Atomistic First Principles Modeling of

Single Donor Spin-Qubit

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Abstract

Quantum technology is attracting great attention in academia, government institutions and policy-making bodies, as well as industry. Quantum technology includes quantum computing, quantum communication and quantum sensing. These technologies exploit the peculiarities of quantum physics to achieve very substantial performance gains over their classical counterparts. From the hardware point of view, the basic unit in a quantum computer is the qubit, implemented in controllable quantum two-level systems. Qubit also plays an important role in the repeaters of quantum internet. There are many ways to implement a physical qubit. The solid-state spinqubit is one of the most popular realizations, which uses the two spin states of the spin-1/2 particles. Typically, the spin-1/2 particle is confined in a gated semiconductor quantum dot or artificial atom whose linear dimension is a few tens to a few hundred nanometers. In a very interesting recent effort, researchers realized spin qubits based on donor impurities in crystal silicon. A donor impurity is a real atom, therefore the donor spin-qubit is in the atomic limit as far as the dimension is concerned. Just like the gated artificial atom, quantum transport in and out of the donor atom region is in the sequential tunneling regime where the physical quantity of importance is the addition energy which measures how much energy is required to add an electron into the qubit system. The addition energy is usually experimentally measured to map out the operational voltages of the spin-qubit devices.

In this work, we attempt to predict the addition energy of donor spin-qubits from atomistic first principles without any phenomenological parameters. To this end, our method proceeds in three steps. First, for a given donor spin-qubit structure, for instance, the phosphorus impurity in bulk silicon (P-in-Si), the single-particle Kohn-Sham eigenstates are self-consistently determined by density functional theory (DFT). Second, the Kohn-Sham eigenstates with low eigen-energies identified to be impurity states, are selected as the basis set for the exact diagonalization calculation of the many-body Hamiltonian of the qubit. Here, the identification of the localized impurity states is carefully carried out. Third, the many-body interaction energy is solved by exact diagonalization. As an example, we apply this first principles theoretical framework to the P-in-Si spin-qubit, the first principles addition energy is predicted to be 48.9 meV. This is in excellent quantitative consistency with the experimentally measured value of 47 ± 3 meV. Due to its first principles and atomistic nature, the theoretical framework established in this work can be applied to a broad range of materials for implementing spin-qubit devices.

Résumé

La technologie quantique suscite un grand intérêt dans le milieu universitaire, les institutions gouvernementales et le milieu politique ainsi que dans le secteur industriel. La technologie quantique englobe l'informatique quantique, la communication quantique et la détection quantique. Ces technologies exploitent les particularités de la physique quantique pour obtenir des gains de performance très significatifs par rapport à leurs équivalents classiques. Au niveau du matériel, l'unité de base d'un ordinateur quantique est le qubit; ce dernier est mis en œuvre dans des systèmes quantiques à deux niveaux contrôlables. Le qubit joue également un rôle important dans les répéteurs de l'internet quantique. Il existe de nombreuses façons de mettre en œuvre un qubit physique. Le qubit de spin à l'état solide est l'une des réalisations les plus populaires, utilisant les deux états de spin des particules de spin 1/2. En général, la particule de spin 1/2 est confinée à proximité d'une grille dans une boîte quantique semi-conducteur ou dans un atome artificiel dont la dimension linéaire est de quelques dizaines à quelques centaines de nanomètres. Dans de très intéressants travaux récemment réalisés, des chercheurs ont réalisé des qubits de spin à base d'impuretés donneuses dans du silicium cristallin. Une impureté donneuse est un véritable atome, et donc le qubit de spin donneur est dans la limite atomique en ce qui concerne la dimension. Tout comme l'atome artificiel à proximité d'une grille, le transport quantique au travers de l'atome donneur se fait dans le régime de la transition séquentielle o ù la quantité physique importante est l'énergie d'ajout, qui mesure la quantité d'énergie nécessaire pour ajouter un électron dans le système du qubit. L'énergie d'ajout est mesurée expérimentalement pour identifier les tensions de fonctionnement des dispositifs basés sur les qubits de spin.

Dans ce travail, nous tentons de prédire l'énergie d'ajout des qubits de spin donneurs à partir de premiers principes atomiques, sans aucun paramètre phénoménologique. Notre méthode a trois étapes. Premièrement, pour une structure de qubit de spin donneur donnée, par exemple l'impureté de phosphore dans le silicium massif (Pdans-Si), les états propres de Kohn-Sham à une particule sont déterminés de manière auto-cohérente par la théorie de la fonctionnelle de la densité (DFT). Deuxièmement, les états propres de Kohn-Sham avec de faibles énergies propres identifiées comme étant des états d'impureté sont sélectionnés comme base pour le calcul de diagonalisation exacte de l'hamiltonien à plusieurs corps du qubit ; l'identification des états d'impureté localisés est effectuée avec grande attention. Troisièmement, l'énergie d'interaction à plusieurs corps est résolue par diagonalisation exacte. À titre d'exemple, nous appliquons ce cadre théorique de premiers principes au qubit de spin P-dans-Si, et l'énergie d'ajout de premier principe prédite est de 48.9 meV. Ceci est en excellente concordance quantitative avec la valeur mesurée expérimentalement de 47 ± 3 meV. Puisqu'il est basé sur les premiers principes atomistiques, le cadre théorique établi dans ce travail peut être appliqué à un large éventail de matériaux pour la mise en œuvre de dispositifs basés sur les qubits de spin.

Statement of Originality

This work attempts to establish a new theoretical framework based on atomistic first principles, for predicting the addition energy in single donor spin-qubits, using a combined approach of density functional theory (DFT) at the single particle level followed by exact diagonalization at the many-body level of the electron-electron interactions. To the best of my knowledge, this atomistic first principles method is original. As I demonstrate, it gives quantitative predictions of the addition energy without any phenomenological parameters. I have carried out all the calculations reported in this document, verified the correctness of the combined modeling, interpreted the calculated data, compared to the measurements, and abstracted the important steps for quantitative calculations of the addition energy of donor based spin-qubits. The results will be the content of a manuscript to be submitted to a refereed journal in 2023.

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Lastly, I would like to thank my parents, whose love supports me throughout my life. No words can express my gratitude for their wholehearted support throughout my academic career.

Physical Constants and Units

1 Å	=	$10^{-10} {\rm m}$
a_0 (Bohr radius)	=	0.5292 Å
m_e (electron mass)	=	$9.1096 \times 10^{-31} \text{ kg}$
e (electron charge)	=	$1.6 \times 10^{-19} {\rm C}$
h (Planck's constant)	=	$6.626\times 10^{-34}~{\rm J\cdot s}$
ϵ_0 (vacuum permittivity)	=	$8.854 \times 10^{-12} \ \mathrm{F} \cdot \mathrm{m}^{-1}$

Atomic units are used in chapter 2 of this thesis. In this system of units, $e = m_e = \hbar = 1$.

1 unit of Length	—	a_0	—	0.5292 Å
1 unit of Mass	=	m_e	=	$9.1096 \times 10^{-31} \text{ kg}$
1 unit of Charge	=	e	=	$1.6 \times 10^{-19} {\rm C}$
1 unit of Energy	—	1 Hartree	_	27.2 eV

Introduction

1

The advent of quantum technology has attracted great attention in academia, industry and government [1]. Quantum technology encompasses a broad range of disciplines including quantum computing [2], quantum communication [3] and quantum sensing [4]. These technologies harness the special properties of quantum phenomena to operate. For instance, quantum computing uses quantum superposition and entanglement to perform data processing, which can lead to exponentially more efficient computation for certain algorithms in comparison to classical computers [2]. Quantum communication builds on quantum laws to ensure completely secure encrypted data transmission, as well as realizing multiple combinations of data bits simultaneously in the information stream [3]. Quantum sensing applies quantum principles that govern the physics inside individual atoms to detect electric and magnetic fields in an exponentially more accurate and efficient manner, in comparison to classical sensors [4]. Quantum technology represents a new and exciting research direction of both fundamental science and practical technology.

Quantum computing is an idea that uses quantum phenomena to perform logical computation. A classical digital computer uses bits, i.e., zeros and ones, to carry out the computation. If we are able to replace the classical bits with quantum bits (qubits) whose physical state represents both zero and one simultaneously, in principle one can carry out multiple classical computations simultaneously thereby increasing the computational efficiency. This kind of "entangled state" is ubiquitous in the quantum world due to the quantum superposition principle [6]. Harnessing the superposition of



Figure 1.1: A quantum computer based on a ³¹P dopant array in silicon bulk, envisioned by Kane[5]. A-gates are used to manipulate electron spins. B_{ac} is used to rotate nuclear spins. J-gates are used to perform two-qubit operations. A magnetic field *B* is used to ensure electrons occupy the lowest energy states. Figure courtesy of Reference [5].

states, quantum computing can be exponentially faster than classical computers for certain computations such as prime number factorization [7], database searching [8], simulation of quantum systems [9][10] and other tasks that can be mapped into these algorithms. The history of quantum computing goes back to 1980 when Paul Benioff proposed that a quantum version of a classical computer, such as a Turing machine, is feasible [11]. In 1982, Richard Feynman argued that some problems would be calculated more efficiently using quantum-evolution-based computers than classical computers [9]. In 1984, David Deutsch gave an important proposal widely considered to be the first design of a quantum computer, where he proved that if a qubit can undergo some simple operations called quantum "gates", any unitary operation can be done, making quantum computing practically possible [12][2].

The central unit in all the quantum hardware is the qubit that can be implemented in many different ways and materials [13]. Superconducting qubits are implemented in superconducting electronic circuits via a ground state and an excited state as the two-level system [14]; trapped ion qubits are implemented by ions trapped in free space with electromagnetic fields [15]; the optical lattice quantum computers use atomic states of neutral atoms trapped in a optical lattice as the two-level system [16]; and spin-qubits use the two-states of spin as the two-level system which can be implemented in spatially confined semiconductor structures called quantum dot (QD) or artificial atom [17], etc. While the physics of qubits is well-studied and even produced in many academic laboratories, the industry has additional concerns and requirements regarding the scalability of the qubits to large numbers, the reliability and cost of the qubit hardware, as well as if the well-established semiconductor processes and materials can be harnessed to implement qubits. At present, the most commonly implemented qubit is based on superconductors, while the semiconductor industry is very interested in spin-qubits implemented in semiconductor QDs, due to the mature industrial fabrication and material processes of microtechnology.

This work focuses on spin-qubits. As the name suggests, this qubit hardware utilizes the quantum characteristics of spin which is an intrinsic characteristic of an electron or nuclei as the two-level quantum system. Namely, the two levels are the spin-up and spin-down states of a spin 1/2 particle. An electron has 1/2 spin and many nuclear spins are also 1/2. There are numerous proposals that utilize the electron spin or 1/2 nuclear spin as a spin-qubit [18]. Spin-qubit has a growing popularity in industries because, as we will see later in this chapter, they are mostly based on semiconductors and can operate at higher temperatures than superconducting qubits. The spin-qubits we investigate in this work are the electron spin-qubits based on single donor impurities in silicon, called donor QD. Interestingly, there are already industrial companies dedicating their entire or part of the technology roadmap toward such qubits [19][20]. We shall discuss in the next section the donor-based spin-qubit in Si.

1.1 Spin Qubits Based On Donors In Silicon

Silicon is not only the main material of semiconductor microtechnology, it has a property very useful for building solid-state qubits. Of the 23 known isotopes, ²⁸Si is the most abundant at ~ 92.2% and they have no nuclear spin. In a material, electrons can interact with nuclear spins through the hyperfine interaction [21]. As a result, the random orientations of nuclear spin lead to decoherence of the quantum states of the qubits implemented in the material. This detrimental effect is largely removed in natural Si since it almost has no nuclear spin [17][18]. In addition, technology already exists to use the isotope effect to remove the nuclear spin of almost all Si atoms [22]. In this section, we briefly review the spin-qubit implementation based on donor impurities in Si.

1.1.1 Kane Model of Nuclear Spin Qubit

The first qubit based on donor impurities in silicon was proposed by Bruce Kane [5] in 1998. Kane's model used the nuclear spin of the donor atom, instead of its electron spin, to implement the qubit. In this proposal, Kane envisioned a quantum computer based on a ³¹P dopant array in Si bulk, schematically shown in Figure 1.1 [5]. In this model, the hyperfine interaction couples the electron spin and the nuclear spin [21]. Because electrons are sensitive to external electric fields, by changing the voltage of the metallic A-gates lying on top of the P dopant (see Figure 1.1), one controls the electrons and, through the hyperfine interaction, controls the spin resonance of the nuclear spin of the P dopant. With the help of an a.c. magnetic field B_{ac} , one can rotate the nuclear spins at resonance to perform single-qubit operation [5].

Importantly, different nuclear spins belonging to different P dopants are indirectly coupled due to hyperfine interactions with the same electron to generate electronmediated nuclear spin coupling. With the J-gates lying between adjacent P dopants as seen in Figure 1.1, one can turn on and off this coupling by controlling the electron wavefunction overlap of nearby donors [23]. Doing so, two-qubit "controlled rotation" operations could therefore be realized. As such, both single-qubit and two-qubit operations could be done so that all quantum operations are achieved [5].

As explained above, the choice of Si as the host material is not arbitrary as Si minimizes the decoherence effect due to its zero nuclear spin. Furthermore, Si has small spin-orbit coupling, further decreasing the decoherence effect [18]. In fact, electron spins in Si tend to have a longer relaxation time than in many other semiconductor materials [18][24] and it is perhaps more interesting to use electron spins as the qubit, as we discuss in the next subsection.

1.1.2 Electronic Spin Qubit

Around the same time as Kane proposed his nuclear spin-qubit, another form of spinqubit was proposed by Loss and DiVincenzo [25]. Rather than using the nuclear spins as qubits, Loss and DiVincenzo proposed using electronic spins [25]. The electron spin-qubit they envisioned was based on confining an electron inside a quantum dot (QD) or "artificial atom". A QD is usually created using two-dimensional electron gas confined in a heterostructure of semiconductor materials, where the confinement is electrostatically defined by several metallic gates [18][26]. The electrons trapped inside the QD occupy bound states that are localized inside the QD. Electrons can tunnel in and out of the QD controlled by applying gate voltages [27]. An illustration of the confinement potential and the bound states of a QD is in Figure 1.2. When there are electrons in the QD, electron spins can be manipulated by the technique of electron spin-resonance (ESR) that forces electrons to a given spin eigenstate [28]. Such a gated QD implements a spin-qubit [29]. With an array of these spin-qubits, a quantum computer may be realized which is illustrated in Figure 1.3. However, this form of gated QD spin-qubit has a linear size of a few tens to a few hundred nanometers [18], much larger than a field effect transistor of modern computers. Furthermore, since gated QD is lithographically and electrostatically defined, it is



Figure 1.2: A qualitative illustration of the confinement potential of a quantum dot and the bound states [18]. The green wavefunctions represent bound states in a quantum dot, and the excessive electrons tunneled into the quantum dot through the gates would occupy these states. The spins of electrons in these states can be used as a two-level system for the qubit. Figure courtesy of Reference [18].

difficult to create many gated QDs in exactly the same size and shape, thus the device-to-device variability is large. Despite these issues, gated QDs provide the main hardware implementation of the spin-qubits at the present time.

While a gated QD is an artificial atom, a donor impurity in Si is a real atom, and one may consider a single donor impurity to be the smallest possible QD [17]. The donor atom can trap excess electrons in the localized impurity states, similar to electrons trapped in the QD states. By applying some gate voltages, electrons can tunnel in and out of these impurity states, and the electron spins can also be manipulated by ESR. An illustration of the impurity states of a donor-in-silicon system is plotted in Figure 1.4. Comparing with Figuire 1.2, the similarities between a gated QD and a donor are seen. In Figure 1.4, while Kane uses the nuclear spins (in blue) as the two-level qubits, one may also use the electron spins (in red) as the two-level qubits. Indeed, after Kane's original proposal, many other proposals were made using electron spins in a donor-in-silicon system as qubits [30][31]. Due to the similarity between a donor-in-silicon system and a gated QD, the former may be called "donor-QD" [32]. Donor-QD is obviously harder to fabricate than gated-QD, but as spin-qubit it has



Figure 1.3: A illustration of an array of quantum dots and gates as the quantum computer hardware implementation [18]. The gates surrounding the quantum dots control the sequential tunneling of electrons into and out of the bound states. Figure courtesy of Reference [18].

several unique advantages. First, arrays of gated-QDs have proven to be extremely difficult to produce, arrays of donor-QDs have already been fabricated using As impurities in Si [33], suggesting an advantage for scaling up the qubits. Second, since donor atoms of a given type (i.e. P, As, etc) are identical, the properties of donor-QDs are more uniform than gated-QDs. Finally, atomic defects can be arranged very close to each other, even down to a single bond length, as demonstrated experimentally on Si surfaces [34], suggesting that very closely coupled donor-QDs can be fabricated.

