimental results of Refs. [9, 10].

The spin splitting has been measured for heavy-holes in GaAs quantum wells through Shubnikov-de Haas oscillations [28]. Provided similar measurements could be performed with a typical confining electric field and range of sheet density as given in Fig. 4.5, the value of χ determined here could be confirmed.

Heavy-hole relaxation time, T_1

In Ref. [10], the relaxation time T_1 has been measured for a quantum-dot-confined heavy-hole spin as a function of the out-of-plane magnetic field, B. The measurements reveal the dependence $T_1 \propto B^{-5}$, which is characteristic of a relaxation channel dominated by phononassisted spin flips driven by either a linear spin-orbit coupling or by a cubic Dresselhaus spin-orbit coupling (this dependence is, however, inconsistent with a cubic Rashba spin-orbit coupling). The observation that the cubic Dresselhaus spin-orbit coupling can be neglected when calculating heavy-hole spin splittings (see Fig. 4.3) provides some evidence that it can also be neglected in the context of spin relaxation. Moreover, because the linear Dresselhaus spin-orbit coupling dominates the linear Rashba spin-orbit coupling (see Appendix 4.D), it is plausible that the former is responsible for T_1 in Ref. [10]. Provided the linear Dresselhaus term (β) controls T_1 in this experiment, we can use the measured value as a quantitative check on our prediction for the value of β shown in Fig. 4.4.

In the limit of a weak out-of-plane magnetic field B (hole Zeeman energy, $g\mu_B B$, small compared to the orbital level spacings E_x , E_y , for an elliptical dot) and for coupling to piezoelectric phonons (which dominates for weak magnetic fields), the relaxation rate due to phonon-assisted spin flips driven by linear Dresselhaus spin-orbit coupling is given by [29]

$$\frac{1}{T_1} \simeq \frac{4(eh_{14}\beta)^2}{105\pi\hbar^4\rho c_t^5} \left(1 + \frac{3c_t^5}{4c_l^5}\right) (g\mu_B B)^5 \left(\frac{1}{E_x^4} + \frac{1}{E_y^4}\right).$$
(4.47)

In this equation, $h_{14} = 1.4 \times 10^9 \,\mathrm{V/m}$ is the piezoelectric potential, $\rho = 5300 \,\mathrm{kg/m^3}$ is



Figure 4.5: Total spin splitting, Δ , (blue line) and spin splitting assuming $\chi \to 0$ (yellow line). For this choice of electric field ($E_z = 9 \times 10^6 \text{ V/m}$), β_{χ} is the largest contribution to the spin splitting (see Fig. 4.4). The top horizontal axis indicates the hole sheet density, $n_p = k_{\parallel}^2/(2\pi)$, associated with a Fermi wavevector, $k_F = k_{\parallel}$. The material parameters used (for GaAs) are displayed in Table 4.2.

the material (GaAs) density, $c_t = 3350 \text{ m/s}$ is the transverse acoustic phonon velocity, $c_l = 4730 \text{ m/s}$ is the longitudinal acoustic phonon velocity, g = 1.35 is the heavy-hole out-ofplane g factor [10], and E_x , E_y are the lowest two orbital level spacings for a quantum dot defined by parabolic confinement along the x- and y-directions.

The measurements of Ref. [10] yield $T_1 = (2.5 \,\mu \text{s} \cdot \text{T}^5)B^{-5}$. Using the range of coefficients presented in Fig. 4.4, $\beta \simeq 0.35$ -0.40 meV nm, and for an anisotropic quantum dot with orbital level spacings $E_x \simeq E_y/3 \simeq 0.3 \text{ meV}$ (see the supplementary material of Ref. [30]),⁶ we obtain $T_1 \simeq (1.7-2.2 \,\mu \text{s} \cdot \text{T}^5)B^{-5}$, remarkably close to the measured value.⁷ This level of agreement suggests that the model presented in Sec. 4.4, which includes the dipolar spin-orbit coupling, may indeed give a highly accurate value for the linear Dresselhaus spin-orbit coupling.

