

Computing Wavefunctions of Silicon Donor Qubits with Density Functional
Theory

By
Yousif Waleed Almulla

A THESIS

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Silicon based quantum computing is an attractive approach to large-scale quantum computation due to the significant success of the modern semiconductor fabrication industry. Despite many advances in silicon quantum computing since its inception in 1998, there remains no software for efficiently designing candidate silicon quantum computing devices. Such a development involves modeling the coherence times of qubits and the fidelity of quantum gate operations in a qubit system, and would accelerate progress towards designing a scalable quantum computer. The quantum computing group at Oak Ridge National Laboratory propose designing a computational workflow for gauging qubit coherence and gate fidelity for Kane's proposal of silicon quantum computing. Kane's model uses electron and nuclear spin states of a P donor atom implanted into a silicon lattice as a qubit, and an oscillating magnetic field to perform quantum gate operations on said qubit. Thus, a computational workflow must consider the electronic structure of a Si:P quantum device, and the wavefunction of the donor electron. This thesis focuses on the donor wavefunction and electronic structure calculations.

The electron density at the phosphorous core gives an approximation to the Fermi contact interaction between nuclear and electron spin states, and is therefore vital to calculating solutions of the time-dependent Hamiltonian representing single-qubit gate operations in Kane's model. We use the Vienna *ab-initio* Simulation Package (VASP) implementation of density functional theory to compute the valence electron wavefunction of a phosphorous defect in a 1.08 nm silicon nanocluster, and the charge density of this electron. We find the electron density to be orders of magnitude below the true electron charge density at the phosphorous nucleus. These data suggest that the pseudo-wavefunctions used by VASP are not accurate enough to inform a silicon quantum computing modeling code.

Key Words: density functional theory, quantum computing, silicon qubit

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Honors Baccalaureate of Science in Physics and Honors Baccalaureate of Science in Mathematics project of Yousif Waleed Almulla presented on May 22, 2018

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I understand that my project will become part of the permanent collection of Oregon State University Honors College. My signature below authorizes release of my project to any reader upon request.

Yousif Waleed Almulla, Author

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Physical Constants

Planck's Constant	$\hbar = 1.05 \times 10^{-34} \text{ m}^2\text{kg/s}$
Permittivity of Free Space	$\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$
Permeability of Free Space	$\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$
Mass of Electron	$m_e = 9.11 \times 10^{-31} \text{ kg}$
Mass of Proton	$m_p = 1.67 \times 10^{-27} \text{ kg}$
Charge of Electron	$e = 1.60 \times 10^{-19} \text{ C}$
Electron Gyromagnetic Ratio	$\gamma_e = 28.025 \text{ GHz T}^{-1}$
Nuclear Gyromagnetic Ratio	$\gamma_n = 17.235 \text{ MHz T}^{-1}$

Chapter 1

Quantum Computing and Kane's Proposal

Computers in the future may weigh no more than 1.5 tons.

- Popular Mechanics, 1949

1.1 Quantum Computing Today

We've done a little better than Popular Mechanics imagined. But how much better can we do? And why do we need to? Consider a finite dimensional quantum system, such as the spin state of an electron. The state space of single-electron spin is 2-dimensional, in that every spin state can be written as a linear combination of the spin-down state, $|\downarrow\rangle$, and the spin-up state, $|\uparrow\rangle$. Suppose one wanted to simulate n interacting electron spin states on a classical computer. An arbitrary single state looks like

$$|\psi\rangle = \alpha |\downarrow\rangle + \beta |\uparrow\rangle,$$

where α and β are complex numbers. Such a state is called a quantum bit, or *qubit*, since it represents one 2-dimensional unit of "quantum information", analogous to a classical bit. If we call two states that differ only by overall phase equivalent, it takes only one number to represent a single state. This is reasonable because an overall phase shift produces equivalent observables. When considering n such states (potentially coupled), there are 2^n total possible spin configurations, and hence an arbitrary n -electron spin state must be represented with 2^n complex coefficients:

$$|\psi^n\rangle = \alpha_1 |\downarrow, \dots, \downarrow\rangle + \alpha_2 |\uparrow, \dots, \downarrow\rangle + \alpha_3 |\downarrow, \uparrow, \dots, \downarrow\rangle + \dots + \alpha_{2^n} |\uparrow, \dots, \uparrow\rangle.$$

To model $|\psi^n\rangle$, a classical computer algorithm must store $2^n - 1$ values (minus one due to equivalence up to phase), or it needs to know something about the quantum system so that it can further reduce the quantity of numbers it must store. Conversely, a universal quantum computer—one capable of simulating any quantum mechanical process—could explicitly simulate the system of n particles and use statistical sampling to compute the property of interest. This suggests that for some problems, it may take exponentially less computational resources for a classical computer to accomplish the same task as a quantum computer. Realizing this, Richard Feynman posited that utilizing quantum systems for computation might be the only way to efficiently simulate quantum mechanics, a problem that has proved (empirically) untenable for classical computers [4]. Tantalized by this idea, computer scientists defined a new complexity class of problems decidable by a universal quantum computer (QC): Bounded-Error Quantum Polynomial time (**BQP**). A problem is in **BQP** if there exists a quantum algorithm that *terminates in polynomial time*,¹ and solves the problem with an *arbitrarily high probability of being correct*. We say an algorithm is **efficient** when it satisfies the first property.

Today, scientists have shown that QCs are able to solve many important problems that have proved difficult classically, including efficient integer factoring and searching through an unstructured search space [7, 25]. Respectively, the quantum algorithms for these problems run exponentially and quadratically faster than their modern classical counterparts. Our laptops and iPhones run fast enough that such a speedup is hardly noticeable to us locally—but that is not where the real societal impact lies. The consequences of solving problems with these levels of speedup are on the large scale, manifesting most in the computational sciences and through efficient solutions to what were previously the most expensive computational problems that universities, industry, and national labs could tackle. Instead of taking 100 days to match patterns in an enormous genome dataset, it would take 10 days with a universal QC; this alone could revolutionize computational biology, helping us to identify mutations, find common DNA patterns in cancer patients, and expedite feature finding in machine learning algorithms for genomics. These are the benefits for just *one* field.

The quest to develop a universal QC is well underway. In 2017, both IBM and Intel unveiled 17 qubit processors. Yet, this is after nearly two decades since the first experimental implementation of a QC, which operated with two qubits [2]. What has been holding progress back?

¹An algorithm terminates in polynomial time if the number of steps the algorithm runs in is polynomial in the length of its input string. The input string encodes the algorithm's input, which to a programmer is usually an array or other data structure.

1.1.1 Decoherence

Quantum systems are sensitive to outside energy fluctuations because the time-evolution of a wavefunction is dependent on the Hamiltonian of a system by Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle. \quad (1.1)$$

The Hamiltonian and initial quantum state $|\psi(0)\rangle$ are the parameters controlled to quantum compute. The information which one desires to compute over is encoded into a qubit state which becomes $|\psi_0\rangle$, and the physical system is programmed so that H evolves $|\psi_0\rangle$ to a state that, when measured, gives the desired output with high probability. Since outside noise perturbs H , the initial quantum state will evolve differently based on how much noise it is exposed to and what that noise looks like. This process of a quantum state evolving to an unknown state over time is termed quantum **decoherence**.

The larger a quantum system, the more difficult it is to isolate from its environment, and hence the faster decoherence occurs. Because the only differences between classical and quantum computation are the properties of superposition and entanglement, decoherence can completely diminish the relative advantage of quantum computing. Decoherence is the fundamental obstacle to building a large (and functional) quantum computer.

1.2 A Proposal for Silicon Quantum Computing

1.2.1 Kane's Model

The term **coherent** is used to describe a qubit that is "in the state it's supposed to be in"—i.e., one that has not been decohered by its environment. In 2014, Muhonen et al. measured coherence times of 30 seconds for nuclear-spin states and 0.5 seconds for electron-spin states of isotopically pure phosphorous (^{31}P) in an isotopically pure silicon (^{28}Si) lattice (denoted Si:P) [21]. Since nuclear states can be made so resistant to decoherence, they are a natural target for quantum computing applications.

Kane's proposed building a quantum computer which utilizes the nuclear spin states of an array of ^{31}P donors in Si:P as qubits. The main challenge in using

nuclear spins for quantum computation is measuring the spin states. Kane circumvents this issue by transferring nuclear spin polarization to the valence electron spin state of ^{31}P via the hyperfine interaction. Further, in semiconductors the donor electron wavefunction permeates significant distance through the crystal lattice [9]. This implies that two nuclear spin states could interact with the same electron spin state, manifesting in what Kane terms "electron-mediated" nuclear spin coupling. The strength of the hyperfine interaction can be controlled by applying a voltage to pull the electron wavefunction away from the nucleus (to which it is attracted if the donor is positively charged without the electron) [9]. Similarly, Loss and DiVincenzo famously showed that electron-mediated nuclear coupling can be turned on and off with external electromagnetic fields [16].

Kane suggested that a constant, global microwave magnetic field B_{AC} could be used to flip nuclear-spins at resonance [9]. The mechanism tunes qubits into resonance by creating a local change in electric field through "A-gates", which induces a Stark shift of the quantum state's energies [15]. Because quantum gate operations are required to be unitary (i.e. reversible) transformations on qubits, we require that electrons in the ground-state are non-degenerate. This is accomplished by applying a constant global magnetic field B_0 [9]. Figure 1.1 depicts the original Kane architecture with two qubits. The A gates in Figure 1.1 perform single-qubit operations on the nuclear-spin of a P donor.

But single qubit operations are not sufficient for universal quantum computation; some mechanism to control entanglement between multiple qubits is also necessary. Entanglement allows a quantum computer to store information "globally", in the sense that a measurement on one state can provide information about *all* the states it's entangled with. In order to perform two-qubit gate operations on nuclear-spin states, Kane's model scales the electron-electron interactions of neighboring P dopants via a "J-gate". The J-gate carries a variable electrostatic potential that controls the **exchange interaction** between neighboring indistinguishable electrons. Perturbation theory tells us that the interaction energy J between electrons is proportional to the wavefunction overlap, in addition to the interaction potential of the two states [17]. Thus, a stronger applied potential increases qubit coupling, while a weaker interaction potential reduces qubit coupling. If the potential $J = 0$ is applied, then the qubits do not interact and operate alone, meaning the A-gate can perform single-qubit operations [3].