1.2 Experimental fabrication of the donor-QD spin-qubits

As discussed above, fabricating electron donor-QD qubits is challenging. It requires the ability to place the donor atom and the surrounding metal gates with atomic precision [18][36]. Atomic precision techniques for placing donor impurities in silicon have been developed using the scanning tunneling microscopy (STM) tip [37]. Notably, in 2012, Simmons et al. fabricated a single-atom transistor, with a single phosphorous (P) impurity acting as a donor sitting inside a silicon bulk. Figure 1.6 shows an STM image of such a transistor. Simmions et al. were able to place the single P impurity into silicon with atomic precision, using the hydrogen-resist lithography to control the dissociation of PH₃ by ejecting a specific silicon atom at the



Figure 1.4: A qualitative illustration of the confinement potential and the energies of the impurity states of a donor atom in silicon [18]. The blue arrows represent nuclear spins in the Kane proposal of qubits. The red arrows represent electron spins which can be used as the two-level system for the qubits. Figure courtesy of Reference [18].



Figure 1.5: An illustration of a potential quantum computer implementation made of an array of electron spin qubits based on donors in silicon [18]. The gates on top of the donors and the SiO_2 layer are used to tunnel electrons into the impurity states, and also used to control the spin of the electrons in the impurity states. The readout of electron spin qubit is easier than nuclear spin, and can be done by using a nearby single electron transistor [35]. Figure courtesy of Reference [18].



Figure 1.6: A scanning tunneling microscope image of the phosphorous single impurity atom transistor [38]. The G1 and G2 are gates that are in the same plane as the P dopant. The S and D are source and drain leads. These electrodes are highly phosphorous-doped regions in a monoatomic layer, which are highly conductive, and thus can be used to tunnel electrons into and out of the impurity states of this transistor. Inside the white rectangle is a single phosphorous impurity atom. Figure courtesy of Reference [38].

surface and replacing it with the P atom. The G1 and G2 in Figure 1.6 are gates that are in the same plane as the P dopant. The S and D are source and drain leads. These electrodes are heavily phosphorous-doped regions in a monoatomic layer, which are highly conductive, thus can be used to tunnel electrons into and out of the impurity states of this transistor. We see that this single-atom transistor is indeed a donor-QD discussed above, which forms the basis of a single spin qubit. Simmons et al. could control and observe electron states with 0, 1, and 2 conduction electrons occupying the impurity states in this system [38]. In 2019, using the same fabrication technique, Simmons et al. fabricated a two spin-qubits system using P dopants in silicon, and successfully realized the two-qubit SWAP gate operation [32].

In 2020, Stock et al. proposed [39] a method to place a single As dopant into

silicon with atomic precision using lithography. The procedure uses the dissociation of AsH_3 to place a single As atom in the silicon lattice. Such a system could become a single donor-QD with the addition of gates and be used as spin qubits. Apart from the electron spin-qubit, using As as a nuclear spin-qubit is also interesting. As has a 3/2 nuclear spin, which is not exactly a two-level system that a qubit requires. But there are ways to perform two-level operations on a 3/2 nuclear spin and treat it as a two-level qubit [39]. In addition, it is possible to make the As donor-QD a 4-level quantum computation unit due to the spin 3/2 property, potentially making it even more efficient for some calculations [40][41]. Indeed, it appears that As donor-QD is another excellent candidate dopant to implement spin-qubits in Si [39].

1.3 Sequential tunneling and the addition energy

For both gated-QD and donor-QD, electrons (and/or holes) tunnel in and out of the QD during device operation. In the case of donor-QD, electrons are tunneled into the impurity states one by one from the outside world, controlled by the gate voltages surrounding the donor-QD [38]. This quantized tunneling of one electron at a time is the sequential tunneling [17].

Experimentally, sequential tunneling is marked by the Coulomb diamond diagram due to the Coulomb blockade effect. As we saw earlier, a spin-qubit is surrounded by source/drain leads and several plunger gates, i.e. Figure 1.6. If the qubit is in the sequential tunneling regime, when varying the voltages between the source and drain V_{bias} or sometimes denoted as V_{SD} , and varying voltages between the gates V_g , there is a transport regime where no current flows through the donor-QD. The reason is that the electron already inside the donor-QD repels the electrons outside the donor-QD by Coulomb interactions, blocking the motion of electrons going through the QD. At some specific V_{bias} and V_g values, sequential tunneling resumes and a current flows through the QD. If we plot the differential conductance dI/dV_{bias} (where I is the current) as a function of V_g and V_{bias} , a diagram that has consecutive diamond's shape appears where the diamond surrounds areas of zero conductance. This is called the Coulomb blockade diamond diagram [42]. Figure 1.7 shows the Coulomb blockade diamond diagram measured in the single-atom transistor of P-in-Si [38]. From this diagram, the area with a bright color indicates that with this V_g and V_{bias} , we would have a large conductance, and the dark area whose boundary gives a diamond shape indicates that there is no conductance. This diagram signifies sequential tunneling because going from one diamond to the next diamond indicates that the system gained one electron, which is only possible with sequential tunneling. For example, in Figure 1.7, we observe the diamonds labeled by D^+ , D^0 , and D^- . These dark areas with small differential conductance signify that there are 0, 1, or 2 conduction electrons occupying the impurity states in the donor-QD [38]. A more detailed discussion of the Coulomb diamonds will be provided in Chapter 3.

For a QD (or spin-qubit) in the sequential tunneling regime, a physical quantity of utmost importance is the addition energy E^{add} , or called the charging energy E_c . It is related to how electrons interact in the QD, and how much energy is needed to sequentially tunnel the next electron into the QD. It is defined as the difference between the electrochemical potential μ_1 , which is the energy required to add one electron into a zero electron QD, and electrochemical potential μ_2 , which is the energy required to add another electron into a one-electron QD [42]. This important quantity can be measured. In a Coulomb diamond diagram, it is simply the V_{bias} value (times electron charge) at the apex of the diamond. For example, in Figure 1.7, the apex height of the D^0 diamond is measured to be 47 ± 3 mV, indicating an addition energy of this value. We shall prove this equality in Chapter 3. Because of its importance to sequential tunneling and QD-based qubits, the addition energy is measured in all experimentally fabricated QD spin-qubits. It gives indications of whether an impurity or several impurities have successfully been placed into bulk silicon and more importantly, provides information on the operation of the qubits [32][38][43].



Figure 1.7: The Coulomb diamond diagram in Simmons et al.'s single-atom transistor [38]. The differential conductance dI/dV_{bias} is plotted as a function of V_g and V_{bias} . The diamonds as labeled by D^+ , D^0 , and D^- signify that there are 0, 1, or 2 conduction electrons occupying the impurity states in the donor-QD. The addition energy is obtained from the apex height of the diamond to be 47 ± 3 meV. Figure courtesy of Reference [38].

Theoretical calculation of the addition energy of spin-qubits is very important for quantum technology hardware designers and manufacturers. In advanced semiconductor integrated circuit and chip manufacturing, the software tools of technology computer-aided design (TCAD) [44] have been playing critical roles for decades. We expect that to establish the quantum technology manufacturing, a quantum version of the TCAD tool is needed and such a tool must be able to predict how qubits behave before fabrication and in particular, accurate prediction of the addition energy is the first task for the quantum-TCAD (QTCAD).

To this end, extensive theoretical investigation has been carried out to determine the addition energy of QD in the sequential tunneling regime. Perhaps the most widely applied theoretical approach is the envelope function theory [42][45] based on the effective mass theory of solid-state physics. For the donor-QD, this approach treats the dopant as a hydrogen-like atom and electrons take an effective mass of the host material [42]. More details of this method are reviewed in Chapter 3. The envelope function theory gives a crude estimate of the addition energy of, for example, a P donor-QD to be around 29 meV, with the first chemical potential at around -31meV and the second chemical potential at around -2 meV [45][46]. Clearly, these values do not agree with the experimental data shown in Figure 1.7. In this approach, all the material properties are only included by the effective mass model and in the coefficient of the 1/r central potential of the hydrogenic model. Unless these and other phenomenological parameters are well-fit to measured data or adjusted, it is hard to make quantitative predictions. Another method for calculating the addition energy is the atomistic tight binding (TB) method [47] where a parameterized Hamiltonian matrix allows the calculation of the eigenstates of the QD. The advantage of the TB method is that it is computationally efficient thus very large atomic structures can be calculated. However, to obtain accurate results, careful adjustments of the Hamiltonian matrix elements by numerical data fitting is necessary [48] which is a very tedious task. With a well-fit TB model, it is possible to make predictions of the addition energy close to the measured value [49].

We conclude that to design spin-qubits for quantum technology, the best approach is a first principles theory and modeling tool. This approach should account for the material details of the devices and the strong electron-electron interactions in the QD qubits, so that the addition energy of the QD is predicted without any phenomenological parameters. In the rest of this thesis, we shall establish this first principles approach, by combining the density functional theory (DFT) with an exact diagonalization method.

1.4 Thesis Organization

In Chapter 2, we shall introduce the theory of DFT [50] and its practical implementation RESCU [51]. For the donor-QD, turns out that the simulation supercell must include a very large number of atoms to reduce the finite-size effect of the results. Our in-house DFT package RESCU can handle such large systems due to its innovative numerical mathematics and parallel algorithms.

In Chapter 3, we shall first establish the theory behind the observed Coulomb diamonds and addition energies, followed by introducing the exact diagonalization method and its implementation in the QTCAD electronic package. Because the Hamiltonian is exactly diagonalized, the most accurate calculation of the many-body states can be achieved [52].

In Chapter 4, we combine the DFT and QTCAD method to determine the addition energy of P-in-Si single donor spin-qubit. We shall show that this first principles approach predicts the addition energy in excellent agreement with the corresponding measured data.

Finally, the last chapter is reserved for a brief summary and outlook of this work.

$\mathbf{2}$

Density Functional Theory

As introduced in the last chapter, the goal of this work is to establish an atomistic first principles framework for quantitative predictions of addition energy of donor-QD-based spin-qubits. As a specific example, we shall investigate the experimentally fabricated P-in-Si device [38] in Chapter 4. The density functional theory (DFT) shall be used as the first step in our framework to determine the donor impurity states which will play the role of basis functions for calculating the many-body Hamiltonian. DFT is the most widely used first principle approach in matreial physics. The theoretical foundation of DFT was first introduced by Hohenberg and Kohn [53] in 1964. The theoretical formulation of DFT was reduced to many software packages in the past several decades, including well-known packages VASP [54], SIESTA [55], RESCU [51], etc. In this chapter, the theory of DFT and implementation details are reviewed. In particular, the RESCU method will be introduced which is the DFT software used in our calculation due to its capability of solving very large atomic supercells.

2.1 Born-Oppenheimer Approximation

DFT is a ground-state theory. In any material, there are Coulomb interactions between electrons, between nuclei, and between electrons and nuclei. The many-body Schrödinger equation is:

$$\left[\sum_{i} -\frac{1}{2}\nabla_{i}^{2} + \sum_{I} -\frac{1}{2M_{I}}\nabla_{I}^{2} + \sum_{i>j} \frac{1}{|\mathbf{r_{i}} - \mathbf{r_{j}}|} - \sum_{i,J} \frac{Z_{I}}{|\mathbf{r_{i}} - \mathbf{R_{J}}|} + \sum_{I < J} \frac{Z_{I}Z_{J}}{|\mathbf{R_{I}} - \mathbf{R_{J}}|}\right] \Psi_{gs}(\{r_{i}\}, \{R_{I}\}) = E_{gs}\Psi_{gs}(\{r_{i}\}, \{R_{I}\}) .$$

$$(2.1)$$

In Eq. 2.1, atomic units (a.u.) are used: $m_e = 1$, e = 1, $\hbar = 1$. Lower case indices such as *i*, indicate the *i*-th electron; upper case indices such as *I*, indicate the *I*-th nuclei. E_{gs} is the eigen-energy that satisfies this equation. The many-body wavefunction Ψ_{gs} depends on the electron positions, $\{r_i\}$ and nuclei positions $\{R_I\}$. M_I is the mass of the *I*-th nuclei and Z_I is the atomic number of the *I*-th nuclei, i.e. the number of elemental charges. The five terms in the Schrödinger equation correspond respectively to: the electron kinetic energy, the nucleus kinetic energy, the electron-electron interaction, the electron-nucleus interaction, and the nucleus-nucleus interaction. This is an extremely difficult many-body problem to solve because the Hilbert space grows exponentially with the number of particles. If there are N_{atom} atoms and N electrons, the exact numerical solution of this equation has been done for a very small number of atoms even for hydrogen, $N_{atom} \sim 5$. For materials physics, some approximations must be made to reduce the complexity of the computation.

The first approximation to make is to "freeze" the nuclei. Because nuclei have a large rest mass compared with electrons, the nuclei move much slower than electrons. From the electrons' perspective, nuclei can be seen as fixed in space, i.e. "frozen", they only produce a static Coulomb potential to the electrons. The Born-Oppenheimer ansatz [56] therefore assumes,

$$\Psi_{gs}({\mathbf{r}_{\mathbf{i}}}, {\mathbf{R}_{\mathbf{I}}}) = \Psi_{e}({\mathbf{r}_{\mathbf{i}}}, {\mathbf{R}_{\mathbf{I}}})\Psi_{n}({\mathbf{R}_{\mathbf{I}}}) .$$
(2.2)

In this approximation, the ground-state wavefunction is split into an electron part Ψ_e , and a nuclei part Ψ_n . As a result, the original Schrödinger equation Eq. 2.1 is

separated into two, one for the nuclei and the other for electrons.

$$\left[\sum_{i} -\frac{1}{2}\nabla_{i}^{2} + \sum_{i>j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i,J} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{J}|}\right] \Psi_{e}(\{\mathbf{r}_{i}\}, \{\mathbf{R}_{I}\})$$

$$= \epsilon_{0}(\mathbf{R}_{I})\Psi_{e}(\{\mathbf{r}_{i}\}, \{\mathbf{R}_{I}\})$$
(2.3)

$$\left[\sum_{I} -\frac{1}{2M_{I}}\nabla_{I}^{2} + \sum_{I < J} \frac{Z_{I}Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} + \epsilon_{0}(\mathbf{R}_{I})\right]\Psi_{n}(\{\mathbf{R}_{I}\}) = E_{gs}\Psi_{n}(\{\mathbf{R}_{I}\})$$
(2.4)

Where Eq. 2.3 is for electrons and Eq. 2.4 is for nuclei. Here ϵ_0 is the ground state energy of the electron Schrödinger equation Eq. 2.3. For materials physics, we are interested in electrons which makes bonding between atoms and other electronic properties, therefore Eq. 2.3 will be the focus. We will drop the subscript *e* without causing confusion in the rest of the thesis. Because the nuclei are considered to be frozen, {**R**_I} dependence will also be dropped in Eq. 2.3. From here, $\Psi({\bf r}_i)$ denotes the many-body electron wavefunction in Eq. 2.3. Unfortunately, even with the Born-Oppenheimer approximation, the Hilbert space still grows exponentially with the number of electrons, which requires further approximations to reduce.

2.2 Hohenberg-Kohn Theorem

The problem of solving the electron Hamiltonian Eq. 2.3 is greatly simplified by introducing an energy functional, as proposed by Hohenberg and Kohn [53]. Hohenberg-Kohn theorem is the theoretical foundation of DFT [53], which has two parts [53]:

Theorem 1 (Hamiltonian-density bijection). Consider the class of Hamiltonians defined as $\hat{H} = \hat{T} + \hat{V} + \hat{U}$, where

$$\hat{T} = \frac{1}{2} \int d\mathbf{r} \nabla \hat{a}^{\dagger}(\mathbf{r}) \cdot \nabla \hat{a}(\mathbf{r})$$
(2.5)

$$\hat{V} = \int d\mathbf{r} v_{ext}(\mathbf{r}) \hat{a}^{\dagger}(\mathbf{r}) \hat{a}(\mathbf{r})$$
(2.6)

$$\hat{U} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\hat{a}^{\dagger}(\mathbf{r})\hat{a}^{\dagger}(\mathbf{r}')\hat{a}(\mathbf{r}')\hat{a}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$
(2.7)

that have a unique ground state (\hat{a} and \hat{a}^{\dagger} are the annihilation and creation operators respectively). There exists a bijection (one-to-one correspondence) between the set of ground state densities ρ of this class of Hamiltonians and the set of external potentials v_{ext} defined uniquely up to a constant.