4.4.3 Comments on the model

The model presented in this section attempts to capture the main features of the spin-orbit coupling for GaAs heavy holes confined to an asymmetric quantum well. Earlier works have calculated the heavy-hole spin splitting accounting for many-body effects by using a potential calculated self-consistently under the Hartree approximation (accounting for charges in both the inversion and depletion layers of an AlGaAs-GaAs heterojunction) [31–33]. However, in these studies, bulk-inversion asymmetry was neglected. More recently, heavy-hole spin splittings have been computed using wavefunctions obtained from a variational solution to the Poisson and Schrödinger equations [27]. This procedure was shown to give results consistent with experiments, even in the parameter regime where the perturbation theory that projects the full Hamiltonian onto the lowest heavy-hole subband breaks down. While the theory presented Ref. [27] includes bulk-inversion asymmetry by considering the terms \mathcal{H}_1 and \mathcal{H}_3 , \mathcal{H}_E is neglected.

^{6.} The device investigated in Ref. [30] was fabricated with the same procedure as the device studied in Ref. [10]. In the supplementary material of Ref. [30], the quantum-dot spectrum is calculated based on a theoretical model and simulations of the quantum-dot device. The orbital level spacings, E_x and E_y , were extracted from this spectrum [Fig. 1(a) of the supplementary material of Ref. [30] at B = 0].

^{7.} The range of values reported here would overlap with the measured value if, e.g., the true level spacing were larger than the estimated value ($E_x \simeq 0.3 \text{ meV}$) by only 3%. Moreover, the hole-spin Zeeman splitting is comparable to the orbital level spacing for the range of magnetic fields ($B \simeq 0.5 \text{ T} - 1.5 \text{ T}$) studied in Ref. [10]. For this range of magnetic fields, there could be a substantial (order unity) correction to Eq. (4.47).

The potential considered in this paper is a triangular well $[U(z) = eE_z z]$ which we take to represent the total effective potential experienced by holes at the heterointerface. Although we have not fully accounted for many-body effects, the benefit of using an analytic form for the potential is that the spin-orbit couplings and spin splitting can be investigated analytically. Other works have adopted a similar approach. For example, in Ref. [34], the spin-orbit coupling has also been calculated starting from the Luttinger Hamiltonian. However, in this reference terms involving bulk-inversion asymmetry were neglected $(\mathcal{H}_1, \mathcal{H}_3, \mathcal{H}_E \to 0)$. If bulk inversion asymmetry is neglected in our model, the linear spin-orbit coupling vanishes and we find only a cubic Rashba heavy-hole spin-orbit coupling with coefficient γ_1^R , consistent with the results of Ref. [34]. In Ref. [35], the heavy-hole spin-orbit couplings were calculated using a similar procedure to that described in Sec. 4.4: The Schrieffer-Wolff transformation was applied to \hat{H} to obtain the effective heavy-hole Hamiltonian \hat{H}_{HH} . Although bulk-inversion asymmetry was included in Ref. [35] through the spin-orbit parameters β_{C_k} and β_{b1} , the parameters β_{χ}, β_0 , and β_{b2} were neglected. In the present case, we find there is a range of electric field E_z for which β_{χ}, β_0 , and β_{b2} give the dominant contribution to the linear Dresselhaus spin-orbit coupling (and are all of the same order, see Figs. 4.4, 4.5).

While the Hamiltonian matrix \mathcal{H} [Eq. (4.23)] includes terms that describe bulk-inversion asymmetry, certain terms that describe structure-inversion asymmetry are neglected (these are the k-linear terms listed in Table 6.5 of Ref. [1]). The dominant term among those that have been neglected has a coefficient r_{41} (see Sec. 6.3.3 of Ref. [1] and Ref. [35]) and off-diagonal matrix elements $\sim r_{41}E_zk_{\parallel}$. This term couples the same valence-band states as the term with coefficient b_{41} in Eq. (4.26), and which has off-diagonal matrix elements $\sim b_{41}\eta_2k_{\parallel}$. For GaAs, we find that $|r_{41}|E_z < |b_{41}|\eta_2$ for the range $10^6 \text{ V/m} \leq E_z \lesssim 10^7 \text{ V/m}$ considered here. Because terms that depend on b_{41} are neglected (they lead to spin-orbit couplings that are smaller than those considered in Secs. 4.4.1 and 4.4.2, see Appendices 4.E and 4.D for justification), this justifies neglecting the contributions described above in the present work.