1.2.2 Achievements to Date in Silicon Quantum Computing

Multiple groups have demonstrated coherent manipulation of single-electron spin qubits bound to phosphorous donors, as well as electrical state measurement through

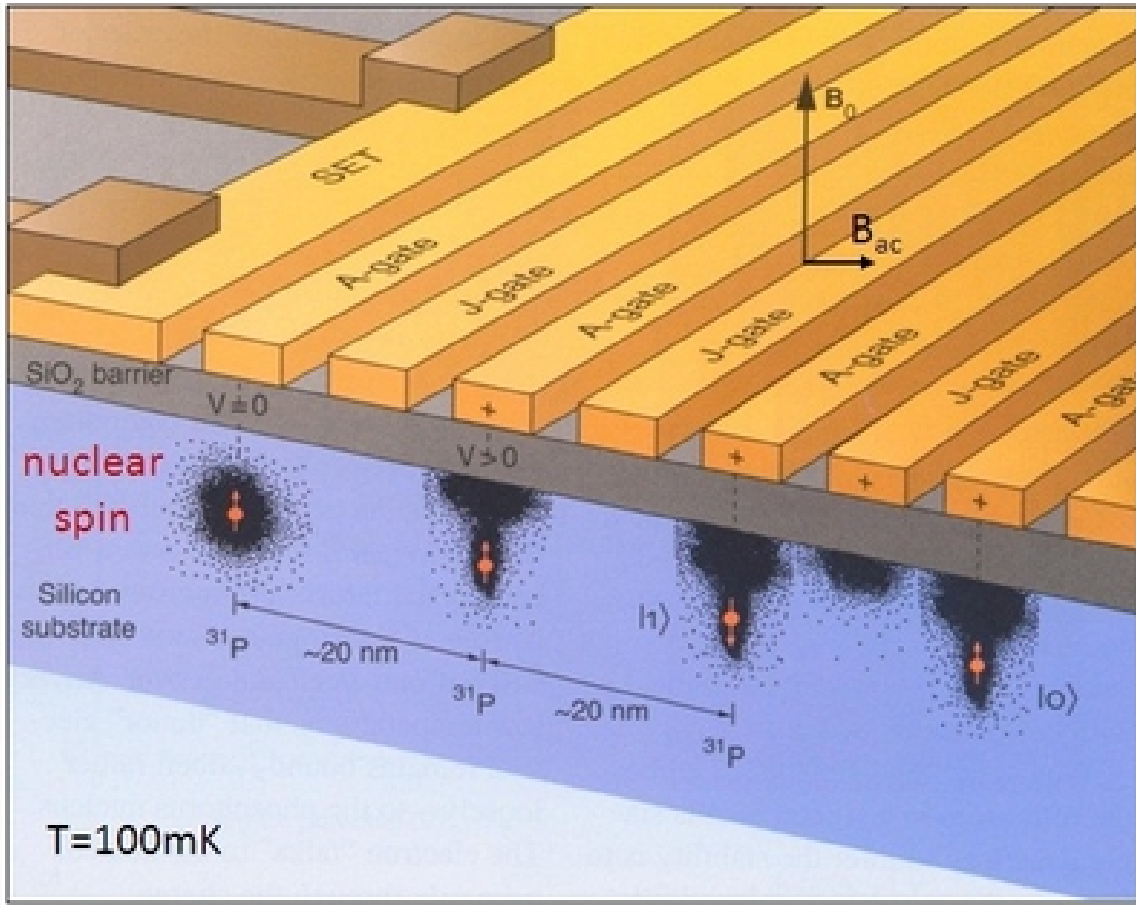


FIGURE 1.1: A cross-section of Kane's proposed architecture for silicon quantum computing. Adjacent donors are spaced apart by 20 nm. An insulating oxide layer is added on top of the ^{28}Si . The A gates carry voltage to alter the Larmor frequency of an individual donor, so there is one A gate above each dopant. The J gate carries a potential which draws adjacent donor electrons near each other to effect a spin-spin interaction; this implements two-qubit computer operations.

single-shot read out [23, 20, 19]. There are two popular approaches to state readout, but both techniques use a process termed spin-to-charge conversion. This involves electrostatically coupling and tunnel-coupling the donor electron to the **conductive island** of a single electron transistor (SET). This has been implemented successfully [20]. If the electron is in state $|\uparrow\rangle$, a current pulses through the SET; if not, no current passes through the SET.

As of 2015, A -gate control of electron and nuclear-spin states of ^{31}P in silicon has been demonstrated [15]. Further, a major roadblock of silicon-based quantum

computing is dopant placement. If there is any uncertainty around the defect's position, state manipulation and measurement will be thrown off due to an incorrect consideration of the Fermi contact interaction (discussed in Section 1.3.1.3). In 2012, Fuechsle et al. used a combination of scanning tunneling microscopy and hydrogen-resistant lithography to develop a single-atom transistor with a phosphorous dopant deterministically placed with a spatial accuracy of one lattice site [5].

There remain many obstacles to large-scale quantum computing, but these developments taken together suggest that Si:P architectures remain a viable medium for scalable quantum computing.

1.3 Project Goal

This thesis has two goals. The first is to present research progress in fulfillment of the physics degree at OSU. The second goal is to provide an introduction to density functional theory that is accessible to undergraduates studying physics, chemistry, or chemical engineering.

1.3.1 Research Goal

The research goal of this project is to write a workflow that can efficiently compute the donor wavefunction in silicon-based QC devices to high accuracy. This is desirable because it will allow researchers to simulate quantum gate operations on silicon donor qubits in a computationally efficient manner, helping to guide engineers and physicists in building programmable quantum architectures that are resistant to decoherence.

This work is a precursor to further research at Purdue University in the Nano-electronic Modeling Group. I use the highly accurate, but computationally slow, method of density functional theory (DFT) to compute the donor wavefunction of a small (109 atom) single qubit silicon device (the nanocluster in Figure 1.2). These wavefunction data are intended to be used for optimizing the much less accurate, but *fast*, technique of tight-binding in the NEMO-3D software created by the Nano-electronic Modeling Group for calculating the electronic structure of Si:P quantum devices.

1.3.1.1 Methods Summary

Density functional theory (DFT) is a mathematical formalism for finding an approximate ground-state wavefunction (from quantum mechanics) for many-body systems, say of N electrons and M atomic nuclei (not in general identical). The equation for finding wavefunctions of atomic systems is the eigenvalue equation,

$$H|\psi\rangle = E|\psi\rangle, \quad (1.2)$$

where H is a Hamiltonian operator (i.e. energy landscape operator), E is an energy eigenvalue of the Hamiltonian, and $|\psi\rangle$ is the wavefunction of the system being modeled [11]. I use a software implementation of DFT called Vienna *ab-initio* Simulation Package (VASP) to calculate the wavefunction of a phosphorous valence electron for a phosphorous dopant in an isotopically pure silicon lattice, a well-known semiconductor material. This work is done with a quantum computing group at Oak Ridge National Laboratory whose goal is to create a computational workflow for modeling quantum computing operations efficiently [8]. In the quantum computing regime this work is focused on, one important operation is using external electromagnetic field variations to change the spin of the phosphorous valence electron [8]. This is really an operation on the electron's wavefunction, and so I also analyze the wavefunction and charge density outputs of VASP to decide whether or not they are accurate enough approximations to be used in the proposed computational workflow.

1.3.1.2 Accuracy Requirements

Figuring out the degree of accuracy necessary to effectively model Si-based quantum computers is nontrivial, and it is not clear that there is any quantitative way to put an exact bound on it. The consequence of interest is error-propagation throughout a quantum computer. We can see immediately that errors will indeed propagate from the Schrödinger equation (Eq. 1.1) with a linear approximation:

$$|\psi(t + \Delta t)\rangle \approx (I + \frac{-i\Delta t}{\hbar}H) |\psi(t)\rangle$$

since quantum gate operations are dictated by the Hamiltonian as discussed briefly in Subsection 1.1.1.

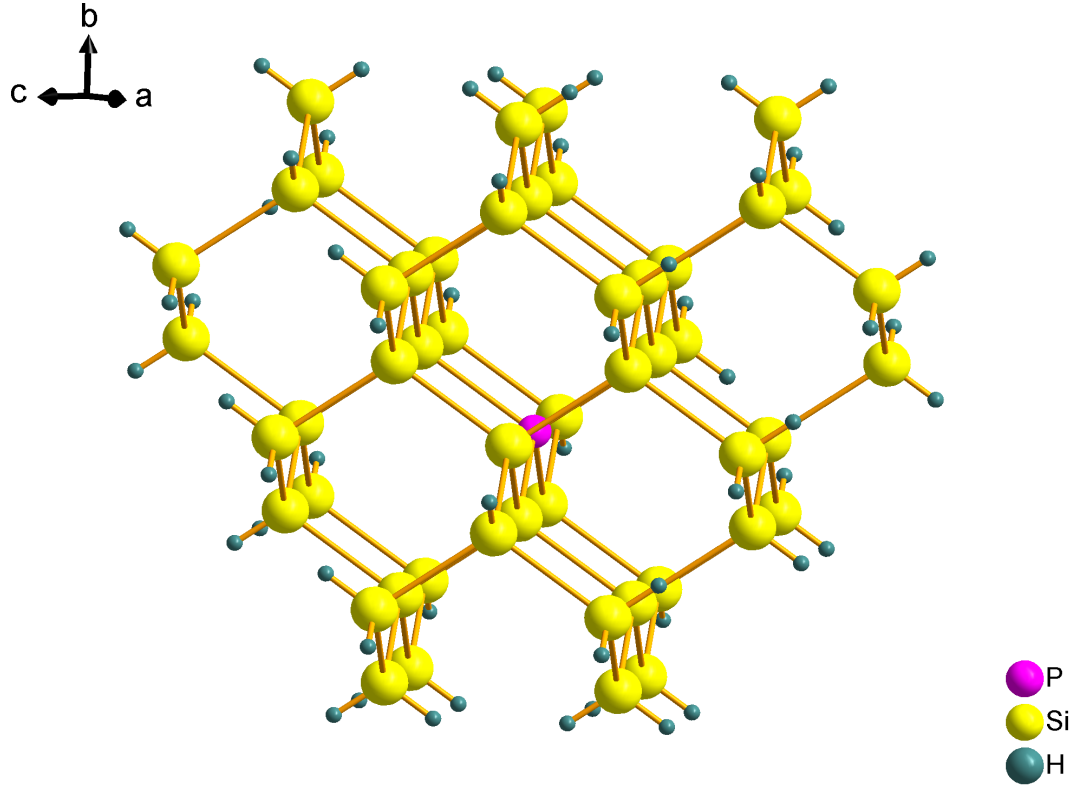


FIGURE 1.2: A 1.08 nm radius single donor quantum "device". The cluster is hydrogen-passivated all around in order to stabilize the surface. Si bulk has a face-centered cubic crystal structure.