Theorem 2 (Universal functional). Consider the following universal functional

$$F[\rho] = \langle \Psi | T + U | \Psi \rangle \tag{2.8}$$

and the energy functional

$$E[\rho] = F[\rho] + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r})$$
(2.9)

 $E[\rho]$ assumes its minimum value at the ground state density, and the minimum value is the ground state energy, with the following constraint $\int d\mathbf{r}\rho(\mathbf{r}) = N$.

Note that the Hamiltonian in Eq. 2.3 is of the form in Theorem 1 which works on a many-electron system. If the creation and annihilation operators are for electrons, the first term corresponds to \hat{T} in Eq. 2.5, the second term corresponds to \hat{U} in Eq. 2.7, and the third term corresponds to a \hat{V} in Eq. 2.6. Theorem 1 also produces a corollary, which gives a bijection between the set of ground state densities and the set of ground state wavefunctions. At zero temperature (ground state), the expectation value of an observable is a functional of the ground state wavefunction, therefore it is also indirectly a functional of the ground state density. Hence, by solving the ground state density, one will be able to obtain the expectation values of any physical observable. In this chapter, zero temperature is assumed unless explicitly stated otherwise.

Theorem 2 states that one can solve for the ground state density and energy by minimizing the total energy. The functional $F[\rho]$ is only a functional of the density and

possibly derivatives of the density, as will be discussed later. Reducing the problem of solving the many-body wavefunctions to solving the electron density drastically simplifies the theory, making it possible to solve realistic materials physics problems.

2.3 Kohn-Sham Equation

The Hohenberg-Kohn theorem stated that one can determine the ground state density and energy by minimizing a total energy functional. This leads to the Kohn-Sham equation [50] that solves the minimization problem. The Kohn-Sham equation is the central piece of DFT [50]. Kohn and Sham rewrote the total energy in Eq. 2.9 to the following form,

$$E[\rho] = T_0[\rho] + V[\rho] + U_H[\rho] + E_{xc}[\rho]$$
(2.10)

where

$$V[\rho] = \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) , \qquad (2.11)$$
$$U_H[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} ,$$
$$E_{xc}[\rho] = F[\rho] - T_0[\rho] - U_H[\rho] .$$

Here, $T_0[\rho]$ is a non-interacting single-particle kinetic energy term, to be specified later. It is not intuitive to part out this single-particle term from the many-body problem, but it is the key to the derivation of the Kohn-Sham equation. $U_H[\rho]$ is the classical Coulomb interaction between electrons, called the Hartree energy. $V[\rho]$ is the external potential that accounts for the Coulomb interaction due to the nucleus and any other externally applied potentials. $E_{xc}[\rho]$ is called exchange-correlation energy which includes quantum interactions such as the exchange and corrections to the $T_0[\rho]$ term. The name of exchange-correlation comes from the fact that this energy is related to the exchange-correlation hole, which can be interpreted as the joint probability of finding an electron at a point given that there exists another electron at another point [57]. To minimize the total energy, a functional derivative of Eq. 2.10 is taken and set to zero,

$$\frac{\delta E[\rho]}{\delta \rho} = \frac{\delta T_0[\rho]}{\delta \rho} + v_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[\rho]}{\delta \rho} = 0 , \qquad (2.12)$$

where v_{ext} is from the functional derivatives of $V[\rho]$ in Eq. 2.11. At the energy minimum, the functional derive of Eq. 2.12 vanishes, leading to the Kohn-Sham equation as we derive below.

To this end, note that if the functional derivative is done for a non-interacting system, which only includes the first and second term in Eq. 2.10, one would obtain

$$E[\rho] = T_0[\rho] + V[\rho] , \qquad (2.13)$$

$$\frac{\delta E[\rho]}{\delta \rho} = \frac{\delta T_0[\rho]}{\delta \rho} + v_{ext}(\mathbf{r}) = 0 . \qquad (2.14)$$

Eq. 2.12 and Eq. 2.14 has the same form with the following replacement:

$$v_{ext}(\mathbf{r}) \to v_{eff}(\mathbf{r}) \equiv v_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[\rho]}{\delta \rho}$$
 (2.15)

Clearly, the problem of the non-interacting system in an external field v_{ext} can be solved by which the single-particle wavefunctions are obtained. Therefore, the same form of Eq. 2.12 and Eq. 2.14 suggests that the interacting system can be solved in the same way, by replacing the external potential v_{ext} with an effective potential v_{eff} defined in Eq.2.15. To simplify notation, let's define a Hartree potential

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(2.16)

and an exchange-correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho} . \qquad (2.17)$$

Following the above discussion, a Hamiltonian for non-interacting single-particles can be written with an effective potential $v_{eff} = v_{ext} + v_H + v_{xc}$, obtaining the Kohn-Sham equation,

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) , \qquad (2.18)$$

which is in effect a non-linear Schrödinger equation. The electron density is

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) . \qquad (2.19)$$

Here, we assume there are N electrons in the material, thus the summation is up to N.

Now, the many-electron Hamiltonian in Eq. 2.1 is transformed into a singleparticle effective Hamiltonian in Eq. 2.18. In the Kohn-Sham equation, ψ_i is called Kohn-Sham wavefunctions or Kohn-Sham orbitals in the literature. Strictly speaking, ψ_i is not the true wavefunctions of the original Schrödinger equation, therefore it is also called the auxiliary wavefunctions. Since ψ_i does give the physical quantity of electron density through Eq. 2.19, in the rest of this thesis we shall not make the distinction between auxiliary and true wavefunctions explicitly.

In the practical algorithms for solving the Kohn-Sham equation, since v_{eff} depends on ρ which is obtained by solving the Kohn-Sham equation, a self-consistent solution process is needed. Namely, from an initial ρ_0 , the Kohn-Sham equation is solved to obtain a new ρ_1 . ρ_1 is again used to solve the Kohn-Sham equation to obtain a ρ_2 . This process is repeated until some convergence criteria are met at which the resulting density and total energy do not change very much from those of the previous iteration step. The ground state energy is calculated from the energy functional Eq. 2.10,

$$E[\rho] = \sum_{i} \int d\mathbf{r} \psi_{i}^{*}(\mathbf{r}) (-\frac{1}{2} \nabla^{2}) \psi_{i}(\mathbf{r}) + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] + \sum_{I < J} \frac{Z_{I} Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} .$$
(2.20)

The first term is the non-interacting kinetic energy term $T_0[\rho]$ discussed earlier. The nuclear energy is now added as the last term. Noting that the Kohn-Sham equation gives

$$\int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \; .$$

Summing over ϵ_i , using Eq.2.19 and 2.16, one obtain

$$\sum_{i} \epsilon_{i} = T_{0}[\rho] + V[\rho] + 2U_{H}[\rho] + \int d\mathbf{r} v_{xc}(\mathbf{r})\rho(\mathbf{r})$$

Using this result, the total energy functional in Eq. 2.20 is rewritten into the following simpler form:

$$E[\rho] = \sum_{i} \epsilon_{i} - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} v_{xc}(\mathbf{r})\rho(\mathbf{r}) + E_{xc}[\rho] + \sum_{I < J} \frac{Z_{I} Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} .$$

$$(2.21)$$

2.4 Periodic Boundary Conditions

A three-dimensional (3D) crystal solid is made of primitive cells periodically extending in 3D to infinity. Figure 2.1 plots a periodic lattice in 1D. In DFT calculations, larger supercells can also be used to build the periodic crystal lattice, namely the supercell forms the periodic unit of the solid while the primitive cell is the smallest possible supercell. To deal with periodic structures, the DFT equations should satisfy the periodic boundary condition at the supercell boundaries.



Figure 2.1: A typical periodic 1D crystalline potential. The red dots are individual ions. The individual potentials of the middle ion are the yellow curves. When these ion form a crystal, the blue curve is the total potential along the line of the ions, which is periodic.

For a Hamiltonian with periodic potential, by Bloch's theorem the wavefunction obeys [58]

$$\psi_{\mathbf{k}i} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}i}(\mathbf{r}) , \qquad (2.22)$$

where **k** is the reciprocal lattice vector and $u_{\mathbf{k}i}(\mathbf{r})$ a supercell periodic function, i.e. $u_{\mathbf{k}i}(\mathbf{r}) = u_{\mathbf{k}i}(\mathbf{r} + \mathbf{R})$ where **R** is the cell vector of the supercell. The electron density can be written as

$$\rho(\mathbf{r}) = \frac{1}{V_{r.c.}} \int_{r.c.} d\mathbf{k} \sum_{i} u_{\mathbf{k}i}^*(\mathbf{r}) u_{\mathbf{k}i}(\mathbf{r}) . \qquad (2.23)$$

Substituting Eq.2.22 into Eq. 2.18, the periodic version of the Kohn-Sham equation is obtained:

$$\left[-\frac{1}{2}\left(\nabla + i\mathbf{k}\right)^2 + v_{eff}(\mathbf{r})\right]u_{\mathbf{k}j}(\mathbf{r}) = \epsilon_{\mathbf{k}j}u_{\mathbf{k}j}(\mathbf{r}) , \qquad (2.24)$$

Here, $v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$, but the potential terms are all cell-periodic. For each **k** in the reciprocal space, this equation is solved to obtain all the periodic functions $u_{\mathbf{k}j}(\mathbf{r})$, for $j = 1, 2, \dots N$. This way, the calculation of the infinitely large crystal lattice - practically impossible to do, is reduced to the solvable problem of the finite supercell by sampling many **k** values. Regarding the total energy Eq.2.21, from Eq. 2.23 it is replaced by the following,

$$E[\rho] = \frac{1}{V_{r.c.}} \int_{r.c.} d\mathbf{k} \sum_{i} \epsilon_{\mathbf{k}i} - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} v_{xc}(\mathbf{r})\rho(\mathbf{r}) + E_{xc}[\rho] + \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{J}}|} .$$

$$(2.25)$$

As will be discussed in Chap.4, for large supercells with more than 10000 atoms, the reciprocal space is in fact extremely small. For such large systems, the Γ -point which is at $\mathbf{k} = 0$, is sufficient to represent the reciprocal space, thus only the Kohn-Sham equation at the Γ -point needs to be solved. On the other hand, when the supercell is not very large, for example, a few to a few tens of atoms, one needs to make a \mathbf{k} sampling and solve Eq. 2.24 for different values of \mathbf{k} .

2.5 Exchange-Correlation Potential

An important term in the Kohn-Sham equation is the exchange-correlation potential. Unfortunately, this term and/or the exchange-correlation functional are unknown except for very special cases such as the uniform electron gas [59] for which the electron density is a constant. For a real material such as Si, the exact form of the exchange-correlation potential is unknown and must be approximated. Let's denote the exchange-correlation energy E_{xc} to be a functional of the electron density,

$$E[\rho]_{xc} = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r})$$
(2.26)

where ϵ_{xc} is the energy density due to the exchange-correlation effect. It is then a problem to find approximations of ϵ_{xc} . Here, the two most widely used approximations in practical calculations of DFT will be discussed.
2.5.1 Local Density Approximation

The local density approximation (LDA) is a completely local approximation where ϵ_{xc} is only a functional of the electron density $\rho(\mathbf{r})$. For a uniform electron gas where $\rho = \rho_o$ is a constant - independent of \mathbf{r} , ϵ_{xc} as a function of the constant ρ_o can be derived analytically at the limit of high density by perturbation theory [60]. When the density is non-uniform, LDA assumes that the form of ϵ_{xc} versus $\rho(\mathbf{r})$ does not change from that of the uniform electron gas. At the limit of very low electron density, turns out that the kinetic energy of the electrons scales to zero much faster than the potential energy terms, and electrons form Wigner crystals [61]. In this limit, ϵ_{xc} can also be analytically derived [61]. In between the high and low density limits, quantum Monte Carlo simulations give numerical curves of ϵ_{xc} versus density [62]. Fitting the data all the way from low to high densities, the LDA form of ϵ_{xc} versus density is obtained [63]. We refer interested readers to the original literature for the details of these developments in the past several decades.

The LDA exchange-correlation energy has the same form as Eq. 2.26 but ϵ_{xc} is only a functional of $\rho(\mathbf{r})$,

$$E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) . \qquad (2.27)$$

The exchange-correlation potential is obtained using Eq. 2.17 and 2.27,

$$\begin{aligned} v_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho]}{\delta \rho}(\mathbf{r}) \\ &= \frac{\partial}{\partial \rho(\mathbf{r})} \int d(\mathbf{r}') \rho(\mathbf{r}') \epsilon_{xc}(\rho(\mathbf{r}')) \\ &= \epsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \epsilon_{xc}(\rho)}{\partial \rho}(\mathbf{r}) \;. \end{aligned}$$

In the literature, the LDA exchange-correlation is written as the sum of an exchange term and a correlation term $E_{xc} = E_x + E_c$. Using the form of the electron gas [59],

$$E_x = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int d\mathbf{r} \rho(\mathbf{r})^{\frac{4}{3}}$$

Regarding the E_c , one of the widely used form is due to Perdew and Wang [63],

$$\epsilon_c = -2A(1+\alpha_1 r_s)) \log\left(1 + \frac{1}{2A\left(\beta_1 r_s^{\frac{1}{2}} + \beta_2 r_s + \beta_3 r_s^{\frac{3}{2}} + \beta_4 r_s^{p+1}\right)}\right)$$

where A, α_1 , β_1 , β_2 , β_3 , β_4 , and p are parameters determined by quantum Monte-Carlo simulations and $r_s = (4\pi\rho/3)^{-1/3}$. The values of these parameters can be found in Reference [63]. E_c can be obtained from ϵ_c with an integral similar to Eq. 2.27.

LDA is a very widely used exchange-correlation functional due to its simplicity. It can also give reasonably accurate results in practical DFT calculations regarding total energy, forces and electronic structures for many materials. Nevertheless, for materials where the electron density is not very uniform, e.g. molecules, interfaces, etc., a natural extension of the completely local LDA is to include some semi-local terms, as we discuss below.

2.5.2 Generalized Gradient Approximation

The generalized gradient approximation (GGA) is a semi-local functional where the exchange-correlation is not only a functional of ρ , but is also a functional of the gradient of ρ , $\nabla \rho$,

$$E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) . \qquad (2.28)$$

The exchange-correlation potential is given by Eq. 2.17 and 2.28,

$$\begin{aligned} v_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho]}{\delta \rho}(\mathbf{r}) \\ &= \frac{\partial}{\partial \rho(\mathbf{r})} \int d(\mathbf{r}') \rho(\mathbf{r}') \epsilon_{xc}(\rho(\mathbf{r}'), \nabla \rho(\mathbf{r}')) \\ &= \epsilon_{xc}(\rho, \nabla \rho)(\mathbf{r}) + \rho \frac{\partial \epsilon_{xc}(\rho, \nabla \rho)}{\partial \rho}(\mathbf{r}) - \nabla \cdot \rho \frac{\partial \epsilon_{xc}(\rho, \nabla \rho)}{\partial \nabla \rho}(\mathbf{r}) \;. \end{aligned}$$

The gradient dependency makes GGA more accurate than LDA, especially when the density is not very uniform. Various forms of GGA are possible, in this work we shall use the most popular one proposed by Perdew, Burke, and Ernzerhof (PBE) [64], which has the following form,

$$E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_x^{unif}(\rho(\mathbf{r})) F_{xc}(r_s, \zeta, s)$$
(2.29)

where ϵ_x^{unif} is the exchange energy density of a uniform electron gas, r_s was introduced above, ζ is the relative spin polarization, and s is some dimensionless density gradient. For the exact form of these terms, we refer interested readers to the original literature Reference [64].