Finally, we also note that in the model described here, E_z provides the confinement that lifts the heavy-hole/light-hole degeneracy. Therefore, as E_z decreases, $\Delta_{\rm HL}$ decreases. A smaller splitting, $\Delta_{\rm HL}$, leads to larger corrections to the perturbation theory used to project \hat{H} onto the two-dimensional heavy-hole subspace. This perturbation theory has a small parameter $\varepsilon_{\rm od}/\Delta_{\rm HL}$, where $\varepsilon_{\rm od}$ represents an off-diagonal element of \mathcal{H} (the magnitude of $\varepsilon_{\rm od}$ increases with k_{\parallel}). For $E_z = 10^6 \,{\rm V/m}$ and $k_{\parallel} \lesssim 0.1 \,{\rm nm}^{-1}$, we find $\varepsilon_{\rm od}/\Delta_{\rm HL} \lesssim 0.1$ for all off-diagonal elements $\varepsilon_{\rm od}$. A breakdown of perturbation theory for $k_{\parallel} \gtrsim 0.1 \,{\rm nm}^{-1}$ is consistent with the results shown in Fig. 4.6. See also Appendix 4.C for further discussion of the validity of the perturbation theory.

4.5 Conclusions

We have extended $\mathbf{k} \cdot \mathbf{p}$ theory to account for interband coupling generated by the triangularwell confining potential at a heterointerface. In subspaces where the basis states transform according to the Γ_8 representation of the tetrahedral double group (e.g., the heavy-hole and light-hole states at k = 0 in a III-V semiconductor), this coupling can be parameterized by a single material-dependent parameter χ . Here, we have focused on the valence band of GaAs, but an equivalent analysis could be applied to other materials/bands. Using the Kohn-Sham orbitals from an all-electron density functional theory calculation, we find $\chi = 0.2$ for GaAs. This value for χ leads to a transition dipole of $ea_B\chi \simeq 0.5$ D, only a factor of ~ 2 smaller than that of a hydrogenic 1s to 2p transition. Rabi-frequency measurements for the light-hole to heavy-hole transition in GaAs would allow for χ to be established experimentally. The finite value of χ found here may be important for understanding electric-dipole spin resonance (EDSR) for GaAs hole-spin qubits with heavy-hole light-hole mixing. This EDSR mechanism may even be present in group IV semiconductor nanostructures (silicon, germanium, ...) that are sufficiently strained to significantly break inversion symmetry on the scale of the lattice.

The finite value of $\chi \neq 0$ in III-V semiconductors (or in group IV materials with broken inversion symmetry due, e.g., to strain) leads to a new form of spin-orbit coupling: the dipolar spin-orbit coupling. Because the dipolar spin-orbit coupling has Dresselhaus symmetry, it may be relevant to the measurements of Refs. [9, 10], which show experimental evidence of Dresselhaus spin-orbit coupling. More generally, a better understanding of the pseudospinelectric coupling may explain spin coherence/relaxation (T_2^*/T_1) times, spin-electric coupling for cavity-QED, electric-dipole spin resonance, and spin non-conserving tunnelling in double quantum dot systems.

A central observation of this paper is that the electric-dipole term \mathcal{H}_E results in important

physical consequences. This term leads, e.g., to a modified spin splitting for heavy holes in a two-dimensional hole gas or to driven Rabi oscillations between heavy holes and light holes under the influence of a time-dependent electric field. The electric-dipole term does not vanish at $\mathbf{k} = 0$, unlike all other inter-band terms in conventional $\mathbf{k} \cdot \mathbf{p}$ theory (within the envelope-function approximation). Thus, long-wavelength (small k) properties of holes will generally be influenced by \mathcal{H}_E , even for $k \to 0$, when the standard envelope-function approximation is expected to be accurate.