1.3.1.3 Simulating Kane's Model

It is more instructive to analyze errors in the physical quantities that play important roles in silicon qubit devices. One such quantity is the hyperfine splitting (HFS), the most significant quantity in nuclear spin-electron spin interactions for the Si:P qubit. The isotropic HFS, or **Fermi contact interaction**, is the magnetic interaction between an electron and nucleus when the electron happens to be *in* the nucleus. This interaction is proportional to the **spin density** on the donor atom, where spin density is the difference between the spin-up ($\rho_{\uparrow}(r)$) and spin-down ($\rho_{\downarrow}(r)$) electron states. If $\psi(r)$ is the electron wavefunction, then this difference may be approximated simply by the density of unpaired electrons $|\psi(r)|^2$ bound to the donor atom [8]. In standard units, the isotropic HFS becomes

$$A_{iso} = -\frac{2}{3}\mu_0 \langle \boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_e \rangle [\rho_{\uparrow}(r_0) - \rho_{\downarrow}(r_0)] \approx -\frac{2}{3}\mu_0 \langle \boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_e \rangle |\psi(r_0)|^2 \quad (1.3)$$

where μ_n is the nuclear magnetic moment, μ_e is the electron magnetic moment, and r_0 is the nucleus/donor position.

Turning back to Kane's proposal, a single-donor qubit gate operation is described by the electron and nuclear spin state interaction and the applied electro-magnetic fields as represented by the time-dependent Hamiltonian

$$H(t) = A_{iso}(t) \mathbf{S} \cdot \mathbf{I} + \gamma_e B_0 S_z - \gamma_n B_0 I_z + \gamma_e B_{AC} \cos(\omega t) S_x - \gamma_n B_{AC} \cos(\omega t) I_x \quad (1.4)$$

where $\mathbf{S}, \mathbf{I}, S_{x,z}, I_{x,z}, B_0, B_{AC}$ are the electron spin operator, the nuclear spin operator, the x, z -components of $\mathbf{S}$, the same of $\mathbf{I}$, the globally applied DC magnetic field, and the global oscillating magnetic field respectively [8]. The constants γ_e and γ_n are the gyromagnetic ratios of the electron and nucleus respectively. $A_{iso}(t)$ is simply the time-dependent version of Eq. 1.3, equal to

$$A_{iso}(t) = -\frac{2}{3} \mu_0 \langle \mu_n \cdot \mu_e \rangle |\psi(r_0, t)|^2. \quad (1.5)$$

The isotropic HFS is important because transitions between the nuclear and electron spin states are induced when A_{iso} is set so that the energy gap between spin states equals (up to an $\hbar$) the frequency ω at which the field B_{AC} is driving the spin qubits. Recall that $A_{iso}(t)$ can be controlled by changing $|\psi(r_0, t)|^2$ with the A -gate in Kane's model.

It follows that we need accurate computations of A_{iso} if our goal is to eventually simulate the Hamiltonian $H(t)$ on many qubits, and this implies we need accurate calculations of the unpaired electron charge density at the ^{31}P nucleus core.

1.3.1.4 Density Functional Theory vs. Tight-Binding

Density functional theory and tight-binding are both widely used for calculating the electronic structures of materials, but they excel in different domains. DFT is a first-principles method based on an approximation to the many-bodied Schrödinger equation, and is considered the most accurate technique for chemical modeling [11]. Tight-binding is based on the assumption that electrons are "tightly-bound" to their nuclei, requiring that there are little to no electron interactions with external states or potentials, and thus approximating electron wavefunctions as linear combinations of atomic orbitals of a free atom [26].

Compared to DFT, tight-binding is very fast and can therefore model much

larger systems of atoms. The cost of this increased efficiency is a loss in accuracy. Where physical details are lost due to the tight-binding approximation, DFT can provide those details with its first-principles calculations. Defining N_e to be the number of electrons in a system, the time complexity of DFT algorithms scales like $\mathcal{O}(N_e^3)$, due foremost to the fact that matrix diagonalization has this complexity. With the strength of today's computing resources, DFT is feasible for systems of up to $\sim 10,000$ electrons in size, but becomes unfeasible thereafter [10, 18]. Tight-binding can model upwards of 1 million atoms.

An ideal computational workflow can handle the large systems required to simulate a candidate quantum computing architecture (~ 1 million atoms), without compromising accuracy. Figure 4.4 highlights the discrepancy between DFT and tight-binding for calculating the electron density function (which is the wavefunction multiplied by its conjugate) of a donor electron qubit in a 3.26 nm length Si:P device.

1.3.1.5 Research Question

I am using a DFT implementation with periodic boundary conditions for calculating electron wavefunctions called Vienna *ab-initio* Simulation Package (VASP). The motivation for this is that one can efficiently simulate infinitely large Si:P crystal structures with a periodic approach, and since infinite crystals are an excellent model for realistic-sized crystals, a periodic DFT code might be able to efficiently simulate the electronic structure of a quantum computer based on Kane's model with millions of qubits. Thus my research question is:

Does VASP retain enough detail in its wavefunction calculations in order to be used for simulating Kane's model and qubit operations?

Chapter 2

Density Functional Theory & Band Theory

In this chapter, we introduce the main mathematical and computational tools used to compute wavefunction and electronic structure approximations.

2.1 DFT Formalism

Recall that the time-*independent* eigenvalue Schrödinger equation is

$$H |\psi\rangle = E |\psi\rangle. \quad (2.1)$$

The details of the Hamiltonian H depend upon the system one wishes to model. When modeling N electrons and M nuclei, the exact Hamiltonian is the sum of all kinetic energy and potential energy contributions,

$$H = V_{tot} + K_{tot}. \quad (2.2)$$

We can break K_{tot} into the separate kinetic energy contributions of electrons and nuclei respectively, giving

$$K_{tot} = K_e + K_{nuc} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2} \sum_{n=1}^M \frac{\nabla_n^2}{m_n}. \quad (2.3)$$

Similarly, we can write V_{tot} as the potential energy between all electrons, all nuclei, and all electron-nuclei interactions respectively:

$$V_{tot} = \sum_{i=1}^N \sum_{j=1}^i V_e(\mathbf{r}_i, \mathbf{r}_j) + \sum_{n=1}^M \sum_{l=1}^n V_Z(\mathbf{R}_n, \mathbf{R}_l) - \sum_{i=1}^N \sum_{n=1}^M V_{e,Z}(\mathbf{r}_i, \mathbf{R}_n). \quad (2.4)$$

Here, m_e is electron mass, m_n is the mass of nucleus n , and Z_n is the proton number of nucleus n . In the non-relativistic case, the interaction potentials V are Coulombic:

$$V_e(\mathbf{r}, \mathbf{r}') = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}, \quad V_Z(\mathbf{R}_n, \mathbf{R}_l) = \frac{e^2 Z_n Z_l}{4\pi\epsilon_0 |\mathbf{R}_n - \mathbf{R}_l|}, \quad (2.5)$$

$$V_{e,Z}(\mathbf{r}, \mathbf{R}) = \frac{e^2 Z_n}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R}|}. \quad (2.6)$$

For clarity, note that i indexes over each electron, n indexes over each nucleus in the system, and that $\mathbf{r}$ is used for electron positions whereas $\mathbf{R}$ is used to denote nucleus positions. The wavefunction is $3(N + M)$ -dimensional at this point, since $|\psi\rangle = |\psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M)\rangle$ and each $\mathbf{r}_i, \mathbf{R}_n$ is a 3-dimensional vector in Euclidean space.

One of the most important approximations for simplifying this Hamiltonian is the **Born-Oppenheimer approximation**. The Born-Oppenheimer approximation says that because nuclei move extremely slowly relative to electrons (due to their significantly greater mass), we may suppose the electrons move in a fixed field of nuclei, and hence that the kinetic energy contribution of the nuclei K_{nuc} is zero and the potential energy between nuclei is a constant, $E_{nuc} = \sum_{n=1}^M \sum_{l=1}^n V_Z(\mathbf{R}_n, \mathbf{R}_l)$.

Thus, the Hamiltonian for a general N -electron, M -nucleus system is approximated by

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j=1}^i V_e(\mathbf{r}_i, \mathbf{r}_j) - \sum_{i=1}^N \sum_{n=1}^M V_{e,Z}(\mathbf{r}_i, \mathbf{R}_n) + E_{nuc} \quad (2.7)$$

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j} |\mathbf{r}_i - \mathbf{r}_j|^{-1} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{n=1}^M \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} + E_{nuc}. \quad (2.8)$$

We have partitioned the Hamiltonian into its electronic sub-Hamiltonian H_{elec} and its nuclear sub-Hamiltonian H_{nuc} , where $H_{nuc} = E_{nuc}$ is constant due to the Born-Oppenheimer approximation. Thus, computing $H|\psi\rangle$ has been reduced to computing $H_{elec}|\psi\rangle$. We focus on the electronic contribution from here on out.