2.6 Spin Density Functional Theory

We note that the PBE functional in Eq. 2.29 depends on the spin information through the polarization parameter ζ . Indeed, DFT can be extended to analyze spin-polarized materials. Here we shall discuss the extension of DFT to the collinear spin situation. The way to extend DFT to the non-collinear spin situation will not be discussed. The collinear spin DFT theory takes a similar form as the Kohn-Sham theory [65]. The essence of the collinear spin theory is to separate the density ρ into the spin-up density ρ^{\uparrow} and the spin-down density ρ^{\downarrow} , $\rho = \rho^{\uparrow} + \rho^{\downarrow}$. The exchange-correlation functional depends on both densities. For example, in GGA,

$$E_{xc}[\rho^{\uparrow},\rho^{\downarrow}] = \int d\mathbf{r}\rho(\mathbf{r})\epsilon_{xc}(\rho^{\uparrow}(\mathbf{r}),\rho^{\downarrow}(\mathbf{r}),\nabla\rho^{\uparrow}(\mathbf{r}),\nabla\rho^{\downarrow}(\mathbf{r})) , \qquad (2.30)$$

to be compared with Eq. 2.28 above. The Kohn-Sham equation becomes,

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^{\sigma}(\mathbf{r})\right]\psi_{\mathbf{k}i}^{\sigma}(\mathbf{r}) = \epsilon_{\mathbf{k}i}^{\sigma}\psi_{\mathbf{k}i}^{\sigma}(\mathbf{r}) , \qquad (2.31)$$

where σ is the spin index and

$$v_{xc}^{\sigma}(\mathbf{r}) = \frac{\delta E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}]}{\delta \rho^{\sigma}} .$$
(2.32)

The spin dependent density (spin density) is given by

$$\rho^{\sigma}(\mathbf{r}) = \frac{1}{V_{r.c.}} \int_{r.c.} d\mathbf{k} \sum_{i} \psi^{\sigma*}_{\mathbf{k}i}(\mathbf{r}) \psi^{\sigma}_{\mathbf{k}i}(\mathbf{r}) . \qquad (2.33)$$

Finally, the total energy is,

$$E[\rho^{\uparrow}, \rho^{\downarrow}] = \frac{1}{V_{r.c.}} \int_{r.c.} d\mathbf{k} \sum_{i} \epsilon^{\sigma}_{\mathbf{k}i} - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} v^{\sigma}_{xc}(\mathbf{r})\rho^{\sigma}(\mathbf{r}) + E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}] + \sum_{I < J} \frac{Z_{I} Z_{J}}{|\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{J}}|} .$$

$$(2.34)$$

In the collinear spin situation, the spin-up and -down densities do not directly couple to each other. The Hamiltonian matrix is therefore a block-diagonal matrix: one block for the spin-up channel and the other for the spin-down channel. This means that in practical applications, two separate Kohn-Sham equations are solved for the two spin channels, doubling the computational effort compared with non-spin polarized situations. We mention in passing that for non-collinear spin situations, the two spin channels do directly couple to each other, causing the Hamiltonian matrix to have off-diagonal elements. In that case, the computational effort increases by a factor of eight, since the eigenvalue solvers typically scale as the cubic power of the size of the Hamiltonian matrix.

2.7 Pseudopotentials

In the previous sections, the form of the external potential v_{ext} has not been discussed in detail. A contribution to v_{ext} is the Coulomb potential of nucleus,

$$v_{ext}(\mathbf{r}) = \sum_{I} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$
(2.35)

where \mathbf{r} is the position of the electron and $\mathbf{R}_{\mathbf{I}}$ is the position of the *I*-th nuclei. For practical calculations, this form of the Coulomb potential poses some difficulties because it lacks a characteristic length scale and the potential changes rapidly when \mathbf{r} approaches $\mathbf{R}_{\mathbf{I}}$. This problem is solved by introducing the augmented plane waves [66]. It is noted that the potential near the nuclei is almost spherically symmetric and the potential varies smoothly away from the nuclei. Therefore, one may separate the space into two regions, a nuclei sphere surrounding each nuclei, and an interstitial region in between the nuclei spheres. This way, the basis function can be represented using simple wavefunctions in the interstitial region such as planewaves, and using a linear combination of solutions of the spherical Schrödinger equation inside the nuclei spheres,

$$\phi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{k}\cdot\mathbf{r}} & \mathbf{r} \in \text{interstitial region} \\ \sum_{lm} A_{\mathbf{k}lm} R_l(r,\epsilon) Y_{lm}(\theta,\phi) & \mathbf{r} \in \text{nuclei spheres} \end{cases}$$
(2.36)

where $A_{\mathbf{k}lm}$ are coefficients to be solved by requiring continuity at the boundary of the spheres and interstitial, $Y_{lm}(\theta, \phi)$ is a spherical harmonic of order (l, m), θ and ϕ are the polar and azimuthal angle, respectively.

Using Eq. 2.36, the nuclear potential Eq. 2.35 can be written as

$$v_{ext}(\mathbf{r}) = \begin{cases} \sum_{lm} v_{lm}^{ext}(r) Y_{lm}(\hat{r}) & \mathbf{r} \in \text{nuclei sphere} \\ \sum_{\mathbf{k}} v^{ext}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} & \mathbf{r} \in \text{interstitial} . \end{cases}$$
(2.37)

One may solve the Kohn-Sham equations within the spheres and also in the interstitial

region, demanding the match of the wavefunctions and their derivatives at the spheres' boundaries. Further manipulations can be done regarding the size of the nuclear sphere, namely how many shells of electrons are included inside the nuclear sphere for each atomic species and how many outer shells are left to be in the interstitial region. Because every electron of the atom is included in the calculation, either in the nuclear sphere or in the interstitial region, this is the all-electron approach to solving the Kohn-Sham equation which is numerically exact if all (\mathbf{k}, l, m) are included. In practice, a cut-off to all these parameters must be made and results can be tested against the cut-off for convergence.

For most materials, the bonding of individual atoms to form solids or molecules is dominated by the valence electrons of the atoms. One can therefore distinguish core electrons from valence electrons of the atom, which led to the pseudopotential approximation [67]. In this approximation, one treats nuclei and core electrons as stable ions, and this ionic potential near the central singular region - called the core region, can be replaced by a smooth effective potential. Outside the core region, the pseudopotential is exactly the same as the real potential. This way, core electrons and nuclei charges are "frozen" into the pseudopotential. Because of this, the total number of electrons in the materials simulation problem is drastically reduced which eases the computation burden for solving the Kohn-Sham equations.

In this work, we shall use the norm-preserving pseudopotentials which have the following properties [67]:

- 1. The pseudopotential preserves the spectrum of the reference atomic configuration (the atomic configuration used in the all-electron calculation);
- 2. The valence wavefunctions and pseudo-wavefunctions are identical beyond a cut-off radius r_c . Since r_c depends on the angular momentum quantum number l, we denote this cut-off by r_{cl} to explicitly indicate the l dependence;
- 3. The integrated charge density within r_{cl} is identical by using real wavefunctions

or pseudo-wavefunctions;

4. The logarithmic derivative of the real wavefunctions and pseudo-wavefunctions and its energy derivative agree beyond r_{cl} .

In the above, the pseudo-wavefunction is the solution of the Kohn-Sham equation for a single atom using the pseudopotential of the atom, while the real wavefunction is the solution of the Kohn-sham equation in the all-electron scheme without using the pseudopotential. The reference atomic configuration is obtained by doing an allelectron calculation of a single atom and finding its ground state. The pseudopotential method has been verified to be quite accurate for atomic species from H to Pu [68] in the periodic table. An example pseudopotential and pseudowavefunctions are plotted in Figure 2.2.

The pseudopotential has been generated for most atoms in the periodic table, using the following procedure. One transforms the radial Kohn-Sham equation to the following radial Schrödinger equation,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\kappa(\kappa+1)}{2r^2} + v_{eff}(r)\right]rR_{jl}(r) = \epsilon_{jl}rR_{jl}(r)$$
(2.38)

Here κ is defined as:

$$\kappa = \begin{cases} l & \text{if } j = l - 1/2 \\ -l - 1 & \text{if } j = l + 1/2 \end{cases}$$
(2.39)

A pseudo radial wavefunction $R_{jl}^{PP}(r)$ is created for each (jl) such that it is equal to the $R_{jl}(r)$ solved from the radial Schrödinger equation Eq. 2.38 beyond the cutoff radius r_{cl} . There are many ways to create this radial wavefunction, the one we employed is proposed by Troullier and Martins [69].

The peudopotential is then found by the inversion of Eq.2.38.

$$v_{eff,jl}^{PP}(r) = \epsilon_{jl} + \frac{1}{2} \frac{1}{r R_{jl}^{PP}(r)} \frac{d^2}{dx^2} r R_{jl}^{PP}(r) - \frac{\kappa(\kappa+1)}{2r^2}$$
(2.40)



Figure 2.2: The first 3 panels compare the pseudopotential wavefunctions and the reference atomic configuration for Mo [67] for the 4d, 4p, and 5s orbitals respectively. The solid line is the pseudo wavefunction, and the dotted lines are from the reference atomic configuration. The pseudo wavefunctions are indeed identical to the real wavefunction above the cut-off radius r_c . The last panel compares the pseudopotential for different quantum number l and the reference atomic configuration, and solid lines are pseudopotential. Dotted lines are potential obtained from reference atomic configuration, and solid lines are pseudopotentials. Figure courtesy of Reference [67].

Afterward, the pseudo Hartree potential and the pseudo exchange-correlation potential need to be subtracted to obtain the pseudo external potential which acts on the valence electrons. This procedure is called unscreening,

$$v_{ext,jl}^{PP}(r) = v_{eff,jl}^{PP}(r) - v_{H}^{PP}(r) - v_{xc}^{PP}(r)$$
(2.41)

This step is non-trivial because one needs to alienate the valance term and the core term in the Hartree and exchange-correlation potential to obtain their pseudopotentials. Finally, the (jl) dependence is eliminated by performing a summation over these indices to obtain the $v_{ext}^{PP}(r)$ pseudopotential [68]. It is typically written in two terms, one local and one non-local.

$$v_{ext}^{PP}(r) = v_{loc}^{PP}(r) + v_{nl}^{PP}(\mathbf{r}, \mathbf{r}') . \qquad (2.42)$$

After $v_{ext}^{PP}(r)$ is generated, it is saved into a database for practical applications of DFT in materials simulations.

Substituting $v_{ext}^{PP}(r)$ into the Kohn-Sham equation Eq. 2.18, we obtain

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}\right]\psi_i(\mathbf{r}) + \int d\mathbf{r}' v_{nl}^{PP}(\mathbf{r}, \mathbf{r}')\psi_i(\mathbf{r}') = \epsilon_i \psi_i(\mathbf{r})$$
(2.43)

where

$$v_{eff}(\mathbf{r}) = v_{loc}^{PP}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$
(2.44)

is the local part of the effective potential, and the non-local part of the pseudopotential v_{nl}^{PP} explicitly appears in Eq. 2.43. Again, Eq. 2.43 can be extended into periodic systems and spin systems, similar to that discussed in Sections 2.4 and 2.6, namely

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}^{\sigma}\right]\psi_{\mathbf{k}i}^{\sigma}(\mathbf{r}) + \int d\mathbf{r}' v_{nl}^{PP}(\mathbf{r},\mathbf{r}')\psi_{\mathbf{k}i}^{\sigma}(\mathbf{r}') = \epsilon_{\mathbf{k}i}^{\sigma}\psi_{\mathbf{k}i}^{\sigma}(\mathbf{r}) , \qquad (2.45)$$

where **k** is the reciprocal lattice momentum, σ is the spin index. This nonlinear inte-

gral equation must be solved in some manner to obtain the Kohn-Sham wavefunctions $\psi_{\mathbf{k}i}^{\sigma}$ and eigen-energies $\epsilon_{\mathbf{k}i}^{\sigma}$.

2.8 Basis Sets And LCAO Method

Eq. 2.45 can be discretized in a real space mesh and solved numerically. The real space technique is very accurate if one picks a fine mesh, but a fine mesh leads to large matrices for the eigenvalue problem which presents the bottleneck of this technique. In Reference [51], by an innovative Chebyshev filtering approach, the large eigenvalue problem is drastically reduced and the real space technique can be used to solve supercells having several thousand atoms. Nevertheless, for our work in this thesis (Chapter 4), supercells with over ten thousand atoms need to be solved, which is too large even for the Chebyshev filtering approach. The real space technique is a large basis method for solving the DFT equations. The most popular large basis is the planewaves, used by the DFT packages VASP [54], Abinit [70] and QuantumExpresso [71]. The planewave codes can typically solve supercells with a few hundred atoms. In quantum chemistry, Gaussian basis is the standard [72][73] which has the advantage of partially carrying out analytical derivations of the Hamiltonian matrix elements but again, for crystals, Gaussian basis is limited to solved problems with relatively small supercells.

In our work, we shall use the linear combination of atomic orbital (LCAO) as the basis functions. The numerical atomic orbitals [51] in the LCAO basis are:

$$\phi_{I\mu}(\mathbf{r}) = \zeta_{\mu}(|\mathbf{r} - \mathbf{R}_{I}|)Y_{l_{\mu}m_{\mu}}(\theta, \phi)$$
(2.46)

where I labels the atom and μ labels the atomic orbital of that atom, namely $\mu = s, p, d, \cdots$ to indicate the s-shell, p-shell, d-shell of the atomic configuration. The basis function $\phi_{I\mu}(\mathbf{r})$ is a product of a radial function ζ and a spherical harmonic Y_{lm} . The ζ function is solved numerically and may be put to zero outside some cut-off



Figure 2.3: A numerical atomic orbital of the s-state of the Si atom for different cut-off radius r_c . Figure courtesy of [74].

radius r_c so that two atoms with distances larger than $2r_c$ do not have orbital overlap, this increases the sparsity of the Hamiltonian matrix, thus reduces numerical computation. The spherical harmonic is centered at the nuclei of the atom. Practically, the atomic orbital functions $\phi_{I\mu}(\mathbf{r})$ are generated by solving the Kohn-Sham equation for a single atom using the pseudopotentials defining the atomic core, and saved in a database together with the corresponding pseudopotentials. Because the functions $\phi_{I\mu}(\mathbf{r})$ are the solutions of the Kohn-Sham equation using the pseudopotentials, they are also called pseudo-atomic orbitals in the literature. For material simulations, $\phi_{I\mu}(\mathbf{r})$ and its corresponding pseudopotentials are inputs to the DFT software. An example of such orbitals is plotted in Figure 2.3.

Using $\phi_{I\mu}(\mathbf{r})$ as the basis set, the Kohn-Sham wavefunctions are expanded as a

linear combination of them (LCAO basis set),

$$\psi_i(\mathbf{r}) = \sum_{I\mu} c^i_{I\mu} \phi_{I\mu}(\mathbf{r}) , \qquad (2.47)$$

where $c_{I\mu}^{i}$ are coefficients to be solved via the Kohn-Sham equation.

For crystal supercells satisfying the periodic boundary condition, we construct a new basis set from $\phi_{I\mu}(\mathbf{r})$ that satisfies Bloch's theorem,

$$\bar{\phi}_{I\mu}^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi_{I\mu}(\mathbf{r}) , \qquad (2.48)$$

where $N = \sum_{\mathbf{T}}$ is a normalization factor. With this new basis, the Kohn-Sham wavefunctions are expanded as:

$$\psi^{\sigma}_{\mathbf{k}i}(\mathbf{r}) = \sum_{I\mu} c^{i\sigma\mathbf{k}}_{I\mu} \bar{\phi}^{\mathbf{k}}_{I\mu}(\mathbf{r}) , \qquad (2.49)$$

where $c_{I\mu}^{i\sigma\mathbf{k}}$ are unknown coefficients to be solved by the Kohn-Sham equation.