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Appendices to Chapter 4

4.A Calculating material parameters

To calculate the $\mathbf{k} \cdot \mathbf{p}$, Zeeman-Hamiltonian, and position-operator matrix elements, we start by calculating the Kohn-Sham orbitals from the necessary bands at the Γ point of GaAs. Then, using the group theoretic projection operators (see Ref. [36] and Appendix C of Ref. [8]), we project these orbitals onto states with the appropriate symmetry. For example, one $\mathbf{k} \cdot \mathbf{p}$ matrix element is [1]

$$P = \frac{\hbar}{m} \left\langle S \right| p_x \left| X \right\rangle, \tag{4.48}$$

where $|S\rangle$ is the s-like conduction-band $\mathbf{k} = \mathbf{0}$ Bloch function and $|X\rangle$ is the p-like valenceband $\mathbf{k} = \mathbf{0}$ Bloch function that transforms like the coordinate x under the symmetry operations of the crystal. To evaluate the matrix element, Eq. (4.48), we first calculate the Γ -point Kohn-Sham orbitals for the conduction and valence bands of GaAs. Because the top of the valence band of GaAs is fourfold degenerate, a general valence-band Kohn-Sham orbital will be a linear combination of all four states (two heavy-hole and two light-hole states). Using group-theoretic projection operators [8,36,37], we project the general valence-band Kohn-Sham orbital onto the orbital that transforms like x to obtain $|X\rangle$. Because the GaAs conduction band is s-like (isotropic) the only Γ -point conduction-band Kohn-Sham orbital is $|S\rangle$ and no projection is necessary in this case. Once we obtain $|S\rangle$ and $|X\rangle$, we evaluate P (see Table 4.1). We apply a similar procedure to evaluate the other $\mathbf{k} \cdot \mathbf{p}$ matrix elements, P' and Q [P, P', and Q are defined in Eqs. (3.3a), (3.3b) and (3.3c) of Ref. [1]], as well as κ , q, and χ (see Sec. 4.3). The code used to implement these projections has been made freely available [37].

For all the parameters listed in Table 4.1, we have used the "very high quality" parameter set of the ELK code (vhighq set to .true. in the input file) [19] to calculate the Kohn-Sham orbitals. This set of parameters was shown to yield precise results (which have converged with respect to multiple parameters to within 2% of their asymptotic values, see Ref. [8]) when calculating the hyperfine couplings in GaAs and silicon [8].

4.B Solution to triangular confining potential

Eq. (4.29) can be solved by the envelope functions

$$F_{\nu}^{n}(z) = C_{\nu} \operatorname{Ai}\left(\left[\frac{2m_{\nu}}{\hbar^{2}e^{2}E_{z}^{2}}\right]^{1/3} \left[eE_{z}z - \epsilon_{\nu}^{n}(z)\right]\right), \qquad (4.49)$$

where C_{ν} is a normalizing constant, and Ai(z) is an Airy function. The eigenenergies are given by

$$\epsilon_{\nu}^{n} = -\left(\frac{\hbar^{2}e^{2}E_{z}^{2}}{2m_{\nu}}\right)^{1/3}a_{n},$$
(4.50)

where a_n is the n^{th} zero of Ai(z). If we define

$$\Lambda_{\nu}(z) = \left(\frac{2m_{\nu}eE_z}{\hbar^2}\right)^{1/3} \left(z - \frac{\epsilon_{\nu}^n(z)}{eE_z}\right),\tag{4.51}$$

we can write C_{ν} as

$$C_{\nu} = \left[\frac{(2m_{\nu}eE_z/\hbar^2)^{1/3}}{\operatorname{Ai}'(\Lambda_{\nu}(0)) - \Lambda_{\nu}(0)\operatorname{Ai}^2(\Lambda_{\nu}(0))}\right]^{1/2}.$$
(4.52)