2.1.1 Finding the Ground-State

Finding the ground-state of the quantum system we've been analyzing is of fundamental importance to chemists and physicists because it corresponds to the most stable and hence most likely state that we will find the system in within the real world. Density functional theory focuses on the *charge density* as the central quantity, rather than on the wavefunction as perturbation methods might. A result that provides the groundwork for a computationally feasible method to find the ground-state is the Hohenberg-Kohn Theorem.

Definition 2.1.1. A *functional* is a linear mapping from a vector space to its scalar field.

The Hilbert space $\mathcal{H}$ in which wavefunctions live in is a vector space, so we can think of a functional in this context as a linear transformation which maps wavefunctions to scalars. Similarly, a linear transformation from Euclidean three-space to the real numbers is also a functional.

Theorem 2.1.1 (Hohenberg-Kohn Theorem). *Up to a constant, the ground-state energy of H is a **unique** functional of the ground-state electron density.*

For our system, the electron charge density is given by

$$\rho(\mathbf{r}) = N \int |\psi_{elec}(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N, \quad (2.9)$$

which integrates over all but one spacial vector to give a 3-dimensional charge density. Thus, the Hohenberg-Kohn Theorem says that, up to a constant, there is only one linear mapping from the space of 3-dimensional electron charge densities to the space of energy values which correctly maps the ground-state electron density to the ground-state energy, and maps any other electron density to higher energy values. This is important, because it admits the **variational principle** (sometimes referred to as the Second Hohenberg-Kohn Theorem). Namely, if the energy functional is applied to an electron density that does not minimize the functional, then it cannot be the ground-state density.

It is helpful to write

$$H_{elec} = K + U + V \quad (2.10)$$

where

$$K \equiv -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2, \quad U \equiv \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{j=1}^i |\mathbf{r}_i - \mathbf{r}_j|^{-1}, \quad (2.11)$$

$$V \equiv -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{n=1}^M Z_n |\mathbf{r}_i - \mathbf{R}_n|^{-1}. \quad (2.12)$$

for the electron kinetic energy, electron-electron repulsion potential, and electron-nucleus attraction terms respectively. Because K and U are dependent only on the electron configuration and not the nuclei positions, charges, or masses, the Hohenberg-Kohn theorem implies that V is uniquely determined by the charge density ρ as well. Thus, no two different electron-nucleus potential fields V and V' can give rise to the same ground charge density (unless they differ only by a constant). This suggests that we can find a 3-dimensional function that gives the same ground-state energy and charge density as the $3N$ -dimensional Hamiltonian from Eq. 2.7. Finding a 3-dimensional function ρ which minimizes the energy is easier than finding a $3N$ -dimensional function that minimizes the energy, which is why this theorem is important.

Recalling that expected energy of a quantum state is $E = \langle \psi | H | \psi \rangle$, we can make a few simplifications for the ground-state energy E_0 . Note that $\langle \psi | H | \psi \rangle = \int \psi^* H \psi d^3\mathbf{r}$, so that the total electronic energy is

$$E_{elec} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \int \psi^* \nabla_i^2 \psi d^3\mathbf{r} + \frac{e^2}{2 \cdot 4\pi\epsilon_0} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' - \frac{e^2}{4\pi\epsilon_0} \sum_{n=1}^M Z_n \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_n|} d\mathbf{r}. \quad (2.13)$$

The new factor of $\frac{1}{2}$ in the second term comes from the double-counting of Coulombic repulsion in the double integral (termed the **Hartree energy**).

2.1.2 Kohn-Sham Equations

There is another powerful approximation we can make to simplify the many-body Hamiltonian above called the **mean-field approximation**. This approximation relies on the notion from mean field theory (or self-consistent field theory) which says that many interactions to one body can be replaced with an average or effective interaction. In the context of our many-bodied Hamiltonian (Eq. 2.7), this

means we replace the complicated potential

$$V = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{n=1}^M Z_n |\mathbf{r}_i - \mathbf{R}_n|^{-1} \quad (2.14)$$

with a much simpler "mean field" effective potential V_{eff} .

The motivation for this approximation lays in the fact that it is computationally very difficult to explicitly compute the true many-bodied potential V , due to the combinatorial property that NM Coulombic interactions must be computed *every time* an algorithm needs to calculate an energy value.

Physically, the mean-field approximation amounts to assuming that each electron experiences an equivalent effective potential, and, crucially, that there are *no other electron-electron interactions*. This lets us write the electron wavefunction as

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \varphi_1(\mathbf{r}_1) \varphi_2(\mathbf{r}_2) \cdots \varphi_N(\mathbf{r}_N), \quad (2.15)$$

where each single-electron wavefunction (or **orbital**) $\varphi_i(\mathbf{r})$ satisfies the single electron Hamiltonian

$$H_e \varphi_i(\mathbf{r}) = \left(\frac{p^2}{2m} + V_{\text{eff}} \right) \varphi_i(\mathbf{r}) = E_i \varphi_i(\mathbf{r}), \quad (2.16)$$

where the electron density must satisfy

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2. \quad (2.17)$$

Together, these are the **Kohn-Sham equations** [12].

Due to the **fungibility** of electrons, any permutation of electron positions $\mathbf{r}_1, \dots, \mathbf{r}_N$ in the above single-electron wavefunctions is also a valid one. Thus we must take the quantum mechanical approach of writing $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ as a superposition or linear combination of all such possible permutations of orbitals. Taking into account the **Pauli exclusion principle** for fermions, which says that particles with half-integer spin cannot occupy the same quantum state within a quantum system, we require moreover that the wavefunction is *antisymmetric*. In the two-particle case, this means we need

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1) \quad (2.18)$$

so that the same state cannot be occupied by more than one fermion. We can then write $\psi(\mathbf{r}_1, \mathbf{r}_2)$ as the following linear combination to satisfy Pauli exclusion:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) - \varphi_1(\mathbf{r}_2)\varphi_2(\mathbf{r}_1)). \quad (2.19)$$

In general, the linear combination of permutations of indistinguishable states that we will use to approximate the N electron wavefunction $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ can be written as a determinant, called the **Slater determinant**. It is defined as

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}. \quad (2.20)$$

This approach reduces calculating the total electron Hamiltonian H_{elec} to solving the much easier single-electron Hamiltonian H_e N times, and will help explain a simplification for crystal modeling in the next section.

Since **bosons** do not follow the Pauli exclusion principle, a many-body boson wavefunction $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ obeys the symmetry condition

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) = \cdots = \Psi(\mathbf{r}_N, \mathbf{r}_{N-1}, \dots, \mathbf{r}_1), \quad (2.21)$$

which is to say that permuting any of the coordinate variables does *not* change the sign of the wavefunction, because bosons are allowed to occupy the same states and the wavefunction does not have to cancel to zero in that case. An interesting discussion of the computational consequences of this fact is included in [Appendix B](#).

The **Kohn-Sham wavefunction** is a single Slater determinant of the set of orbitals which are the lowest energy solutions to the effective orbital Hamiltonian in [Eq. 2.16](#).

2.1.2.1 The Functional

Thus far, the conditions we have shown for the many-body quantum mechanical Hamiltonian amount to the **Hartree-Fock approximation**; this is not yet density functional theory. The key insight that Kohn and Sham made is that we can circumvent the errors from the Hartree-Fock method by introducing a new unknown term called the **exchange-correlation functional**, E_{xc} . The exchange-correlation

term is *defined* by the equality

$$E[\rho] = K_s[\rho] + E_e[\rho] + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d^3\mathbf{r} + E_{xc}[\rho] \quad (2.22)$$

$$\begin{aligned} &= -\frac{\hbar^2}{2m} \sum_{i=1}^N \int \varphi_i^* \nabla^2 \varphi_i d^3\mathbf{r} + \frac{e^2}{2 \cdot 4\pi\epsilon_0} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \\ &\quad - \frac{e^2}{4\pi\epsilon_0} \sum_{n=1}^M Z_n \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_n|} d\mathbf{r} + E_{xc}[\rho], \end{aligned} \quad (2.23)$$

where K_s is the sum of the kinetic energy of each orbital φ_i , E_e is the Coulombic (or Hartree) energy term, and V_{ext} is the "external potential" that each electron feels (normally just the Coulombic potential due to the stationary nucleus field, i.e. Eq. 2.12).

Note that without E_{xc} this equation would not be correct because, in general,

$$\langle \psi | K_e | \psi \rangle = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \int \psi^* \nabla_i^2 \psi d^3\mathbf{r} \neq -\frac{\hbar^2}{2m} \sum_{i=1}^N \int \varphi_i^* \nabla^2 \varphi_i d^3\mathbf{r}. \quad (2.24)$$

Thus we define $E_{xc}[\rho] \equiv \langle \psi | K_e | \psi \rangle - K_s[\rho]$, where $K_s[\rho]$ is the sum of non-interacting orbital kinetic energies and $\langle \psi | K_e | \psi \rangle$ is the true wavefunction's kinetic energy.

$E[\rho]$ is the "functional" in density functional theory.

2.1.2.2 Exchange-Correlation Factors

There are many different exchange-correlation functionals used in DFT, some of the most popular being the local-density approximations (LDA) the generalized gradient approximations (GGA). The LDA functional is based on considering a homogeneous electron gas system of fixed density against a positive background charge which keeps the system neutral. This yields an analytical expression for the LDA exchange-correlation functional [22],

$$E_{xc}^{\text{LDA}} = -\frac{3}{4} \left(\frac{3}{\pi} \right) \int \rho(\mathbf{r})^{4/3} d\mathbf{r}. \quad (2.25)$$

The LDA and GGA approximations are successful in many domains, but often fail to give correct band gap values. So called **hybrid functionals** are defined as linear combinations of certain LDA and GGA functionals, and some are known to calculate correct band gaps for specific materials.

2.2 Band Structures and Conduction Band Minima

An important symmetry within crystals is invariance under certain translations. This is termed **translational symmetry**. Similarly, many crystals also have some rotational and reflection symmetries, for which group-theoretic considerations are required (and which we will not discuss here).

The following sections on Bloch states and electronic band structures use explanations adapted from *Fundamentals of Semiconductors* [30].