To this end, we write the Kohn-Sham equation in a matrix form using an LCAO basis. Multiply $\psi_{i\mathbf{k}}^{\sigma*}$ on the left of Eq. 2.45 and integrate over \mathbf{r} , substituting in Eq. 2.49, divide by $c_{I\mu}^{i\sigma\mathbf{k}*}$, the Kohn-Sham equation reduces to the following matrix form (from now on we shall drop the *PP* superscript on the pseudopotential without causing confusion)

$$\mathbf{H}^{\mathbf{k}}\mathbf{C}^{\sigma\mathbf{k}} = \left[\mathbf{T}^{\mathbf{k}} + \mathbf{V}_{eff}^{\sigma\mathbf{k}} + \mathbf{V}_{nl}^{\sigma\mathbf{k}}\right]\mathbf{C}^{\sigma\mathbf{k}} = \mathbf{S}^{\mathbf{k}}\mathbf{C}^{\sigma\mathbf{k}}\boldsymbol{\epsilon}^{\sigma\mathbf{k}}$$
(2.50)

where $\mathbf{C}^{\sigma \mathbf{k}}$ is defined by rewriting Eq. 2.49 in a matrix form,

$$\Psi^{\sigma \mathbf{k}} = \Phi^{\mathbf{k}} \mathbf{C}^{\sigma \mathbf{k}} , \qquad (2.51)$$

and the following notations are introduced,

$$T_{I\mu,J\nu}^{\mathbf{k}} = \int d\mathbf{r} \bar{\phi}_{I\mu}^{\mathbf{k}*}(\mathbf{r}) \left(-\frac{1}{2}\nabla^{2}\right) \bar{\phi}_{J\nu}^{\mathbf{k}}(\mathbf{r})$$

$$V_{eff\,I\mu,J\nu}^{\sigma\mathbf{k}} = \int d\mathbf{r} \bar{\phi}_{I\mu}^{\mathbf{k}*}(\mathbf{r}) v_{eff}^{\sigma}(\mathbf{r}) \bar{\phi}_{J\nu}^{\mathbf{k}}(\mathbf{r})$$

$$V_{nl\,I\mu,J\nu}^{\sigma\mathbf{k}} = \int d\mathbf{r} d\mathbf{r}' \bar{\phi}_{I\mu}^{\mathbf{k}*}(\mathbf{r}) v_{nl}(\mathbf{r},\mathbf{r}') \bar{\phi}_{J\nu}^{\mathbf{k}}(\mathbf{r})$$

$$S_{I\mu,J\nu}^{\mathbf{k}} = \int d\mathbf{r} \bar{\phi}_{I\mu}^{\mathbf{k}*}(\mathbf{r}) \bar{\phi}_{J\nu}^{\mathbf{k}}(\mathbf{r})$$

$$\epsilon_{ij}^{\sigma\mathbf{k}} = \epsilon_{i}^{\sigma\mathbf{k}} \delta_{ij}$$
(2.52)

Eq. 2.50 is a matrix eigen-value problem which is readily solvable numerically to give the coefficients $\mathbf{C}^{\sigma \mathbf{k}}$ and the eigen-values $\boldsymbol{\epsilon}^{\sigma \mathbf{k}}$. Afterward, the Kohn-Sham wavefunctions are obtained by Eq. 2.49.

2.9 The RESCU electronic package

Having reviewed the main steps and theories of realizing a DFT calculation, in this work we shall apply the RESCU implementation of the DFT [51]. RESCU was developed in my research group. The distinct advantage of RESCU over essentially all other DFT codes in the literature, is that it is a general purpose method optimized for solving very large atomic systems for metals, semiconductors, insulators and molecules. Due to its optimized numerical mathematics and parallel algorithms, the computation scaling of RESCU is roughly $\mathcal{O}(2.3)$ up to supercells having ~ 10,000 atoms, which is much more efficient than the $\mathcal{O}(3)$ scaling of conventional codes. Since the RESCU implementation of DFT is well-documented, we refer interested readers to the original publication [51] and the Ph.D. thesis of Dr. Vincent Michaud-Rioux [75]. In short, the ability to carry out DFT calculations on large systems is critical for the research of this thesis.

2.10 Summary

This chapter is devoted to the theory and important implementation steps of the Kohn-Sham DFT. From the many-body Hamiltonian of a material which includes many electrons and nuclei, the Born-Oppenheimer approximation allows the separation of the electrons from the nucleus where electrons move inside the potential created by the nucleus, i.e. the nucleus are frozen in space positions when we solve the electron system. The Hohenberg-Kohn Theorem is then introduced which links an unknown total energy functional of the system with the ground state electronic density. Picking a particular form of the total energy functional, the Kohn-Sham equation is derived by minimizing the total energy, and the Kohn-Sham equation is the central result of DFT. By introducing a non-interacting reference system, the manybody Hamiltonian is transformed into a mean-field Hamiltonian with the many-body physics casted into an exchange-correlation functional. Multiple ways to approximate the exchange-correlation functional are possible, the most popular ones are the LDA and GGA, due to their relatively simple calculation procedure. The Kohn-Sham equation can be extended to crystals consisting of periodic supercells and materials with spin degrees of freedom. To reduce the number of electrons in a calculation, pseudopotentials are introduced to define the atomic core which includes the nuclei and core-shell electrons, as such only the valence electrons participate in the DFT selfconsistent calculation. Finally, we discussed the LCAO basis using the pseudo-atomic orbitals as the basis function which are used to reduce the Kohn-Sham equation to a matrix eigen-value equation. In Chapter 4, we shall apply the RESCU implementation of the DFT, to solve the electronic structure of a donor impurity in bulk Si and in particular, to determine the localized impurity states.

Addition Energy And Exact Diagonalization

In the last chapter, DFT is introduced as the first principles method to determine single-particle ground states of materials. The mean-field approximation of DFT reduces the original many-body problem to a simpler problem of single particles moving inside the mean-field produced by all the particles. However, the addition energy of a QD has a large contribution from the many-body interaction which cannot be accurately determined via a mean-field theory. In this chapter, we will discuss in more detail the physics of addition energy, its relation to Coulomb diamonds, and the method of exact diagonalization to account for the strong interaction and correlation of the electrons in the QD.

3.1 Many-Body Hamiltonian

The Hamiltonian of a many-body electron system is written as

$$\hat{H} = \hat{H}_0 + \frac{1}{2} \sum_{i,j,\sigma,i\neq j} V_{\text{Coul.}}(\mathbf{r}_i, \mathbf{r}_j)$$
(3.1)

where

$$\hat{H}_0 \equiv \sum_{i,\sigma} \left[-\frac{\hbar}{2m} \nabla_i^2 + U(\mathbf{r}_i) \right]$$
(3.2)

is the non-interacting part of the many-body Hamiltonian. Here, SI unit is employed, the subscript *i* labels the electrons and \mathbf{r}_i is the position of the *i*-the electron, and σ is the spin index of the electron. The second term in \hat{H} is the summation of Coulomb interactions between pairs of the electrons, $V_{\text{Coul.}}(\mathbf{r}_i, \mathbf{r}_j)$:

$$V_{\text{Coul.}}(\mathbf{r}_i, \mathbf{r}_j) = \frac{e^2}{4\pi\varepsilon |\mathbf{r}_i - \mathbf{r}_j|}$$

where ε is the dielectric permittivity of the material.

The above Hamiltonian can be written in the second quantization form in terms of the creation and annihilation operators [76][77],

$$\hat{H} = \sum_{\sigma} \int d\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left[-\frac{\hbar}{2m} \nabla^{2} + U(\mathbf{r}) \right] \hat{\Psi}_{\sigma}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}_{1} d\mathbf{r}_{2} \sum_{\sigma_{1}, \sigma_{2}} V_{\text{Coul.}}(\mathbf{r}_{1}, \mathbf{r}_{2}) \hat{\Psi}_{\sigma_{1}}^{\dagger}(\mathbf{r}_{1}) \hat{\Psi}_{\sigma_{2}}^{\dagger}(\mathbf{r}_{2}) \hat{\Psi}_{\sigma_{2}}(\mathbf{r}_{2}) \hat{\Psi}_{\sigma_{1}}(\mathbf{r}_{1})$$
(3.3)

where $\hat{\Psi}^{\dagger}_{\sigma}(\mathbf{r})$ is a quantum field operator that creates an electron of spin σ at position **r**. Its adjoint, $\hat{\Psi}_{\sigma}(\mathbf{r})$, annihilates an electron of spin σ at position **r**.

Using an orthonormal single-electron basis set $\{\varphi_i(\mathbf{r})\}$, for instance the solutions of \hat{H}_0 in Eq. 3.2, the field operator is expressed as:

$$\hat{\Psi}_{\sigma}(\mathbf{r}) = \sum_{i} \varphi_{i}(\mathbf{r}) \hat{c}_{i\sigma}$$
(3.4)

where $\hat{c}_{i\sigma}$ annihilates an electron of spin σ in the *i*-th basis state. Similarly

$$\hat{\Psi}^{\dagger}_{\sigma}(\mathbf{r}) = \sum_{i} \varphi^{*}_{i}(\mathbf{r}) \hat{c}^{\dagger}_{i\sigma}$$
(3.5)

where $\hat{c}_{i\sigma}^{\dagger}$ creates an electron of spin σ in the *i*-th basis state.

Using the single-particle basis $\{\varphi_i(\mathbf{r})\}\$ and Eq. 3.4 and 3.5, Eq. 3.3 becomes

$$\hat{H} = \sum_{i\sigma} \epsilon_i \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma} + \frac{1}{2} \sum_{ijkl,\sigma\sigma'} V_{ijkl} \hat{c}^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{k\sigma'} c_{l\sigma}$$
(3.6)

where ϵ_i is the *i*-th expectation value of the non-interacting Hamiltonian \hat{H}_0 , corre-



Figure 3.1: An illustration of many-body energy levels of a single impurity spin-qubit [42] for the system with N - 1, N and N + 1 electrons. The lowest energy for the systems with N electron is the ground state energy E_N^0 . The chemical potential μ_N is the difference between the ground state energy of the N and N - 1 electron system. Figure courtesy of Reference [42] with minor changes.

sponding to the single particle state $\{\varphi_i(\mathbf{r})\}$. V_{ijkl} is the Coulomb integrals of the basis set

$$V_{ijkl} = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{e^2}{4\pi\varepsilon |\mathbf{r}_i - \mathbf{r}_j|} \varphi_k(\mathbf{r}_2) \varphi_l(\mathbf{r}_1) . \qquad (3.7)$$

3.2 Addition Energy

The Hamiltonian in Eq. 3.6 can be used to describe electrons trapped in impurity states of a donor QD spin-qubit. After the many-body problem in Eq. 3.6 is solved (see below), the many-body eigen-energies and many-body wavefunctions are obtained. For a *N*-electron system (i.e. *N* electrons trapped in the spin qubit) where *N* is an integer, assuming *n* many-body eigenstates are obtained, we denote E_N^m where $m = 0, 1, 2, \dots n$, to be the energy of the *m*-th many-body states. The lowest of them, E_N^0 , is the ground state energy of the many-body Hamiltonian in Eq. 3.6. An illustration of the many-body energy levels is shown in Figure 3.1.

The chemical potential μ_N is the difference between the ground state energy of the N electron system and that of the N-1 electron system [42].

$$\mu_N = E_N^0 - E_{N-1}^0 . aga{3.8}$$

In the familiar problem of a large number of particles, i.e. N >> 1, for example, the air molecules in a room, the chemical potential μ_N is a constant independent of N. But for our spin-qubit problem involving only one of a few spins inside the QD, μ_N depends on N. With μ_N and μ_{N+1} defined using Eq. 3.8, the addition energy is the difference between them:

$$E_N^{add} = \mu_{N+1} - \mu_N \;. \tag{3.9}$$

In this work, we shall focus on the first addition energy E_1^{add} .

In the experimental gated-QD and/or donor-QD, external gate voltages are applied to control the device (see Figure 1.6 in Chapter 1). In Hamiltonian Eq. 3.2, the potential $U(\mathbf{r})$ depends on the applied gate voltages. Due to the plunger gate voltages, an extra electrostatic potential U_{pg} inside the QD is established on top of the Hartree potential discussed in Chapter 2. U_{pg} satisfies the Poisson equation and can be solved numerically and written as

$$U_{pg}(\mathbf{r}) = -|e| \sum_{i} \phi_{i} \alpha_{i}(\mathbf{r})$$
(3.10)

where ϕ_i is the potential applied at the *i*-th gate, and $\alpha_i(\mathbf{r})$ is some spatial dependent function that is always less than unity. As a result, apparently the quantities ϵ_i , E_N^0 , and μ_N all depend on the gate voltages through the electrostatic potential U_{pg} .

Let's consider the single-particle energies ϵ_i and how it changes with the gate voltages. First of all, even though $\alpha_i(\mathbf{r})$ is in principle spatial dependent, we may ignore this dependence because the gates are significantly larger than the region where electrons are confined. This way, by Eq. 3.10, the gate voltages simply add an offset to the total potential in the Hamiltonian Eq. 3.2. An overall constant potential shift does not change the single-particle wavefunctions φ_i [42]. Assume that when a gate voltage ϕ_i^0 is applied to the gate labeled by *i*, there are a set of single-particle energies ϵ_m^0 where *m* labels the single-particle states. Vary the gates voltage a little to ϕ_i , the single-particle energies become ϵ_m . Taking the expectation value of the Hamiltonian in Eq. 3.3 and assuming the wavefunctions remain the same, one has

$$\epsilon_m = \epsilon_m^0 - e \sum_i (\phi_i - \phi_i^0) \langle \varphi_m | \alpha_i(\mathbf{r}) | \varphi_m \rangle \quad . \tag{3.11}$$

Therefore, the single-particle energies change linearly with the gate voltages. $\langle \varphi_m | \alpha_i(\mathbf{r}) | \varphi_m \rangle$ is called the lever arm of gate *i* acting on state *m*. In most applications, the lever arm can be approximated to be independent of the state, and can simply be denoted as α_i . In practical simulations, once the Poisson equation is solved, the lever arm can be determined.

Let's partition the total energy of the N-electron system E_N^0 as:

$$E_N^0 = \sum_{n=1}^N \epsilon_i^0 + \sum_{n=1}^N V_c(n)$$
(3.12)

where the first term is the non-interacting single-particle energy; the second term accounts for the interactions, and $V_c(n)$ is the Coulomb interaction energy required to add the *n*-th electron to a system with n - 1 electrons. Insert Eq. 3.11 and Eq. 3.12 into Eq. 3.8, we obtain

$$\mu_N = \epsilon_N^0 - e \sum_i \alpha_i (\phi_i - \phi_i^0) + V_c(N) . \qquad (3.13)$$

Substitute Eq. 3.13 into Eq. 3.9, we have

$$E_N^{add} = \epsilon_{N+1}^0 - \epsilon_N^0 + V_c(N+1) - V_c(N) . \qquad (3.14)$$

This result suggests that the addition energy E_N^{add} is independent of the gate voltages ϕ_i if taken the assumption that the lever arm is independent of the state and the state wavefunctions are unchanged with different gate voltages, as we have seen above. If one recalculates ϵ_N from another gate voltage, according to Eq. 3.11 the part depending on the lever arm will be canceled. Similarly, the Coulomb integral in Eq. 3.7 remains unchanged since a constant shift of the potential does not change

wavefunctions. As a result, V_c also remains the same with the change of gate voltages. We conclude that the addition energy E_N^{add} can be obtained without the complications of including the gate voltages in the analysis. In the literature, the number $V_c(N + 1) - V_c(N)$ is defined as the charging energy. Note that the single-particle energies $\epsilon_2^0 = \epsilon_1^0$ due to the spin degeneracy. Therefore, by Eq. 3.14, the first addition energy $E_1^{add} = V_c(2) - V_c(1)$, i.e. it is just the charging energy.

3.3 Coulomb Diamonds

As discussed in Chapter 1, the addition energy discussed in the last section is closely related to the Coulomb blockade effect and the Coulomb diamonds diagram which is measured experimentally. Here we show that the height of the apex of a Coulomb diamonds diagram corresponds to the addition energy.

Consider a QD having a source electrode, a drain electrode and a plunger gate (pg). The externally applied voltages on these electrodes are V_S , V_D and V_{pg} , respectively. If there are more gates, we assume all other gate voltages remain constants. The source and the drain act as electron reservoirs that allows electrons to tunnel into the qubit. If the voltages of the source or the drain are changed by ΔV_S (V_D), the chemical potential of the source or the drain μ_S (μ_D) is raised by $e\Delta V_S(V_D)$. The operation of QD-based spin-qubit is in the sequential tunneling regime where electrons tunnel into and out of the QD one by one. Sequential tunneling is dominated by the Coulomb blockade (CB) phenomena [17]. When transport is Coulomb blockaded, no current flows through the QD. It corresponds to the situation when it is energetically neither favorable to remove one electron nor favorable to add an electron, into the QD. Since no electron is added or removed from QD, there is no current flow through the QD. The CB regime is established when chemical potentials satisfy

$$\mu_N \le \mu_S(\mu_D) \le \mu_{N+1}$$
 (3.15)



Figure 3.2: An illustration of the situation with no conductance and the system will remain in a N electron state [42]. This is because the energy gain in removing an electron from the source or drain μ_S, μ_D is not enough for the energy to put the N + 1-th electron into the system μ_{N+1} . But at the same time, the energy required to put an electron into the source or drain μ_S, μ_D is greater than the energy gain in removing an electron from the system with already N electron μ_N . Therefore no electrons would move into or out of the system, and the system will remain in a N electron state, meaning there will be no current or conductance. Figure adapted from Reference [42] with minor changes.