4.C Contributions to the heavy-hole spin splitting from higher subbands

In the approach described in the main text, the full Hamiltonian \mathcal{H} [Eq. (4.23)] is projected onto the lowest subband to obtain the four-dimensional Hamiltonian, \hat{H} . \hat{H} is then projected onto the heavy-hole subspace using perturbation theory (Schrieffer-Wolff transformation) to obtain an effective two-dimensional Hamiltonian, \hat{H}_{HH} [Eq. (4.35)]. To verify the spin-splitting obtained from the Schrieffer-Wolff procedure (green line in Fig. 4.6), we have numerically diagonalized the four-dimensional Hamiltonian arising from the lowest subband, \hat{H} , resulting in the spin splitting shown in the blue line of Fig. 4.6. To address the effect of the first



Figure 4.6: Heavy-hole spin splitting in GaAs computed by diagonalizing the effective 2 × 2 Hamiltonian obtained from the Schrieffer-Wolff transformation, as described in the main text (in green), by diagonalizing the 4 × 4 Hamiltonian in the lowest valence-band subband (in blue), and by diagonalizing the 8 × 8 Hamiltonian in the two lowest valence-band subbands (in yellow). The top horizontal axis indicates the hole sheet density, $n_p = k_{\parallel}^2/(2\pi)$, associated with a Fermi wavevector, $k_F = k_{\parallel}$. All calculations were preformed for a triangular well with electric field $E_z = 10^6 \text{ V/m}$ with material parameters used (for GaAs) given in Table 4.2.



Figure 4.7: Linear spin-orbit coupling coefficients. The magnitude of the Dresselhaus coefficient (in blue), β , is larger than the magnitude of the Rashba coefficient (in yellow), α , for all values of E_z considered. The values for the material parameters (for GaAs) are listed in Table 4.2.

excited subband, we have also numerically diagonalized the eight-dimensional Hamiltonian, giving the yellow line shown in Fig. 4.6. From Fig. 4.6, perturbation theory breaks down at large k_{\parallel} ($k_{\parallel} \gtrsim 10^{-1} \,\mathrm{nm^{-1}}$). For the analysis presented here to give quantitatively accurate results, we therefore require $k_{\parallel} \lesssim 10^{-1} \,\mathrm{nm^{-1}}$. For a two-dimensional hole gas with Fermi wavevector $k_{\rm F} = k_{\parallel}$, this implies a low sheet density, $n_p \lesssim 10^{-11} \,\mathrm{cm}$.

4.D Linear Rashba spin-orbit coupling

In addition to the linear Dresselhaus spin-orbit coupling discussed in Sec. 4.4.2, a linear Rashba spin-orbit coupling can be derived from the same model:

$$\hat{H}_R = i\alpha \left(k_+\sigma_+ - k_-\sigma_-\right),\tag{4.53}$$

where α is the linear Rashba spin-orbit coupling coefficient. This coefficient depends on the strength of the electric field, E_z , as well as the material-specific parameters χ , C_k , b_{41} , b_{42} , b_{51} , b_{52} and γ_2 . In Fig. 4.7 we compare the value of α to the linear Dresselhaus coefficient, β . We find that (for the values of E_z considered) $|\alpha| \leq 10\% |\beta|$. For simplicity, We neglect the linear Rashba spin-orbit coupling in the analysis presented in the main text. However, we note that the linear Rashba coefficient could be calculated and included in the analysis. The procedure to do so would be similar to that outlined in Sec. 4.4: project the Hamiltonian \mathcal{H} onto the lowest subband subspace to obtain \hat{H} , perform the Schrieffer-Wolff transformation on the Hamiltonian \hat{H} to project it onto the heavy-hole subspace, and then collect the terms linear in k_{\parallel} that possess Rashba symmetry [Eq. (4.53)].