2.2.1 Bloch Functions

When a particle resides in a periodic potential V , its wavefunctions can be written as a linear combination of **Bloch functions**. Particles in large crystals reside in such an approximately periodic potential ("approximately" because real crystals are not infinite and near the surface this breaks down). Suppose the mean-field potential from the single-electron Hamiltonian in Eq. 2.16 represents a one-dimensional crystal lattice potential with a translational period of R , so that $V(x) = V(x + nR)$ for all integers n . We can understand Bloch functions by defining a translation operator T_R which maps any function $f(x)$ to

$$T_R f(x) = f(x + R). \quad (2.26)$$

Now we define a function $\varphi_k(x)$ by

$$\varphi_k(x) = u_k(x)e^{ikx} \quad (2.27)$$

where $u_k(x)$ is a function with the same periodicity as the potential V , so that $u_k(x) = u_k(x + nR)$ for all n . If we multiply $\varphi_k(x)$ by $e^{-i\omega t}$, we will have a plane wave whose magnitude is modulated by the periodic function $u_k(x)$. We call $\varphi_k(x)$ a Bloch function, which by definition of our operator satisfies

$$T_R \varphi_k(x) = \varphi_k(x + R) = e^{ikR} \varphi_k(x). \quad (2.28)$$

This implies that $\varphi_k(x)$ is an eigenfunction of T_R with eigenvalue e^{ikR} . Since H_e is invariant under spacial translation, the Hamiltonian commutes with T_R . It follows from quantum mechanics that the eigenfunctions of T_R form a basis for the eigenspace of H_e . Therefore any wavefunction $\varphi(x)$ that is an eigenstate of H_e can

be written as a sum of Bloch functions

$$\varphi(x) = \sum_k c_k \varphi_k(x) = \sum_k c_k e^{ikx} u_k(x) \quad (2.29)$$

where $\{c_k\}$ are complex constants. Extrapolating from this 1-dimensional case, we find that 3-dimensional single-electron wavefunctions can also be written as linear combinations of Bloch functions, but that they are indexed by 3-dimensional **wave vectors** $\vec{k}$ rather than scalars k . An energy plot of a state such as that in Eq. 2.29 versus $\vec{k}$ is termed the **electronic band structure** of the crystal that is being modeled.

This allows us to write the one-electron orbital solutions to the Kohn-Sham equations over a **plane wave basis set**.

2.2.2 Conduction Band Minima

The **conduction band** in a band structure is defined to be the lowest range of vacant electronic states at absolute zero temperature. Analogously, the conduction band is the first energy band directly above the **Fermi level**. The **conduction band minima** (c.b.m.) of a band structure are simply the energy minima along the conduction band in a crystal.

See Figure 2.1 for a visualization of a silicon crystal's six c.b.m.

2.3 Pseudopotentials

The true Coulombic potential creates electron wavefunctions that are highly oscillatory near ion cores, with many roots (or nodes). To describe these wavefunctions correctly, a large set of plane waves—or Fourier modes—is required. A **pseudopotential** is an effective potential made to replace the all-electron potential in the many-body electron Hamiltonian, with core states "frozen" so that only valence electron interactions must be computed explicitly. The potential from frozen core electrons is included together with the nuclei potential term.

By freezing non-valence electrons and requiring that pseudo-eigenstates and true all-electron eigenstates have the same energies and amplitudes outside a certain cut-off radius r_c from an ion core, the pseudopotential method provides faster algorithm convergence while retaining precise observable values on the large scale.

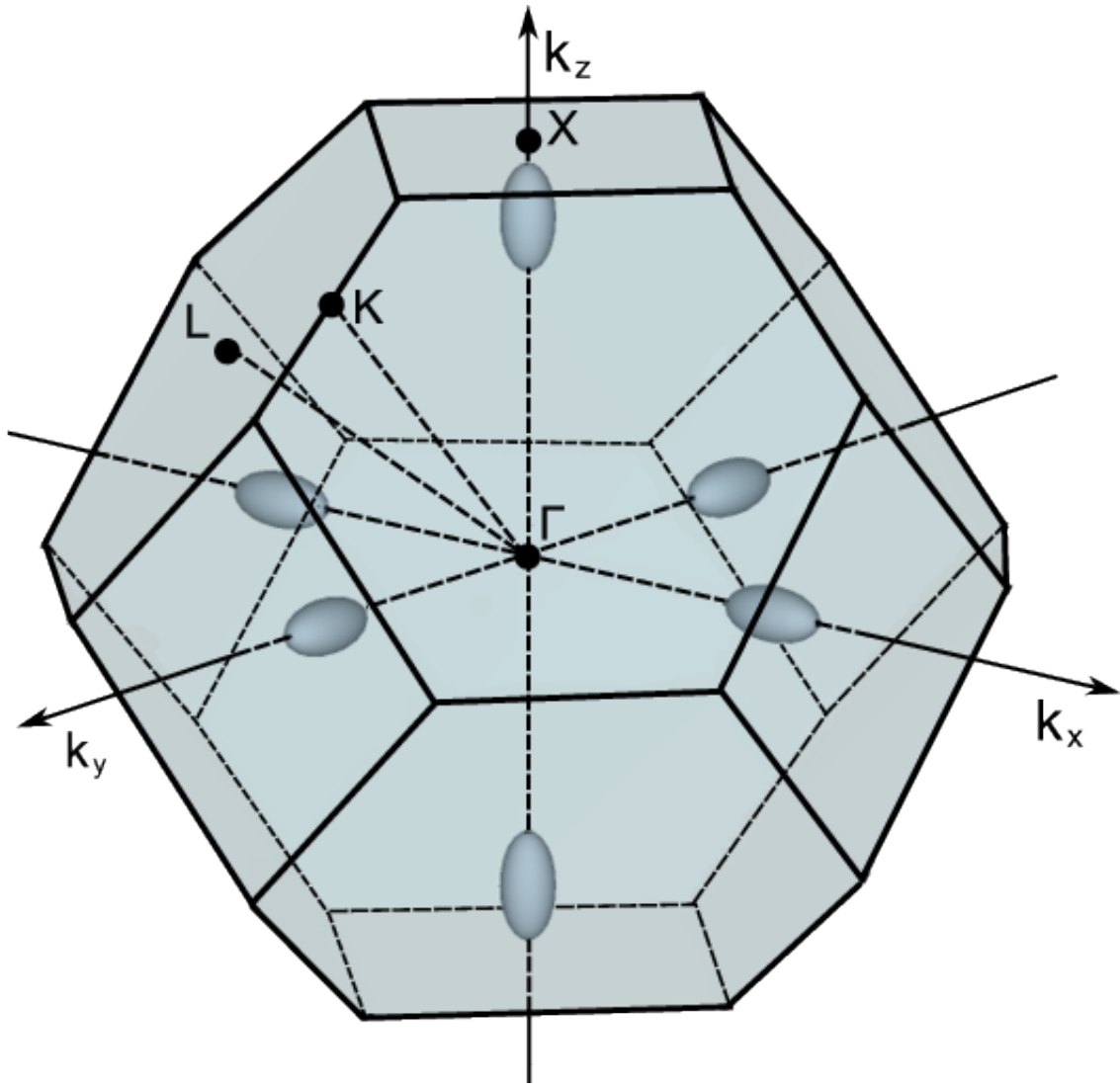


FIGURE 2.1: Six degenerate energy surfaces corresponding to the conduction band minima of an unstrained silicon lattice.

The Kohn-Sham equations need only be solved for valence electrons with this method, with a much smaller reciprocal space grid (i.e. fewer Fourier modes/-coefficients). As a side note, this also explains the neglect of relativistic effects in the Kohn-Sham equations, because relativistic effects are negligible on valence electrons [24].

The plane wave coefficients are computed in $\vec{k}$ -space (reciprocal space) because certain operations are much more efficient in this basis. For example, the orbital

kinetic energy operator is diagonal in this basis, due to the fact that

$$k = \frac{p}{\hbar} \quad (2.30)$$

where p is momentum. This reciprocal/momentum-space is also the Fourier space of the spacial model, which is why a consideration of the number of Fourier modes required to accurately describe a wavefunction is required. Integrals over real-space operators can be done efficiently using fast Fourier transforms.

The clear disadvantage of this method is that all information of the true electron wavefunction near nuclei is lost. This has negative consequences for the calculation of properties such as hyperfine parameters and forces within the cut-off radii.

2.3.1 The Projector Augmented-Wave Method

The project augmented-wave (PAW) method is a generalization of the pseudopotential method in DFT which makes similar inner-core approximations and gains the same computational speed-up while making it possible to recover the true wavefunction information within the cut-off radius around each ion. A complete description of this method is out of the scope of this thesis. See Carsten Rostgaard's paper for a self-contained explanation of the technique [24].

For this work, we just note that the DFT implementation utilized (VASP) uses the PAW method.

Chapter 3

Methodology

3.1 Vienna *ab-initio* Simulation Package

VASP is a computational DFT implementation for modeling molecular dynamics through plane wave electronic structure calculations.

3.1.1 Functionals Used

I use VASP with the LDA, GGA, B3LYP, and HSE06 functionals to compute wavefunctions and band structures of a pure silicon lattice. Motivated by the finding that the HSE06 hybrid function is the only one which computes the band gap of silicon correctly, I also use HSE06 in VASP when conducting the Si:P electronic structure calculations. The HSE06 hybrid functional uses Hartree-Fock exchange between electrons with PBE functional contributions [14].

3.1.2 VASP Inputs and Outputs

The inputs to VASP include the following four files:

- KPOINTS: a file listing the $\vec{k}$ -points to be used in the DFT calculation;
- POSCAR: a file defining the elements in the system with the coordinates of each atom (e.g. an array representing Figure 1.2);

- INCAR: a file controlling VASP parameters (such as which energy convergence algorithm to run, the energy convergence threshold, the energy cut-off dictating number of Fourier modes to use in computation, etc.);
- POTCAR: a file containing the element-specific pseudopotentials one would like to use for the DFT algorithm.