This means that the energy gain in removing an electron from the source or drain μ_S , μ_D is not enough to put the N + 1-th electron into the QD which requires energy μ_{N+1} . At the same time, the energy required to put an electron into the source or drain μ_S , μ_D is greater than the energy gain of μ_N in removing an electron from the QD of N electrons. The energetics thus dictates that no electrons would move into or out of the QD, the QD remains in the N electron state and there is no current. A qualitative illustration of the energy diagram of the CB is in Figure 3.2. In this illustration, the QD remains in an N electron state.

In sequential tunneling, current is not Coulomb blockaded when

$$\mu_S \ge \mu_N \ge \mu_D , \qquad (3.16)$$

as schematically shown in Figure 3.3. In Figure 3.3b, the bias voltage is defined as $V_{SD} \equiv V_S - V_D$. Under the condition of Eq. 3.16, as can be seen in all three cases in Figure 3.3, it is energetically favorable to remove an electron from the N electron QD and put it into the drain. Once an electron is removed from the QD, it is energetically favorable to remove and put it into the QD so that the QD has N electrons again. This way, an electron jumps out of the QD followed by an



Figure 3.3: An illustration of the situation with finite conductance. Figure (b) is the common chemical potential situation with a current flow, when $\mu_S \ge \mu_N \ge \mu_D$. Figure (a) and (c) correspond to edge cases when $\mu_S = \mu_N$ and $\mu_D = \mu_N$. [42]. It is energetically favorable to remove an electron from the N electron system and put it into the drain. But once an electron is removed, it is again energetically favorable to remove an electron from the source and put it into the system so that it would have N electrons again. Therefore electrons would tunnel in and out of the system one by one, creating a current. Figure courtesy of Reference [42].

electron jumping into the QD, a finite current thus flows through the QD. Of course, the signs in Eq. 3.16 could be flipped which would also have a current flow: this time from drain to source,

$$\mu_S \le \mu_N \le \mu_D . \tag{3.17}$$

The Coulomb diamonds seen in experimental measurements (see Figure 1.7 in Chapter 1) can now be understood. Note that the boundary of the "diamonds" corresponds to the transition between the situation with a current flow and the situation with no current flow. From Eq. 3.15, 3.16 and 3.17, and from Figure 3.3, we see that for a QD at its N electron state, this transition corresponds to the edge cases when $\mu_S = \mu_N$ for Figure 3.3a and $\mu_D = \mu_N$ for Figure 3.3c.

At zero bias voltage, i.e. $V_{SD} = 0$, $V_S = V_D = V^0$ where V^0 is some value, the chemical potentials of the source and the drain are equal, $\mu_S = \mu_D = \mu^0$ where μ^0 is some constant. One tunes the plunger gate voltage until at some V_{pg}^0 , one has $\mu_S = \mu_D = \mu_N = \mu^0$, meaning that the three chemical potentials align with each other. This situation is shown as the red dot in Figure 3.4 where we plotted the Coulomb diamonds. Assume V^0 for the source and the drain, and V_{pg}^0 for the plunger



Figure 3.4: An illustration of the Coulomb diamonds. The red dot corresponds to the situation when $\mu_S = \mu_D = \mu_N$. The edge cases of $\mu_S = \mu_N$ and $\mu_D = \mu_N$ give two linear relationship between V_{pg} and V_{SD} , acting as sides of the Coulomb diamonds. The hollow dot is the apex of a diamond, which is the intersection between the $\mu_S = \mu_N$ line and the $\mu_D = \mu_{N+1}$, and its height correspond to E_N^{add} [42]. Figure adapted from Reference [42] with minor changes.

gates are used as the starting voltage to calculate ϵ_N^0 in Eq. 3.13. Then with Eq. 3.13 a relationship as the following can be written,

$$\mu_{S} = \mu_{D} = \mu_{N}$$

$$= \mu^{0} = \epsilon_{N}^{0} + V_{c}(N) .$$
(3.18)

We now add a bias voltage. Let us define a unitless quantity $f, 1 \ge f \ge 0$, and for some bias $V_{SD}, V^0 - fV_{SD}$ is applied to the drain, and $V^0 + (1 - f)V_{SD}$ is applied to the source. Experimentally, the value of f is usually 1/2. Following the discussion at the beginning of this section, one has

$$\mu_S = \mu^0 + e(1 - f)V_{SD} \quad , \tag{3.19}$$

$$\mu_D = \mu^0 - efV_{SD} \quad . \tag{3.20}$$

Following the definition of f and Eq. 3.13, at some plunger gate voltage V_{pg} ,

$$\mu_N = \epsilon_N^0 - e \left[\alpha_{pg} (V_{pg} - V_{pg}^0) + (1 - f) \alpha_S V_{SD} - f \alpha_D V_{SD} \right] + V_c(N)$$
(3.21)

where α_{pg} , α_S , and α_D are the lever arms of the plunger gate, the source, and the

drain respectively. Next, consider the edge case where $\mu_S = \mu_N$. One can equate Eq. 3.19 with Eq. 3.21,

$$\mu^{0} + e(1-f)V_{SD} = \epsilon_{N}^{0} - e\left[\alpha_{pg}(V_{pg} - V_{pg}^{0}) + (1-f)\alpha_{S}V_{SD} - f\alpha_{D}V_{SD}\right] + V_{c}(N) .$$
(3.22)

Subtract Eq. 3.18 from Eq. 3.22, we obtain

$$V_{pg} - V_{pg}^{0} = -\frac{1}{\alpha_{pg}} \left[(1-f)\alpha_s - f\alpha_D + (1-f) \right] V_{SD} .$$
 (3.23)

Therefore, for the edge case $\mu_S = \mu_N$, there is a linear relationship between V_{pg} and V_{SD} , which produces a straight line boundary when one plots the current as a function of V_{pg} and V_{SD} . This straight line, together with the line corresponding to $\mu_D = \mu_N$, and two lines coming from the N + 1 electron state corresponding to $\mu_S = \mu_{N+1}$ and $\mu_D = \mu_{N+1}$, form a diamond shape area in which there is no current flow. Outside the diamond area, there is current flow, as shown in Figure 3.4.

Let's write down the equation for the other three lines. Similarly for the edge case of $\mu_D = \mu_N$, equate Eq. 3.20 with Eq. 3.21 and subtract Eq. 3.18, one obtains

$$V_{pg} - V_{pg}^0 = -\frac{1}{\alpha_{pg}} \left[(1 - f)\alpha_s - f\alpha_D - f \right] V_{SD} .$$
 (3.24)

For the case where $\mu_S = \mu_{N+1}$, Eq. 3.21 is rewritten as

$$\mu_{N+1} = \epsilon_{N+1}^0 - e \left[\alpha_{pg} (V_{pg} - V_{pg}^0) + (1 - f) \alpha_S V_{SD} - f \alpha_D V_{SD} \right] + V_c(N+1) . \quad (3.25)$$

Equate to Eq. 3.19 again we obtain

$$\mu^{0} + e(1-f)V_{SD} = \epsilon^{0}_{N+1} - e\left[\alpha_{pg}(V_{pg} - V^{0}_{pg}) + (1-f)\alpha_{S}V_{SD} - f\alpha_{D}V_{SD}\right] + V_{c}(N+1) .$$
(3.26)

Again, subtracting Eq. 3.18 we obtain the linear relationship

$$V_{pg} - V_{pg}^{0} = \frac{1}{e\alpha_{pg}} (\epsilon_{N+1}^{0} - \epsilon_{N}^{0} + V_{c}(N+1) - V_{c}(N)) - \frac{1}{\alpha_{pg}} \left[(1-f)\alpha_{s} - f\alpha_{D} + (1-f) \right] V_{SD} .$$
(3.27)

A similar derivation for $\mu_D = \mu_{N+1}$ gives

$$V_{pg} - V_{pg}^{0} = \frac{1}{e\alpha_{pg}} (\epsilon_{N+1}^{0} - \epsilon_{N}^{0} + V_{c}(N+1) - V_{c}(N)) - \frac{1}{\alpha_{pg}} [(1-f)\alpha_{s} - f\alpha_{D} - f] V_{SD} .$$
(3.28)

The lines corresponding to $\mu_S = \mu_N$ and $\mu_D = \mu_{N+1}$ will intersect at some V_{pg} and V_{SD} . This corresponds to the apex of our diamond, illustrated by the hollow dot in Figure 3.4. To find the height of the diamond's apex, equate Eq. 3.23 and Eq. 3.28 to obtain

$$eV_{SD} = \epsilon_{N+1}^0 - \epsilon_N^0 + V_c(N+1) - V_c(N) . \qquad (3.29)$$

Recall Eq. 3.14, this is equal to E_N^{add} . Interestingly, this apex height is independent of parameters f, α_{pg} , α_S , and α_D . Therefore, the addition energy of the QD can be read from the apex height of the bias voltage in the Coulomb diamond diagram (divided by elementary charge). Therefore, from the experimentally measured diamond shown in Figure 1.7, the addition energy is 47 ± 3 meV.

3.4 Envelope Function Theory

To theoretically predict addition energy, the many-body Hamiltonian in Eq. 3.6 must be solved. One typically proceeds in three steps. The first step is to solve the singleparticle states $\varphi_i(\mathbf{r})$ and energies ϵ_i that appear in Eq. 3.6. The single-particle states $\varphi_i(\mathbf{r})$ form the basis functions of the field operators in Eq. 3.4 and 3.5. The second step is to calculate the Coulomb integrals in Eq. 3.7. Finally, the third step is to carry out exact diagonalization of the many-body Hamiltonian matrix formed by Eq. 3.6 with the single-particle basis set { φ_i }. In this section, we present the envelope function theory to solve the single-particle states, i.e. the first step of the theoretical procedure. As stated in Chapter 1, we shall not use envelope function theory for our work (see Chapter 4) since we wish to do first principles analysis, but it is a very widely used and state-of-the-art single particle theory of semiconductor physics.

The non-interacting Hamiltonian in Eq. 3.2 can be rewritten in terms of H_p - for the perfect crystal which we assume is solved, and a single particle potential U which accounts for any perturbations to the perfect crystal. For the single impurity spin qubits in Si, H_p is the Hamiltonian of the bulk Si; U is a 1/r-like Coulomb potential in the hydrogenic model of the impurity atom. The non-interacting Schrödinger equation is

$$[H_p + U(\mathbf{r})]\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) . \qquad (3.30)$$

Here, H_p gives the band structure of the crystal $E_n(\mathbf{k})$ and the corresponding Bloch wavefunctions $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$, where *n* labels the bands and **k** the momentum.

We expand the wavefunction $\Psi(\mathbf{r})$ in Eq. 3.30 in terms of the Bloch wavefunctions of the perfect crystal,

$$\Psi(\mathbf{r}) = \sum_{n,\mathbf{k}} F_n(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r})$$

= $\sum_{n,\mathbf{k}} F_n(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$. (3.31)

Inserting this in Eq. 3.30,

$$\sum_{n,\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) [E_n(\mathbf{k}) - E + U(\mathbf{r})] F_n(\mathbf{k}) = 0 .$$

Multiply the above equation by $\psi_{n'\mathbf{k}'}(\mathbf{r})$ and integrate over \mathbf{r} , we obtain

$$\sum_{n,\mathbf{k}} [(E_n(\mathbf{k}) - E)\delta_{n\mathbf{k},n'\mathbf{k}'} + U_{n\mathbf{k},n'\mathbf{k}'}]F_n(\mathbf{k}) = 0$$
(3.32)

where $U_{n\mathbf{k},n'\mathbf{k}'}$ is the matrix element for the perturbation potential,

$$U_{n\mathbf{k},n'\mathbf{k}'} = \int d\mathbf{r} \psi_{n'\mathbf{k}'}(\mathbf{r}) U(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) \, .$$

To proceed further, some assumptions are made [42]:

- 1. Assuming that the perturbing potential changes slowly on the scale of the crystal lattice constant, i.e., $U(\mathbf{q})$ is significant only for $q \leq \pi/a$;
- 2. Assuming that the perturbation is small compared to the typical energy scale in the semiconductor crystal, i.e. the band gap;
- 3. Assuming that the coefficients $F_n(\mathbf{k})$ to have significant value only near some band minimum \mathbf{k}_m , e.g. the Γ -point where $\mathbf{k} = 0$.

With these reasonable assumptions, it can be proved that the perturbation will not mix states of different bands, and $U_{n\mathbf{k},n'\mathbf{k}'} \simeq U(\mathbf{k}' - \mathbf{k})\delta_{nn'}$. The detailed derivations can be found in Reference [42]. Eq. 3.32 can thus be written as,

$$\sum_{\mathbf{k}} [(E_n(\mathbf{k}) - E)\delta_{\mathbf{k},\mathbf{k}'} + U(\mathbf{k} - \mathbf{k}')]F_n(\mathbf{k}) = 0.$$
(3.33)

Because only **k** that is near the band minimum is important, an approximation can be made such that $u_{n\mathbf{k}}(\mathbf{r}) \simeq u_{0\mathbf{k}}(\mathbf{r})$. Substitute this into Eq. 3.31,

$$\Psi(\mathbf{r}) = u_{0\mathbf{k}}(\mathbf{r}) \sum_{\mathbf{k}} F_n(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} = u_{0\mathbf{k}}(\mathbf{r}) F_n(\mathbf{r})$$
(3.34)

where $F_n(\mathbf{r})$ is the Fourier transform of $F_n(\mathbf{k})$. $F_n(\mathbf{r})$ is called the envelope function, and is the key in the envelope function theory.

Using the approximation near the conduction band minimum and assuming a

parabolic band dispersion there, namely

$$E_c(\mathbf{k}) = E_c + \frac{\hbar^2 k^2}{2m^*}$$

where E_c is the conduction band minimum and m^* is the effective mass of electron. Substituting this into Eq. 3.33, we obtain

$$\frac{\hbar^2 k^2}{2m^*} F_c(\mathbf{k}) + \sum_{\mathbf{k}'} U(\mathbf{k}' - \mathbf{k}) F_c(\mathbf{k}') = (E - E_c) F_c(\mathbf{k}) .$$
(3.35)

Fourier transform this equation to real space leads to,

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + E_c + U(\mathbf{r})\right]F_c(\mathbf{r}) = EF_c(\mathbf{r}) . \qquad (3.36)$$

Eq. 3.36 is an effective Schrödinger equation for the envelop function, and the crystal potential inside H_p disappears but its effect is accounted for by the effective mass. The potential in Eq. 3.36 is an effective potential $E_c + U(\mathbf{r})$. This way, the Hamiltonian of a perturbed crystal is transformed into a free particle Hamiltonian for the envelope functions inside an effective potential.

This is especially useful for analyzing single impurity spin-qubits, because the perturbing potential is simply a 1/r Coulomb potential in the hydrogenic model of the impurity atom. This way, the effective Schrödinger equation Eq. 3.36 becomes a hydrogen Hamiltonian with an effective mass which can be solved in closed form. Note that the hydrogen-like problem, even with interactions, is well known [45]. Therefore the many-body energies and the addition energy can be obtained by solving this known problem. While theoretically useful, the envelope function theory for the donor-QD relies on material parameters (e.g. effective mass) and assuming the impurity to be hydrogen-like, as well as other approximations mentioned above. As a result, it predicts the addition energy of phosphorous single impurity is Si to be 29 meV [45], to be compared to the experimentally measured value of 47 ± 3 meV [38].

3.5 Exact Diagonalization

Instead of using the hydrogenic model to deal with the single impurity atom in a host material, we may use the exact diagonalization technique to solve the manybody Hamiltonian in Eq. 3.6 [52]. In particular, we shall use the QTCAD spinqubit simulator [77] for our numerical calculations. The many-body Hamiltonian is written in the basis set spanned by $\{\varphi_i(\mathbf{r})\}$ defined in Section 3.1. To solve the many-body Hamiltonian exactly, the basis set should in principle be complete. Exact diagonalization is based on the assumption that by truncating the complete basis set into a smaller set containing n_{states} states, the solution of the problem does not change significantly. The validity of this assumption can be verified by increasing n_{states} and checking the convergence of the solution. The result of such a convergence check will be presented in Chapter 4.