4.E Additional cubic spin-orbit coupling

In addition to the cubic spin-orbit couplings discussed in Sec. 4.4.1 (γ_1^R , γ_1^D , and γ_2^D) there are extra small terms that we discuss here for completeness. According to the model presented in Sec. 4.4, the cubic Rashba spin-orbit coupling coefficient is given by,

$$\gamma^R = \gamma_1^R + \gamma_2^R, \tag{4.54}$$

where γ_1^R is given by Eq. (4.37) of the main text and

$$\gamma_2^R = \frac{4b_{41} + 7b_{42} - 2b_{51} + 2b_{52}}{32\Delta_{\rm HL}} \xi$$

$$\times \left(3b_{52}\eta_3 - 2\sqrt{3}C_k\eta_1 + \sqrt{3}E_z ea_B\chi\xi\right).$$
(4.55)



Figure 4.8: Cubic spin-orbit coupling coefficients $-\gamma_1^D$ (in yellow), $-\gamma_3^D$ (in green), and γ_2^R (in blue) as a function of electric field, E_z . $|\gamma_1^D|$, is orders of magnitude smaller than the dominant cubic spin-orbit coupling term characterized by γ_1^R (see Sec. 4.4.1), however it is larger (in magnitude) than both γ_3^D and γ_2^R , for the values of E_z considered here. The values for the material parameters (for GaAs) are listed in Table 4.2.

Similarly, the Dresselhaus spin-orbit coupling has an additional contribution:

$$\gamma^D = \gamma_1^D + \gamma_2^D + \gamma_3^D, \tag{4.56}$$

where γ_1^D is given by Eq. (4.38) of the main text, γ_2^D is given by Eq. (4.39) of the main text, and

$$\gamma_3^D = \frac{3}{16}(b_{51} + 3b_{52} - b_{42}). \tag{4.57}$$

As shown in Fig. 4.2, for the range of electric fields considered, the cubic spin-orbit coupling parameters satisfy $|\gamma_1^R| \gg |\gamma_2^D| > |\gamma_1^D|$. The additional terms contributing to γ^R and γ^D (γ_2^R and γ_3^D) are even smaller (in magnitude) than γ_1^D (see Fig. 4.8) over the range of electric fields considered and are therefore neglected throughout the main text.

References for Chapter 4

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5 Conclusion

Spins confined to semiconductor nanostructures have a broad range of applications. These include, but are not limited to, sensing, classical spintronics, and quantum information processing. These applications rely on knowing the state of the confined spins. Therefore, understanding the spin dynamics in semiconductor nanodevices is an important problem. In this thesis, we have investigated two factors that influence these dynamics: the hyperfine and spin-orbit interactions. In Chapter 2, we calculated the hyperfine couplings for electrons and holes in GaAs and silicon using the Kohn-Sham orbitals from DFT. The results are consistent with electron Knight-shift measurements. For holes, experiments are limited and a direct comparison between the DFT and experimental values is not yet possible. In Chapter 3 we estimated the hyperfine coupling for boron acceptors in silicon, whose value remains an open question. Because the envelope function approximation breaks down in this system, we based the estimate on the experimentally determined phosphorus donor hyperfine coupling. We also demonstrated how measurements of hole spin echo envelope modulations could be used as a direct measure of the hole-hyperfine interaction for boron acceptors in silicon. Finally, in Chapter 4, we went beyond the envelope function approximation to calculate the electric-dipole coupling between the heavy-hole and light-hole bands in GaAs. This coupling leads to a new linear Dresselhaus spin-orbit term in the heavy-hole subspace, the dipolar spin-orbit coupling, which may be important to understand recent experimental results.

The work presented in this thesis can be extended in different ways to further understand the hyperfine and spin-orbit interactions in semiconductor nanosystems. For instance, in Chapter 3 we focused on hole spin echo envelope modulations due to the hyperfine coupling between a light hole and a single boron nuclear spin in silicon. This theory can be extended to understand the echo envelope signal based on coupling to multiple nuclear spins. Such an analysis could be applied to quantum dots (or other nanostructures where the envelope function approximation is valid) to determine the hole hyperfine couplings in GaAs, silicon, and/or germanium from measurements of hole spin echo envelope signals. The results of such a measurement could be compared to the hyperfine parameters computed in Chapter 2 to validate the predictions for holes.