The output of VASP includes more files than it is instructive to include here. Instead, I focus on the files which are used in this research project. The two files of interest are

- OUTCAR: holds all the information necessary to construct a band structure plot based on the k -points that are provided for the DFT calculation;
- WAVECAR: a file written in binary that contains the plane wave coefficients of each electron orbital and its occupancy.

3.1.3 VASP Wavefunctions

As motivated in Chapter 2, VASP writes wavefunctions in terms of a plane wave basis. Thus an orbital from VASP is written as

$$\varphi_{\vec{k},\nu}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \left(\sum_{|\vec{G}| < G_{cut}} C_{\vec{G},\vec{k},\nu} \exp(i\vec{G} \cdot \mathbf{r}) \right) \exp(i\vec{k} \cdot \mathbf{r}) \quad (3.1)$$

where ν is the band number and with $\vec{k}$ specifies the state's energy, and G_{cut} is a cut-off magnitude for the basis set size defined by the energy cut-off (E_{cut}) chosen, according to

$$G_{cut} \equiv \frac{1}{\hbar} \sqrt{2m_{eff}E_{cut}}. \quad (3.2)$$

3.1.4 Pseudo-Wavefunctions

Researchers working on workflow are interested in the wavefunctions and charge densities that an all-electron, periodic DFT code might output for Si:P of different sized clusters. The NWChem DFT calculation done in Figure 4.4 is closed boundary (non-periodic) and hence not realistic for any reasonably sized Si:P system. Our group is interested in periodic DFT codes for this reason. Moreover, VASP utilizes the projector-augmented wave (PAW) formalism for its DFT calculations.

This involves the use of *pseudo*-wavefunctions which are highly smoothed within a radius of 1-2 Å from the core of each ion. VASP uses the PAW method because it significantly speeds up computations (but unfortunately this fact also makes VASP unideal for calculating Si-donor qubits, a finding explained in more detail in the Discussion section).

3.2 Programming and Analyses

As part of this project, I wrote Python code and adapted Feenstra & Widom's WAVETRANS code¹ to read the WAVECAR file and output the wavefunction array in 3-space for any real-space mesh desired. My code computes a discrete Fourier transform from reciprocal space (the coefficients VASP outputs in the WAVECAR) to a generalized plane wave solution. This solution is the wavefunction.

My code for wavefunction extraction and visualization is available on GitHub.²

¹<https://www.andrew.cmu.edu/user/feenstra/wavetrans/>

²<https://github.com/almullay/WAVECAR-analysis/tree/master/VASP-wavefunction-visualization>

Chapter 4

Results & Analysis

To corroborate the analysis of my code, I compute wavefunctions and band structures of pure ^{28}Si bulk, the silicon band gap, and the Bloch states of crystalline silicon to compare to literature. Qualitative and quantitative comparisons are made. The P qubit charge density is compared to a similar plot computed by Dr. Jakowski and Dr. Mohiyaddin with NWChem (Figure 4.4). The overall agreement of results suggests that my wavefunction analysis program is working correctly. Despite this, I find that the smoothness approximation used in VASP for inner-core electron wavefunctions gives too much inaccuracy at positions which are important to simulating qubit interactions with external electromagnetic fields.

4.1 Results

4.1.1 Quantitative Comparison

Using the hybrid HSE06 functional in VASP, I computed a silicon semiconductor band gap of 1.15 eV at zero temperature, the band structure of Si bulk over energy bands 1 - 8 (Figure 4.1), wavefunctions and partial charge densities of Si c.b.m. states over silicon's unit cell (wavefunctions available in Appendix A), and the wavefunction and charge density of a single P defect valence electron in Si:P.

In agreement with Koiller et al.'s result, I found that five coefficients in each cbm wavefunction account for approximately 90% of each wavefunction's magnitude [13]. These coefficients correspond to the five reciprocal space indices

$$\vec{G} \in \left\{ \frac{2\pi}{a}(-1, \pm 1, \pm 1), \vec{0} \right\}$$

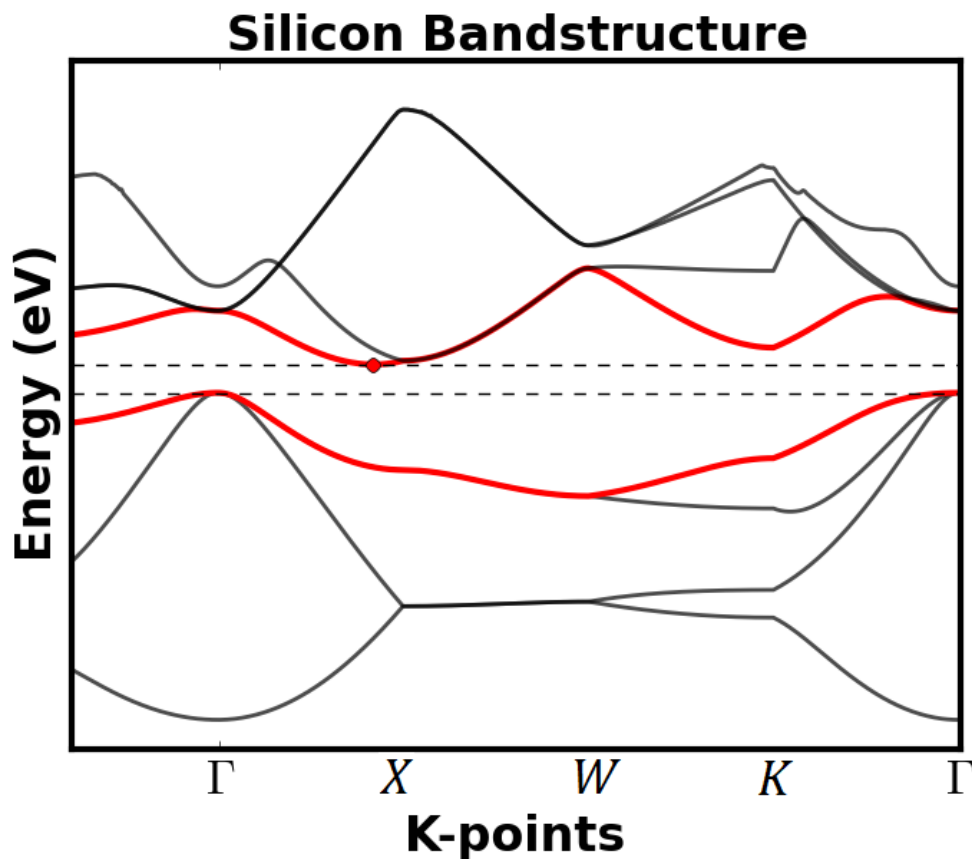


FIGURE 4.1: Si band structure computed with HSE06 hybrid functional in VASP. Valence band and conduction band are in red, with a red point at the conduction band minimum.

where $a = 5.431$ nm is silicon's lattice constant.

Figures ?? and 4.3a represent the charge density function of a phosphorous defect state's valence electron in 1.08 nm Si:P. Because VASP uses pseudo-wavefunctions (discussed in Section 3.1.4), I observe that Figure 4.3a is missing the peaks present in the NWChem DFT plot within Figure 4.4.

In verifying the scale of the wavefunctions calculated, I found that VASP's projector augmented-wave formalism is not norm-conserving (^{31}P valence electron density integrates to 1.03 rather than 1).