Let's truncate the basis set to $\{\varphi_i(\mathbf{r})\}, i \in \{1, ..., n_{\text{states}}\}$. Assume the degeneracy of a basis state is n_{degen} , which for the spin qubits $n_{\text{degen}} = 2$ due to spin degeneracy. The total number of single-particle basis states is then $n_{\text{states}} \times n_{\text{degen}}$. Note that each of the single-electron basis states can only be occupied by one electron, therefore the maximum number of electrons is

$$N_{\rm max} = n_{\rm states} \times n_{\rm degen} \ . \tag{3.37}$$

Exact diagonalization can solve the many-body energies of a system with a maximum electrons number of N_{max} . However, to accurately calculate the energies of a system with N electrons, a large number of $N_{\text{max}} >> N$ is required. The exact N_{max} to obtain an accurate result needs to be found with the convergence test.

To solve for the many-body Hamiltonian, one first breaks it down to $N_{\text{max}} + 1$ many-body subspace, each containing N electrons with $N \in \{0, 1, ..., N_{\text{max}}\}$. The many-body basis set can then be written in the particle-number representation for the N electron subspace. This representation writes a many-body basis state as a binary string with $n_{\text{states}} \times n_{\text{degen}}$ digits, and the *i*-th digit is zero (one) if the *i*-th single-electron state is empty (occupied). This is under the constraint that the number of occupied states should be equal to N. For example, if there are $n_{\text{states}} = 2$ states in the original basis state, and the system has spin degeneracy such that $n_{\text{degen}} = 2$, in the particle-number representation a state is a string of $2 \times 2 = 4$ digits. For the N = 2 electron many-body subspace, for example, the many-body basis set can be written as

$$\{|1100\rangle, |1010\rangle, |1001\rangle, |0110\rangle, |0101\rangle, |0011\rangle\}, \qquad (3.38)$$

The many-body basis state can be defined with fermionic creation operators \hat{c}_i^{\dagger} that create an electron in the *i*-th single-electron basis state. For example,

$$|1100\rangle \equiv \hat{c}_1^{\dagger} \hat{c}_2^{\dagger} |0\rangle \tag{3.39}$$

where $|0\rangle$ is the vacuum state with no electron. Now, suppose one is given a basis set $\{\varphi_i(\mathbf{r})\}\$ which are the solutions of the single particle Hamiltonian in Eq. 3.2. If one chooses n_{states} of the states in this basis set with degeneracy n_{degen} , and the expectation value of the non-interacting Hamiltonian is $\{\epsilon_i\}$, the many-body Hamiltonian Eq. 3.6 can be solved by partitioning it into $N_{\text{max}} + 1$ subspace each with the many-body basis set defined above (i.e. examples in Eq. 3.38, 3.39). After evaluating the Coulomb integral in Eq. 3.7, the many-body Hamiltonian can be written in a matrix form with the many-body basis states. This many-body Hamiltonian matrix is block diagonal due to the partition into many-body subspace. Finally, this matrix eigenvalue problem can be solved numerically to obtain the many-body energies which give the addition energy.

While very accurate, the disadvantage of exact diagonalization is also obvious: it is only computationally tractable for a system with a very small number of electrons. If one wishes to exactly diagonalize a system with a large number of electrons, the many-body basis set, as seen in the example in Eq. 3.38, would grow exponentially. For a QD, this method is computationally feasible with roughly 10 electrons or less. Luckily, for our donor spin-qubit, the calculation of the first addition energy E_1^{add} requires exact diagonalization of a many-body Hamiltonian of only two electrons. The computational complexity is not an issue since only a few single-particle basis functions suffice to converge the result, as will be presented in Chapter 4. The advantage of this method is also obvious. It solves the Hamiltonian exactly, taking care of all Coulomb interactions and exchange-correlation energy exactly. There is no mean-field approximation for the interactions of the electrons. For quantities such as the addition energy which comes from interactions, exact diagonalization gives very accurate results.

3.6 The QTCAD spin-qubit simulator

Having reduced the many-body Hamiltonian Eq. 3.6 into a matrix form, we carry out exact diagonalization using the QTCAD spin-qubit simulator [77]. QTCAD is a finite-element-method (FEM) simulation platform for quantum technology [77]. It is mainly used to aid the fabrication process of QD based spin-qubits. QTCAD has an exact diagonalization module that calculates the many-body physics of systems having a few electrons.

The original workflow of QTCAD is to create a 3D numerical mesh and define an external potential for the QD, the QTCAD simulator solves the electrostatic properties self-consistently by the Poisson and Schrödinger equations within the envelope function theory. Assuming that the envelope functions are good representations of the QD states, these functions are taken as the single-electron basis set described in Section 3.5 to perform exact diagonalization. One obtains the many-body energies and other many-body properties [78][79]. In Chap. 4, we shall use QTCAD to perform exact diagonalization calculations of the donor-QD spin-qubit, in which we employed its exact diagonalization module without doing the envelope function calculation.

3.7 Summary

In this chapter, we showed that solving the many-body Hamiltonian of electrons is essential for calculating the addition energy in QD. The addition energy is shown to be related to the experimentally measurable Coulomb diamonds in the sequential tunneling transport through the QD which is dominated by Coulomb blockade. A theory that is widely used to solve the single-particle states in semiconductors is the envelope function theory, and these single-particle states serve as the basis functions for exactly diagonalizing the many-body Hamiltonian. Finally, the QTCAD spinqubit simulator which we shall employ to do the exact diagonalization is very briefly introduced.

In the next Chapter, we shall analyze the single donor spin-qubit in Si. Instead of solving the single-particle states by envelope function theory, we shall solve them by DFT so that the material properties of the donor-QD are included at the atomic level. Afterward, we exactly diagonalize the many-body Hamiltonian using the QTCAD simulator to predict the addition energy.

4

Addition Energy of Single Donor QD in Si

We have so far established a theoretical approach for first principles prediction of addition energy of single donor quantum dots. In this Chapter we shall investigate the experimental system [38] of a single P dopant in bulk Si. Similar single atom QDs were fabricated using As atoms [39] as well. In a recent work [80], a large database with over 50,000 single-atom or few-atom impurities in bulk Si, diamond and SiC, was theoretically proposed for applications in quantum technology, providing a large and exciting material platform for practical implementation of spin-qubits in the atomic limit. We select P-in-Si for our investigation since experimental transport measurements were accurately carried out for this system [38]. In particular, the first addition energy in the transport measurements was reported [38] to be 47 ± 3 meV (see Figure 1.7 in Chapter 1). This value was argued to be consistent with the ionization energy of P atoms in Si which were measured by optical techniques a long time ago [45]. Using the first principles approach, here we attempt to predict the addition energy to directly compare with the measured data without phenomenological parameters.

Our calculation proceeds in two steps, as shown in Figure 4.1. First, we determine the P impurity states in the crystal fields of bulk Si using DFT. A surprising result is that unless the Si supercell is very large, > 10,000 atoms, the impurity states are not accurately determined due to the finite-size effect. We monitored the finite-size effect by calculating the addition energy versus the supercell size until the results converges to a stable value. The technical difficulty of handling a huge number of atoms in DFT is solved by the RESCU method [51] reviewed in Chapter 2. Second, taking the localized impurity states obtained by DFT as the basis set, we carry out many-body analysis by exact diagonalization using the QTCAD method reviewed in Chapter 3, which gives the addition energy of the single P-donor QD. Note that the many-body theory can use any basis set, for example, the Gaussian functions, finite-difference grids, planewaves, etc., but using the DFT states as the basis has the great advantage of automatically including the detailed ground state properties of the material system without resorting on any phenomenological parameters. Our first principles theory and simulation predicts the addition energy to be 48.9 meV for the P-in-Si system, in very good agreement with the measured data.

4.1 DFT analysis of the impurity states

In our DFT analysis using the RESCU package [51], the exchange-correlation is treated at the GGA level (see Section 2.5.2), the atomic cores are defined by the Trottier-Martin (TM) norm-conserving pseudopotentials (Section 2.7), and the LCAO basis is at the level of double-zeta with polarized (DZP). For the large supercells (see below), it is necessary to use the LCAO basis to construct a Hilbert subspace for solving the eigenvalue problem of Kohn-Sham equations. We used a Pulay mixing method [81] for the self-consistent DFT iteration. The mixing determines how charge density $\rho(\mathbf{r})$ is updated after each self-consistent step, which is necessary to overcome numerical instabilities due to charge sloshing. In Pulay mixing, a mixing history of six steps was used which we found to be a good compromise between computer memory consumption and numerical stability. The real space potential (i.e. Hartree) in the Kohn-Sham Hamiltonian Eq. 2.16 in Chapter 2 is calculated in a real space cubic mesh of 206^3 which we tested to be fine enough for all the systems investigated. Finally, due to the large supercells, only the Γ -point is sampled in the Brillouin zone during the DFT self-consistent iterations which is justified in Section 2.4. After the Kohn-Sham Hamiltonian is converged, a full band structure can be obtained.

The P-in-Si system is a cubic supercell of Si consisting of N atoms where N ranges



Figure 4.1: An illustration of the workflow of our method.



Figure 4.2: The P-in-Si cubic supercell with 10648 atoms used in the DFT calculation. A 3D view of the supercell is shown in this figure, and a zoomed view in the center box is expanded in the inset. The Si atom in the center of the supercell is replaced by a phosphorous impurity atom, indicated by the yellow atom in the illustration. All others are silicon atoms. This supercell has a side length of 5.97 nm.

from a few hundred to 10,648 atoms. The Si atom in the center of the supercell is replaced by a phosphorous impurity atom. A 3D view of the supercell is shown in Figure 4.2, and a zoomed view in the center box is expanded in the inset. The atom marked yellow in the supercell is the phosphorous atom, all others are silicon atoms. For the pristine Si lattice, we use the experimentally known lattice constant of 5.429 angstroms. When a P impurity is present, in principle a structure relaxation is desired. A previous work showed [82] that the structural relaxation gave slightly less than 1% change in the formation energy for a Si supercell with 431 Si atoms and one P impurity. Since we are working with much larger systems, we shall use the unrelaxed structure for our DFT calculations and ignore the small effects due to relaxation.

The DFT calculation was carried out by the Béluga computer cluster of the Digital Research Alliance of Canada. We used 10 computation nodes each with 40 computing cores and 186G of memory. The DFT self-consistent calculation of the largest system, 10,648 atoms, required 72 wall-clock hours and 23 self-consistent steps to converge. Afterward, we obtain the wave functions of the Kohn-Sham states at the Γ -point.
As discussed in Section 3.5 and 4.1, we need to use the impurity states as the basis set for exact diagonalization calculation of the many-body Hamiltonian Eq. 3.6 in Chapter 3. The impurity states are solutions of the Kohn-Sham Hamiltonian Eq. 2.18 in Chapter 2 and localized around the impurity. As discussed in Section 3.4, the impurity states have energies near the conduction band minimum. As an example, it can be shown that the 1s impurity state (in a hydrogenic impurity model) in the envelope function approach for conduction electrons is at the six-fold degenerate conduction band minimum of Si. The degeneracy is lifted and split into a singlet A_1 state with the lowest energy, a triplet T_2 state and a doublet E-state [46][83]. The lowest energy A_1 state is most important for our problem, since it is the state in which the first and second conduction electron most likely occupy, and the first addition energy is mostly contributed from the interactions of the first and second conduction electron. For very large supercell sizes, the Brillouin zone shrinks to essentially zero, i.e. to the Γ -point [84]. Therefore, we may inspect the Kohn-Sham states near the conduction band minimum at the Γ -point. In the following discussion, we shall continue to use A_1 , T_2 to indicate impurity states even though they will come from DFT calculations. For the P-in-Si system, the Fermi level is calculated to be at -3.3eV and the energy of the A_1 state is 0.0148 eV above the Fermi level. The probability density of the A_1 state, i.e. the absolute square of the Kohn-Sham wavefunction $|\psi_{A_1}|^2$ is plotted in Figure 4.3 for the (001) and (011) views. The yellow surface is the isosurface for the probability density of 7.3×10^{-13} in atomic units, i.e. the energies are in Hartree and the lengths are in Bohr. A two-dimensional slice of the probability density through the phosphorous impurity atom in the [100]-[010] plane is shown in Figure 4.4. Indeed, the A_1 state is localized around the phosphorous impurity atom, spreading around 2-3 nanometers around the impurity, similar to other DFT calculated results [84].

After visually inspecting the Kohn-Sham states to find the localized ones surrounding the P impurity, we further confirm them quantitatively. Since the atomic orbital of the P impurity must contribute more significantly to the impurity state than those from the Si atoms, using Eq. 2.47 in Chapter 2, the coefficients $\sum_{\mu,I=\text{P atom}} c_{I\mu}^i$ in Eq. 2.47 must be significant. As the Kohn-Sham states are normalized, $\sum_{I\mu} (c_{I\mu}^i)^2 = 1$, and for the largest system there are more than 10000 atoms, we thus practically define that an atomic orbital is significant if

$$c_P = \sum_{\mu,I=P \text{ atom}} \left(c_{I\mu}^i\right)^2 \gg 10^{-4}.$$
 (4.1)

This way, we find that the A_1 state identified above indeed has a high value of $c_P = 0.0092$, i.e. the atomic orbitals of the P impurity contribute to this Kohn-Sham state most significantly, much larger than all other atomic orbitals. Following the same procedure, we identified other impurity states at higher energies: 0.052, 0.0804, and 0.133 eV above the Fermi level. The (001) views of two such impurity states are shown in Figure 4.5 at energies 0.052 and 0.133 eV, respectively. Since the Kohn-Sham state at energy of 0.052 eV is found to be 3-fold degenerate, we assign them to be the T_2 states discussed above. Other Kohn-Sham states have larger mixing of the atomic orbitals of P and Si atoms, and could not be unambiguously identified as impurity states. Nevertheless, as presented in the next Section, the Kohn-Sham state A_1 is of the utmost importance to the addition energy, while states with energies above T_2 have a negligible contribution.

4.2 Addition Energy

As presented in the last section, we used the RESCU electronic package [51] to solve Kohn-Sham wavefunctions of the P-impurity states, which serve as the single-particle basis set for the many-body calculation of the addition energy of the single P-impurity QD in Si. To this end, we apply the QTCAD spin-qubit simulation package [77] to exactly diagonalize the many-body Hamiltonian Eq. 3.6 in Chapter 3. The combined RESCU/QTCAD approach provides an atomistic and first principles view of the electron-electron interactions in the P-in-Si system.



Figure 4.3: The probability density $|\psi_{A_1}|^2$ of the A_1 state of a N = 10648 supercell plotted in VESTA. The yellow surface is the isosurface for the probability of 7.3×10^{-13} in atomic units. Figure (a) is a (001) view. Figure (b) is the (011) view, in which the supercell is rotated 45 degrees along the x-axis from the perspective of (a).



Figure 4.4: A two dimensional slice of the probability density $|\psi_{A_1}|^2$ slicing through the phosphorous impurity atom in the [100]-[010] plane in atomic units.



Figure 4.5: The (001) view of the probability density $|\psi|^2$ of two chosen impurity states of a N = 10648 supercell plotted in VESTA. The yellow surfaces are the isosurface for the probability of 7.3×10^{-13} in atomic units. The chosen states are: (a). One of the T_2 impurity states with an energy of 0.052 eV above the Fermi level (b). An impurity state with an energy of 0.133 eV above the Fermi level.

To proceed with the RESCU/QTCAD combined analysis, two transformations of data must be done. First, a transformation of physical units is necessary since RESCU used atomic units (a.u.) while QTCAD uses SI units. Apart from simple relationships for energy and length between a.u. and SI, the wavefunctions receive a transformation factor. Noting that the wavefunctions are normalized,

$$\int_C \psi(\mathbf{r})^{\dagger} \psi(\mathbf{r}) d\mathbf{r} = 1$$

where C is supercell. Therefore, going from a.u. to SI units, a multiplicative factor a_{renorm} is required to transform the wavefunctions:

$$a_{\rm renorm} = \sqrt{\frac{1}{a_0^3}}$$

where a_0 is the Bohr radius

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2m_e}$$

Second, while the QTCAD package is a finite-element method (FEM) solver which

usually requires a 3D FEM mesh, the wavefunctions from the RESCU package are stored in a 3D hyperrectangle mesh. To this end, we applied the open-source mesh generator GMSH to create a 3D hyperrectangle mesh with 206³ nodes for the QTCAD solver to receive the P-impurity wavefunctions from RESCU.