The calculation presented in Chapter 2 can also be extended to account for strain. The symmetry of the hyperfine Hamiltonian can be drastically different depending on the subspace under consideration. For example, in GaAs and silicon, while the conduction-band hyperfine Hamiltonian is isotropic, the heavy-hole hyperfine Hamiltonian is Ising-like (highly anisotropic). The symmetry of the hyperfine Hamiltonian can greatly influence the spin dynamics: e.g. in contrast to isotropic hyperfine Hamiltonians, Ising hyperfine Hamiltonians can be exploited to extend coherence times with a properly chosen applied magnetic field [105]. Thus, it would be interesting to investigate (perhaps using DFT) how strain modifies the crystal eigenstates and, in turn, the symmetries of the effective hyperfine Hamiltonian (in relevant subspaces). Such an investigation could lead to an understanding of how to strain different crystals to achieve advantageous effective hyperfine Hamiltonians.

In Chapter 4, we listed the important heavy-hole spin-orbit couplings present in an asymmetric GaAs quantum well. This list includes the dipolar spin-orbit coupling which may be necessary to obtain a quantitatively accurate description of the heavy-hole system. Recent measurements of the heavy-hole relaxation time, T_1 [53], and heavy-hole leakage current in the Pauli spin-blockade regime [106] have been shown to be consistent with a heavy-hole spin-orbit coupling that is almost entirely Dresselhaus-like. We hypothesized in Chapter 4 that since the Rashba and Dresselhaus spin-orbit couplings dominate at large and small k_{\parallel} respectively, that the observables of Refs. [53, 106] are sensitive to the states at small k_{\parallel} . This hypothesis can be tested by computing T_1 [49, 51, 107] and spin-flip tunneling rates [108, 109] in the respective systems and verifying if the results are consistent with the measurements. These calculations could also lead to a deeper understanding of these systems. For example, ascertaining the parametric dependencies of T_1 , accounting for all the spin-orbit coupling terms (including the dipolar spin-orbit coupling), could be useful to determine how to suppress spin relaxation. More generally, understanding the spin-orbit-mediated electric-field couplings in these systems could lead to a better understanding of how to electrically drive Rabi oscillations and manipulate spins.

The theory presented throughout this thesis has been primarily applied to specific materials, i.e. GaAs, silicon, and germanium. However, the methods developed can be generalized and used to calculate hyperfine and spin-orbit parameters for other systems. Thus, these methods could be useful to catalog spin-qubit systems (accounting for e.g. crystaline symmetries, nanostructure geometry, and strain) with respect to their effective hyperfine and spin-orbit Hamiltonians. Such a catalog would allow one to chose the optimal spin-qubit system based on the intended application.

The methods discussed in this thesis can be extended even further, beyond applications to spin qubits. The results for the hyperfine parameters (Chapter 2) and spin-orbit gaps (Sec. 4.3.1) provide some evidence that the DFT procedure we have presented can be used to obtain a fairly accurate description of the wavefunctions (at least near the atomic cores). A crucial component of the DFT procedure of Chapter 2 is DFT+ $\mathbf{k} \cdot \mathbf{p}$, which allows us to extend the accuracy of the $\mathbf{k} = \mathbf{0}$ Bloch functions to all finite \mathbf{k} states. With accurate wavefunctions in hand, matrix elements of general operators can be computed and bulk properties besides hyperfine and spin-orbit couplings can be calculated. These properties include, but are not limited to, polarizabilities, magnetic susceptibilities, and electron-phonon couplings. As touched upon in Sec. 2.5, this procedure may also be useful to calculate topological invariants for candidate topological materials. Thus, the DFT and DFT+ $\mathbf{k} \cdot \mathbf{p}$ procedures are extremely versatile and can potentially be used to predict properties of new or existing materials or to design materials with desired qualities.

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