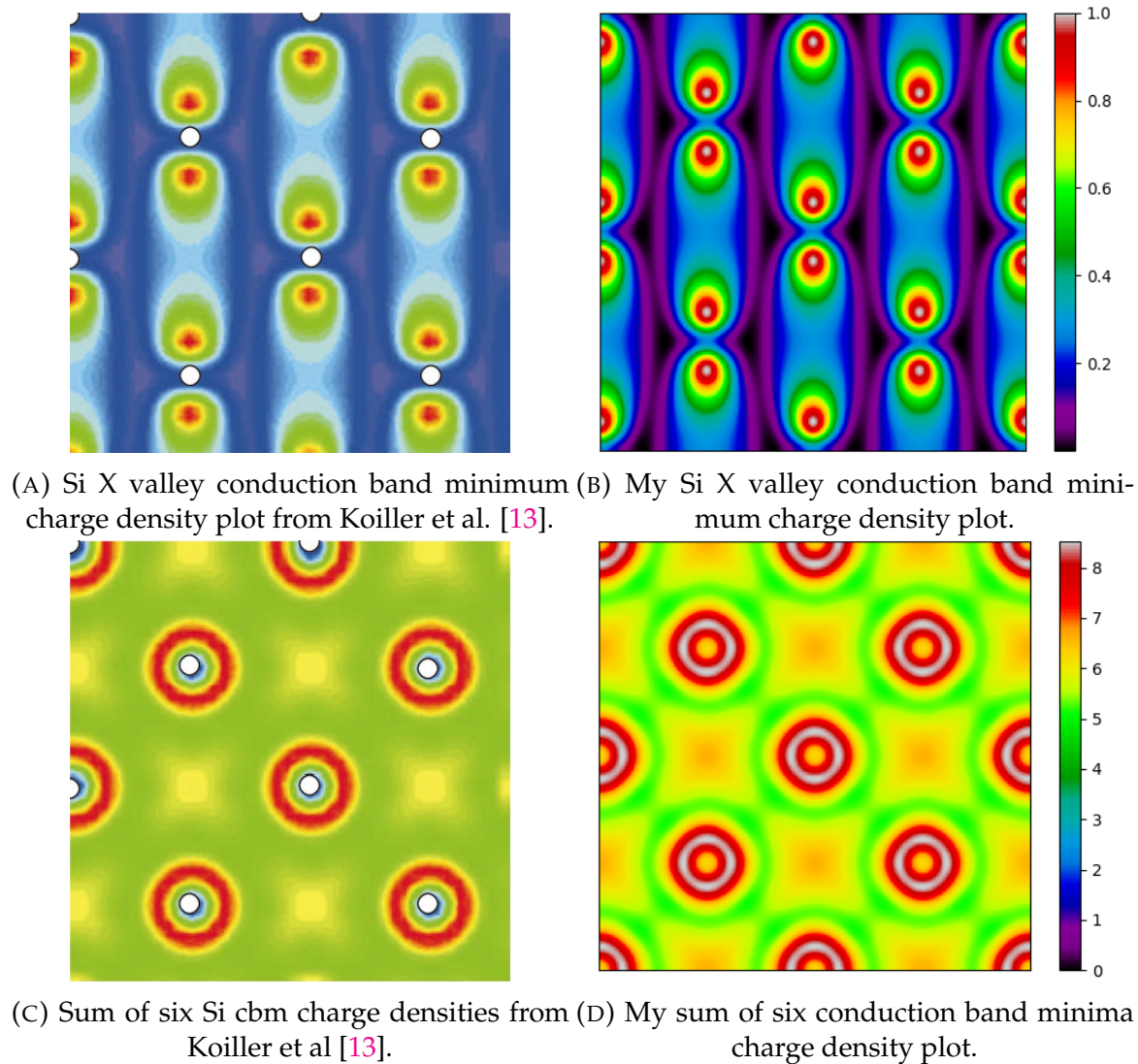


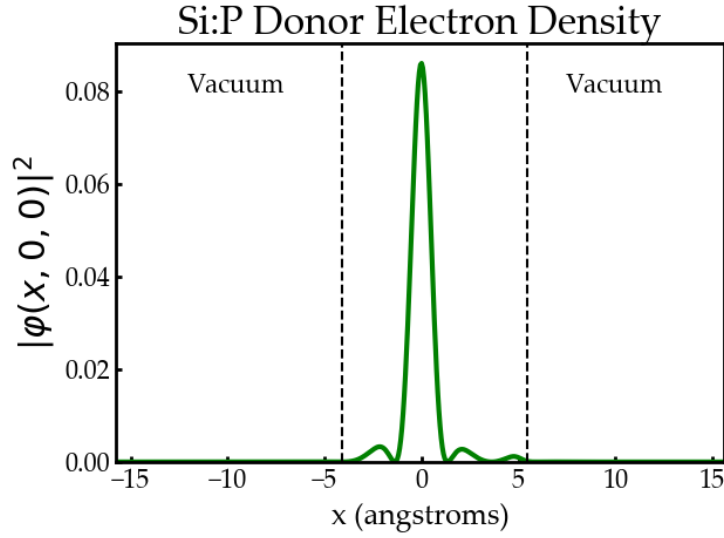
FIGURE 4.2: Though numerical data from Koiller et al. is unavailable, the charge map similarities suggests that my code is working correctly.

4.1.2 Qualitative Comparison

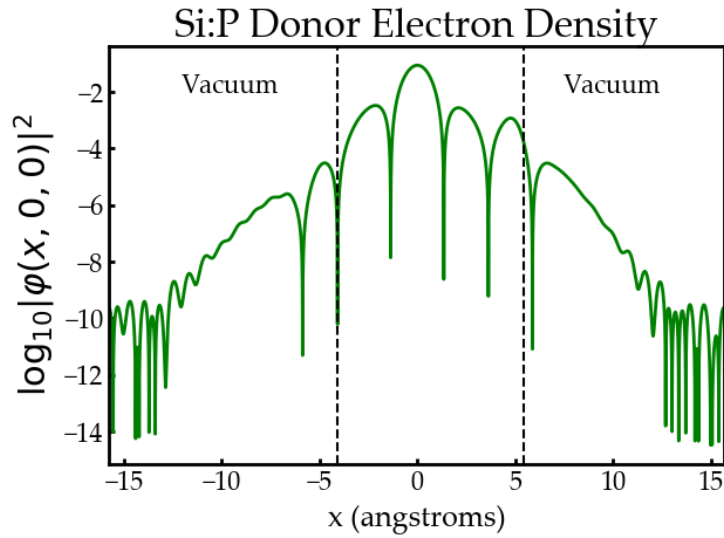
Koiller et al. computed partial charge density color maps in [13]. Figure 4.2 shows a comparison of my charge maps with Koiller et al.'s for the same states.

Gamble et al. have computed the Z valley conduction band minimum wave-function for Si bulk using VASP with an energy cutoff corresponding to 335 plane wave coefficients; see Figure 4.6b for their data [6]. My own calculation in VASP

for the same state used ~ 1000 plane wave coefficients. See Figure 4.6a for my Z valley c.b.m. state. Electron densities for the five other degenerate c.b.m. states are included in Appendix A.



(A) Dopant electron density



(B) Logarithmic electron density.

FIGURE 4.3: (A) is the electron density $|\varphi|^2$ plotted through the P donor at the highest occupied molecular orbital (P's valence electron). This is the quantum state to be used as the computational qubit for Kane's silicon-based quantum computing. (B) is Log base 10 version of Figure (A).

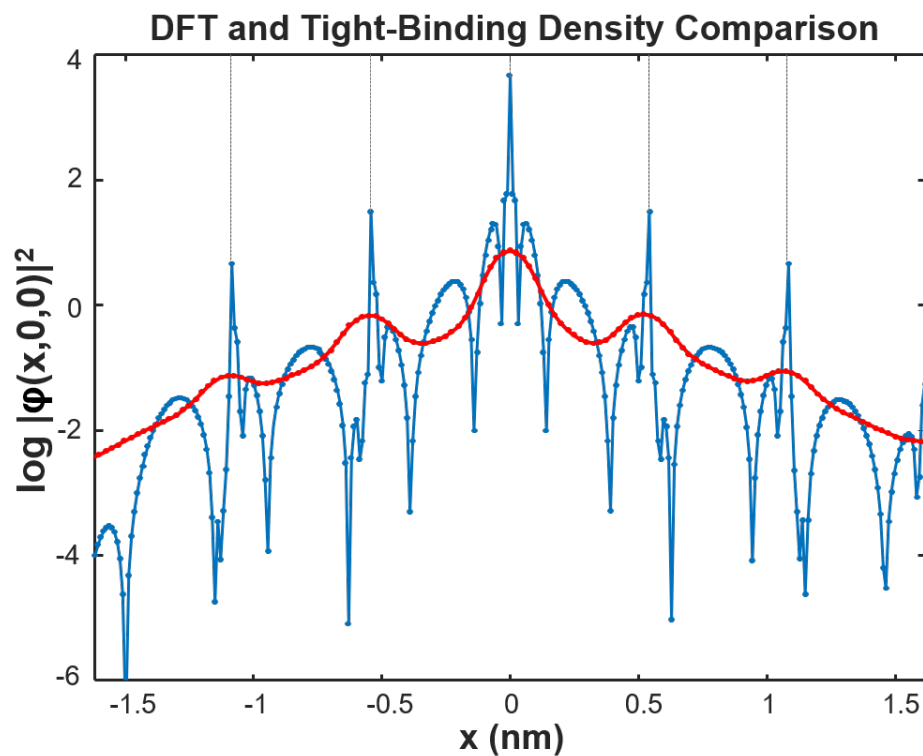
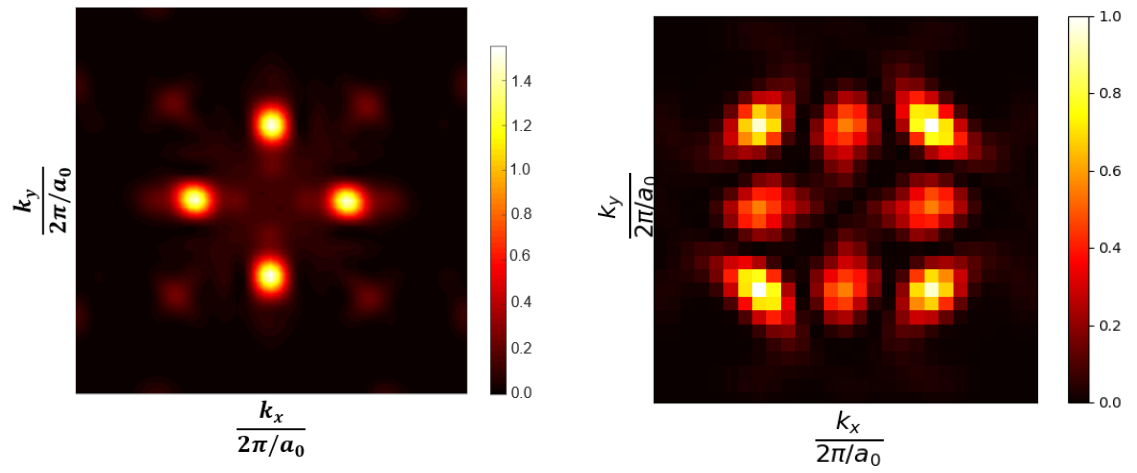
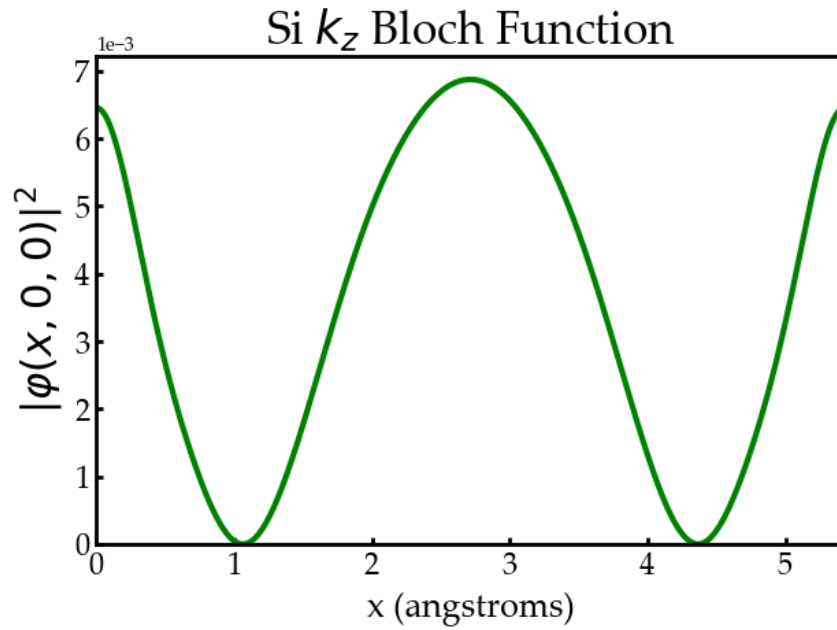


FIGURE 4.4: DFT calculation of P qubit electron density with the NWChem software. Tight-binding calculation of electron density done by the Nanoelectronic Modeling Group at Purdue with their NEMO-3D software. Sources: Dr. Fahd Mohiyaddin, Dr. Jacek Jakowski.