In many-body theory by exact diagonalization, as discussed in Section 3.5, the number of basis functions is critical for obtaining accurate results. The size of the many-body basis set grows exponentially with the increase of the number of electrons and becomes the numerically limiting factor of any method involving exact diagonalization. Fortunately, for QD-based spin-qubits, only a very small number of electrons - one to a few, is confined in the QD. This allows one to achieve accurate results with a small number of basis functions n_{states} . Practically, we increase n_{states} until the predicted addition energy is converged. For $n_{\text{states}} = 1$, only the A_1 impurity state is used (a total of two states due to the spin degeneracy). For $n_{\text{states}} = 4$, the A_1 and T_2 impurity states discussed above, are included in the basis (total of eight states due to spin degeneracy). For the largest Si supercell with N = 10648 atoms, Figure 4.6 plots the calculated addition energy versus n_{states} . We observe that starting from $n_{\text{states}} = 2$, the addition energy quickly converges to a stable value. Here we are focusing on the first addition energy which is mainly contributed from the interactions between the first and second conduction electron (see discussions in Section 3.2), as such it is the single particle states with the lowest energies that dominate the interactions.

Figure 4.6 shows that for the P-in-Si supercell with N = 10648 atoms, the calculated first addition energy converges to a value of $E_1^{add} = 48.9$ meV. This is in excellent consistency to the corresponding experimental result [38] of 47 ± 3 meV, obtained by transport measurements of the P-in-Si single donor transistor. The calculated value of E_1^{add} may also be compared to the optical spectroscopy data [45] of impurities in Si. The optical data gives the binding energy of the first electron in the P-impurity which is essentially μ_1 of Eq. 3.9 in Chapter 3. However, the quantity μ_2 of Eq. 3.9 is unknown from the optical data but it could be obtained by fitting to



Figure 4.6: The resulting addition energy in meV is plotted against n_{states} . One can see that after $n_{\text{states}} = 2$, the resulting addition energy changes very little with increasing n_{states} , signifying the convergence. The converged addition energy is 48.9 meV.

the theoretical results of envelope function theory, leading to a value of ~ 44 meV via Eq. 3.9. While the optical analysis is not from atomic first principles, it does produce an addition energy consistent with the direct transport measurement and our first principles modeling.

So far, we presented the predicted addition energy $E_1^{add} = 48.9$ meV, for the single P-in-Si system with a large supercell having N = 10648 atoms. If one could make accurate predictions with smaller N, a very significant reduction of computation cost would result since the eigenvalue solver in RESCU scales [51] in the range of $\mathcal{O}(N^{2.3})$ to $\mathcal{O}(N^3)$. This is the issue of the finite-size effect. This effect was studied before for structural properties such as the formation energy of single P dopant in bulk Si [82], where the formation energy changes roughly 2.5% when N increases from 53 to 431, seems not extremely significant. However, structural properties are more related to local atomic interactions near the impurity and as long as the periodic images of the P dopant in the periodic supercells do not interact, the size of the supercell is large enough. For our problem, on the other hand, the spatial extension of the impurity states plays a critical role in the value of the addition energy. In other words, the finite-size effect limits the spatial size of the impurity states, making them more localized than they should be, which in turn increases the Coulomb energy of Eq. 3.7 in Chapter 3, leading to a much larger addition energy. The finite-size effect can be estimated from the point of view of the effective Bohr radius of the electron in the material, as discussed in Section 3.4. The electron effective mass of Si is $m = 0.26m_e$, and the relative permittivity of Si is $\varepsilon = 11.7$, using these parameters in a hydrogenic atomic model of the Bohr radius, $a_B = \varepsilon \frac{4\pi\varepsilon_0\hbar^2}{e^2m}$, we obtain $a_B = 2.385$ nm. A more accurate estimate from first principles calculation [84] gave $a_B = 1.8$ nm. Either way, it suggests that to avoid a finite-size effect on the impurity wavefunctions, the supercell should be much larger than ~ 2 nm. With N = 10648 atoms, the linear supercell size is 5.97 nm.

Figure 4.7 shows a (001) view of an impurity state with a supercell of size N = 576. Note that the isosurface of the probability density in this figure is 8.6×10^{-11} in the atomic unit, which is much larger than the isosurface in Figure 4.3, which is 7.3×10^{-13} . This indicates that it is a much more localized impurity state compared to those we found in a N = 10648 supercell, agreeing with our discussion above. Figure 4.8 plots the calculated addition energy versus the supercell size for the P-in-Si system. The results are striking. With N = 576 atoms which are already quite large from the DFT point of view, the addition energy was found to be 160 meV which is more than three times larger than the experimental value. Increasing N to 4000, the addition energy reduces to ~ 110 meV which is still more than twice the experimental value. When N is further increased to 10648 atoms, the addition energy essentially converges to the experimental range [38] of 47 ± 3 meV. We conclude that the finite-size effect is very significant for predicting the addition energies of single impurity QD.

The finite-size effect also gives an indication of the optimal distance between two non-interacting donor QD spin-qubits. On one hand, a large addition energy is unwanted for a spin qubit due to the requirement of a large current during spin transport



Figure 4.7: The (001) view of probability density $|\psi|^2$ of an impurity state of a N = 576 supercell plotted in VESTA. The yellow surface is the isosurface for the probability of 8.6×10^{-11} in atomic units. This impurity state is more localized than impurity states of a N = 10648 supercell, seen in Figure 4.3.



Figure 4.8: The size of our supercell (atom number in the supercell) against the resulting addition energy in meV obtained from our method. A converging trend is obvious.

[49], on the other hand, the distance between nearby spin qubits should be kept small in order to minimize system size when scaling up. The periodicity of the P donor in the DFT calculation in our investigation is physically identical to experimentally placing of an array of P donors in making of a multi qubit quantum computer. The above discussion concludes that the minimal distance for P donors to be placed next to each other without increasing the addition energy is around 5.97 nm.

4.3 Summary

In this chapter, we present the calculated addition energy of the P-in-Si spin-qubit. Our approach is from atomistic first principles by combining the Kohn-Sham DFT method RESCU [51] and the many-body solver in the QTCAD qubit simulator [77]. In general, for practical calculations the first principles analysis of spin-qubit proceeds in three steps. First, for a given device supercell (e.g. P-in-Si), the single-particle Kohn-Sham eigenstates are self-consistently determined by DFT, as discussed in Section 4.1. The RESCU method is critical for this step as it can routinely solve supercells with a very large number of atoms. Second, the Kohn-Sham eigenstates with low eigen-energies identified to be impurity states, are selected as the basis set for the exact diagonalization calculation. For the particular P-in-Si device, the process of identifying the P impurity states is discussed in Section 4.1, where the A_1 and T_2 impurity states are identified by calculating the expansion coefficients of the atomic orbitals of the P-donor in the Kohn-Sham eigenstates. The identification of the impurity states is also assisted by visual inspection of the spatial localization of the states. Third, the selected single-particle basis set is used to solve the many-body interaction energy by exact diagonalization using the QTCAD simulator. An important issue is to make sure that the number of basis functions in the basis set converges the manybody interaction energy. For the P-in-Si device, eight basis functions $(n_{\text{states}} = 4)$ were found adequate to converge the first addition energy.

In typical DFT calculations of structural and electronic properties of crystal solids,

a supercell containing a few tens to a few hundred atoms suffices to generate reasonable results. This size is commensurate with the ability of computational algorithms in almost all DFT codes. Surprisingly, the addition energy we attempt to determine is very sensitive to the finite-size effect of the DFT supercell. For the P-in-Si device, we found that supercells with more than 10,000 atoms are necessary to obtain accurate predictions of the addition energy. This is due to the large effective Bohr radius of the electron in the Si crystal field. Namely, the larger the effective electron Bohr radius, the larger the supercell one must use for the DFT calculation of the impurity states.

Finally, with the large supercells and proper identifications of the donor impurity states, our first principles calculation predicts the first addition energy of 48.9 meV for the P-in-Si device, in very good agreement with the measured data of 47 ± 3 meV, see Section 4.2. This demonstrates that the combined modeling method of RESCU/QTCAD quantitatively captures both the materials physics and the many-body physics, reaching the required accuracy for analyzing donor-QD based spin-qubits. Since this first principles method is general, we expect its broad applications as a designer's tool for many other spin-qubit devices in the atomic limit.

Conclusion

5

Quantum technology has attracted great attention in academic institutions, government labs and policy makers, as well as industry, due to its potential to exploit quantum physics of the superposition principle and entanglement for unprecedented application power. The basic unit in quantum technology is the qubit which is a controllable quantum two-level system. While there are numerous physical realizations of two-level quantum systems, a very popular one is the spin-qubit implemented via spin- $\frac{1}{2}$ particles such as an electron, where the spin-up and spin-down states form the two-level quantum structure. So far, spin-qubit is mostly realized in gated semiconductor QDs which are artificial atoms [18] that trap one of a few electrons into the localized (quasi-) bound states inside the QD. In the device operation, an electron tunnel in or out of the gated QD in the sequential tunneling regime [17] dominated by the Coulomb blockade effect where the charging energy or the addition energy is an important operational parameter of the device.

The gated semiconductor QD is rather large, in the scale of tens to a few hundred nanometers [18]. Since fabricating a large number of such identical gated QDs appears to be difficult to do, proposals have been made for using a single impurity atom as the QD hosted by Si bulk. Using Si as the host material for such donor-QD is extremely important, since the Si material can be purified by isotope effect to have no nuclear spin, thereby removing a serious de-coherence effect due to the hyperfine interaction between the donor-QD and the background nuclear spins. To this end, the first donor-QD was due to Kane [5] who proposed to use the nuclear spin of the phosphor donor atom as the spin-qubits. A better approach may be to use the electron and hole spin of the donor atom as the two-level spin-qubit. In donor-QD spin-qubit, instead of using an artificial atom (QD) to host the spin, one uses a real impurity atom to host it. The donor atom is both small and reproducible due to being simply an atom. So far, several experimental fabrications of donor-QD spin-qubits have been achieved, most notably using phosphorous and arsenic as the donor atom.

In a working donor spin-qubit, the electrons tunnel into the qubit and are trapped in the impurity states one by one through a sequential tunneling process. In this tunneling regime, the addition energy measures the energy required to add one more electron into the donor-QD which is contributed by the interactions of electrons in the impurity states. The addition energy indicates whether or not one has a working spinqubit, and whether a donor is in fact placed correctly in the Si lattice. Furthermore, this value is easy to measure, by plotting the differential conductance as a function of bias and gate voltages. Experimentally, once the Coulomb diamond diagram is measured, the addition energy is simply the height of the apex of this diagram. Due to its importance, addition energy is measured in essentially all experimentally fabricated spin-qubits. A theoretical calculation of the addition energy is therefore important for a designing tool of spin-qubit hardware. Theoretically, the most widely used method to calculate the addition energy is the envelope function theory, which treats the spin-qubit as a hydrogenic atom by neglecting the background silicon potential and treating the donor potential in a simple 1/r form. These approximations lead to errors in the calculated results. Another method is the tight binding model which relies on parameterized Hamiltonian matrix. There have been good predictions of the addition energy using the tight binding method if careful parameterization of the Hamiltonian is done which is a very tedious task that may not even work in the end. Clearly, a method that is both accurate and not relies on phenomenological parameters is needed.

Therefore, it is the purpose of this work to establish and test a theoretical frame-

work to quantitatively predict properties of solid-state spin-qubits from atomistic first principles without any phenomenological parameter. As the first step in this endeavor and without losing generality, we choose the experimentally realized single impurity spin-qubit[38], namely the P-in-Si device as the target of our investigation, and focus on predicting the first addition energy which is a very important spin-qubit property, to directly compare with the measured data. Our first principles theoretical framework encompasses two major techniques: a large-scale Kohn-Sham DFT method (RESCU) [51] to deal with the material and single-particle electronic properties of the device, and a spin-qubit simulator (QTCAD) [77] that takes the Kohn-Sham states as the basis set to accurately predict many-body physics by exact diagonalization. Either of these techniques is the leading tool in their respective research field and combined, we hope to eventually innovate a designer's tool for quantum technology fabrication. Indeed, the combined analysis of the P-in-Si device predicts the first addition energy in excellent quantitative agreement with the measured data.

The theoretical background of DFT and its practical implementation were discussed in Chapter 2. It is a first principles method for calculating the electronic structure of atomic systems by writing the many-body Hamiltonian as a single-particle non-linear effective Schrödinger equation, the Kohn-Sham equation. The eigenstates of the Kohn-Sham equation are the Kohn-Sham states. DFT is a mean-field theory in which the interactions of charges are factored into an effective potential. The Kohn-Sham equation can be solved self-consistently for periodic systems (crystals) and finite systems (molecules) with or without spin degrees of freedom. The effective potential in the Kohn-Sham equation includes an external potential term that comes from the nuclei of the atoms, a Hartree potential term that accounts for the classical Coulomb interaction, and an exchange-correlation potential for the quantum part of the interactions. The exchange-correlation potential is unable to be written exactly, and is approximated using a generalized gradient approximation method in our work. The external potential from the nucleus and the core electrons is approximated using a pseudopotential. In our work, the Kohn-Sham Hamiltonian is reduced to a matrix form using a linear combination of atomic orbital (LCAO) basis set. Our numerical solutions of the Kohn-Sham equation are realized by the RESCU electronic package [51] which can handle a supercell with a very large number of atoms.

Once the impurity states are determined by DFT, they are used as the basis set for calculating the many-body interaction of the donor-QD. As discussed in Chapter 3, the many-body eigen-energies and eigen-functions are obtained by exact diagonalization. The electrochemical potential and the addition energy of the donor-QD are obtained from the many-body energies. The relationship between the electrochemical potential and the sequential tunneling is also discussed, and from there one obtains the equality between the addition energy and the apex height of the Coulomb diamond diagram. In the exact diagonalization of the many-body Hamiltonian, the size of the basis set is important. If the size of the basis is too small, the results are not accurate. If the basis is too large, the computational cost grows exponentially. Fortunately, for the specific problem of spin-qubits, one is concerned with a very small number of electrons in the QD and accurate results can be obtained with a very modest-sized basis set. For the P-in-Si device, a few impurity states from DFT as the basis set suffices to give converged many-body states. In our work, the apply the QTCAD spin-qubit simulator to conduct the exact diagonalization of the many-body Hamiltonian.

In Chapter 4, we apply the combined RESCU/QTCAD framework to investigate the first addition energy of the P-in-Si device. Due to the large effective Bohr radius of electrons in the Si host, very large supercells, containing more than 10,000 atoms, must be used to calculate the impurity states. The A_1 and T_2 impurity states are identified from the Kohn-Sham eigenstates at the conduction band minima, which are used as the basis set in the many-body exact diagonalization calculation. We predict the first addition energy of the P-in-Si device to be converged at 48.9 meV, in good agreement with experimental values of 47 ± 3 meV. This concludes that by combining DFT and exact diagonalization, we reached the desired accuracy to predict addition energy in donor spin qubits.

One of the advantages of our combined RESCU/QTCAD framework is its high accuracy in predicting the addition energy. The accuracy depends on the ability to find accurate impurity states and address the strong interactions of electrons in the QD. Another advantage is that our method is from atomistic first principles, requiring no empirical data or parameter fitting. As such, a broad range of future investigations for different spin-qubits are possible. For instance, experimentally it has been possible to use As impurity as the donor-QD [33] where not only a single As donor but also regular arrays of such donor-QDs can be fabricated. There appear to be reasons that the As impurities are chemically easier to be placed with very high probability at regular locations in the Si lattice, than the P impurities [39]. So far, the addition energy of As-in-Si has not been measured yet, therefore a theoretical prediction prior to the measurement will be very useful. Another interesting problem, which has been achieved experimentally already [32], is to use a small cluster of several impurity atoms as the spin-qubit. In addition, as mentioned above, in Reference [80], over 50,000 different impurity atoms or small clusters of them, in bulk Si, have been identified theoretically and proposed to be useful for quantum technology. Our theoretical framework can be applied to investigate this huge and very exciting material phase space to find the best donor-QD based spin-qubit structures. Finally, a very important next step is to investigate systems with two or more donor-QD spin-qubits.

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