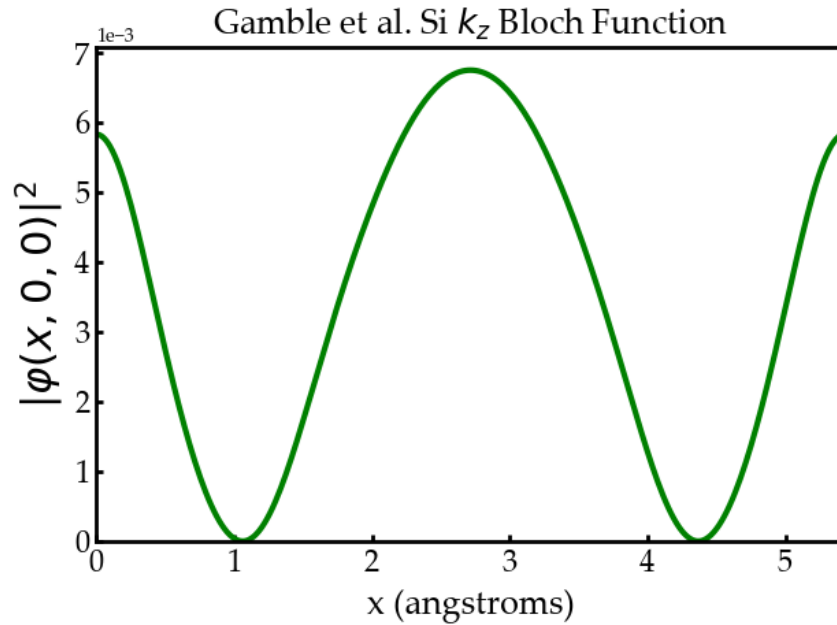


(A) Fourier Transformed tight-binding donor wavefunction. (B) Fourier transformed VASP DFT donor wavefunction.

FIGURE 4.5: Fourier representation comparison between DFT and tight-binding. Vertical and horizontal clusters represent Si c.b.m. contributions. Note that DFT picks up more than just c.b.m. plane waves.



(A) Wavefunction of Z valley c.b.m. computed with my code.



(B) Wavefunction of Z valley c.b.m. computed by Gamble et al. [6].

FIGURE 4.6: Horizontal axis is $\hat{x}$ -direction in unit cell. Green curve is electron density. Blue disks represent silicon ion positions along the $\hat{x}$ -direction. Curves are equivalent up to scale, which has not been confirmed yet.

4.2 Discussion & Conclusion

VASP utilizes the projector-augmented wave formalism for its DFT calculations. This involves the use of pseudo-wavefunctions which are highly smoothed within any radius on the order of 1-2 Å from the core of an ion. This is why the wavefunctions calculated in VASP for a Si:P nanocluster do not show the same order of magnitude or degree of oscillations as provided by the NWChem all-electron code. The main take-away is that one cannot use VASP to model accurate silicon qubit wavefunctions for the purpose of quantum computing simulations because VASP gives grossly smoothed wavefunction values at all nucleus positions as part of the projector-augmented wave approximation. Since an accurate charge density at the donor position is vital to computing the isotropic hyperfine interaction and hence the time-dependent Hamiltonian modeling single-qubit gate operations from Eq. 1.4, it is clear that any post-processing attempt to use VASP wavefunctions for this task will fail.

In principle, since VASP is based on the projector augmented-wave method, it is possible to recover the true electron wavefunctions from the pseudo-wavefunctions that VASP provides. This would require altering VASP's source code to provide the correction term, and is not considered a fruitful direction to move in.

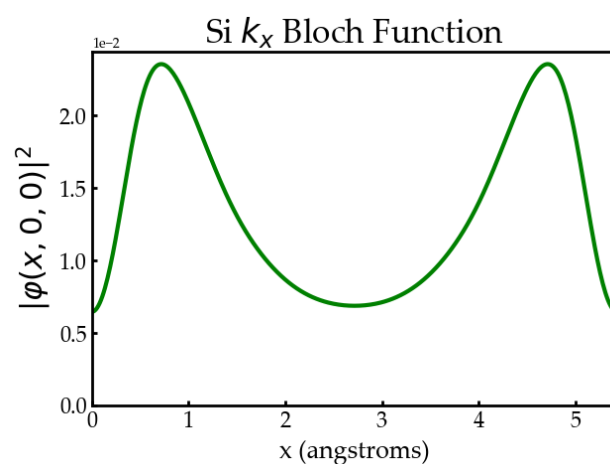
4.2.1 Future Work

The NWChem DFT calculation done for Figure 4.4 is closed boundary (non-periodic) and hence not realistic for any reasonably sized Si:P system. Our group is interested in periodic DFT codes because they can provide more realistic observables for large crystals. Thus our group is looking to analyze the wavefunctions and charge densities that all-electron, periodic DFT codes output for Si:P of different sized clusters—in particular, we'd like to find a code that accurately captures the peaks in the small nanocluster single qubit electron density provided by the NWChem calculation previously shown (Figure 4.4).

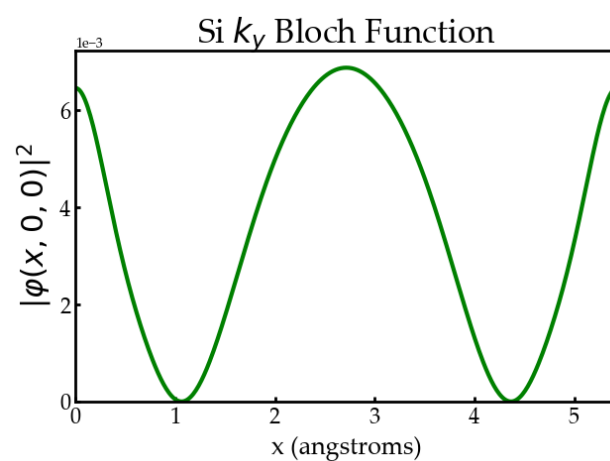
On the suggestion of Dr. Paul Kent, I am looking into linearised augmented plane-wave (LAPW) DFT codes as an alternative which can incorporate all-electron calculations and periodic boundary conditions. Our group at Oak Ridge National Laboratory is also working on a hybrid DFT/tight-binding code which might preserve efficiency and accuracy.

Appendix A

Silicon C.B.M. Wavefunctions



(A) Wavefunction of X valley c.b.m.



(B) Wavefunction of Y valley c.b.m.

FIGURE A.1: Horizontal axis is $\hat{x}$ -direction in unit cell. Green curve is electron density.

Appendix B

The Permanent & Bosonic Computers

In the case of indistinguishable bosons, the linear combination of states that is equated to the total wavefunction Ψ does not need the negative signs introduced by the Slater determinant, which describes a state of indistinguishable fermions that must obey the antisymmetry principle due to Pauli exclusion (see Section 2.1.2). The analogous construction representing bosons is called the **permanent**, a positive analog of the determinant. If A is an $n \times n$ matrix with elements a_{ij} , the permanent is defined as

$$\text{Perm}(A) = \sum_{\sigma \in S_n} \prod_{i=1}^n a_{i,\sigma(i)}. \quad (\text{B.1})$$

Here S_n is the set of permutations over n numbers, so each σ maps index i to some other index j in the matrix. Because all the indistinguishable wavefunctions are being added, a different normalization factor is required for bosons, and we turn out to get

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sqrt{\frac{\prod_{i=1}^N n_i!}{N!}} \text{Perm} \left(\begin{bmatrix} \varphi_1(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{bmatrix} \right), \quad (\text{B.2})$$

where $\{\varphi_i\}$ are single-boson wavefunctions, analogous to the single-electron orbitals from Eq. 2.16.

A final interesting fact is that the permanent function is incredibly difficult to compute. The study of its computation is important in theoretical computer science, and it has been shown that if we could compute the permanent in polynomial time, then we could also compute any problem in the entire **polynomial hierarchy** (an implication of the famous Toda's theorem) [29, 28]. If the reader is familiar

with the $\mathbf{P} = ?\mathbf{NP}$ Millennium prize problem, recall that the complexity class $\mathbf{NP}$ is the first level of the infinite polynomial hierarchy. It is suggested that if $\mathbf{P}$ is indeed equal to $\mathbf{NP}$, a philosophical repercussion would be the downfall of human creativity, due to subsequent advances in technology and efficient problem-solving that would render our brightest and most creative minds obsolete. In a similar vein, if we could create a **bosonic computer** to compute the permanent efficiently, then we could not only solve $\mathbf{NP}$ problems efficiently, but all problems in the polynomial hierarchy.

To get an idea of how bosonic computation might operate, think of preparing a known state of many photons whose probability amplitudes encode the elements of a matrix. Then a repeated construct-and-measure procedure could provide an approximation to $|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$, from which the value of $\text{Perm}(\dots)$ can be approximated by Eq. B.2. Practically, such a method must involve sampling approximate values of $|\text{Perm}(\dots)|^2$ rather than $\text{Perm}(\dots)$ directly. This introduces some limitations on the power of this computing model, made explicit by Scott Aaronson and Alex Arkhipov [1].

From the perspective of $\mathbf{NP}$, the next class up in the polynomial hierarchy ($\mathbf{NP}^{\mathbf{NP}}$) looks like $\mathbf{NP}$ does from the perspective of $\mathbf{P}$, which is to say that the computational gain from $\mathbf{P}$ to $\mathbf{NP}$ is similar to the gain from $\mathbf{NP}$ to $\mathbf{NP}^{\mathbf{NP}}$. This suggests that the world would look radically different as a consequence of the ability to efficiently compute the polynomial hierarchy, due largely to the argument provided above. Notably, constructions in the direction of bosonic computation have been attempted physically by experimentalists [27].

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