QUANTUM COMPUTATION WITH ELECTRON SPINS
OF PHOSPHOROUS DONORS IN SILICON

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Urbana, Illinois
To My Family
Abstract

The discovery of efficient quantum algorithms a decade ago has shown that a quantum computer encoding and processing information quantum mechanically, can solve important problems intractable with conventional computers. The invention of quantum error correction principle, makes quantum computation possibly fault-tolerant against the decoherence of information carriers. Thereafter, intensive research activities have been made toward the implementation of quantum computation with various realistic quantum systems. Among them, the most attractive implementation proposals are using silicon-based materials, which have the advantage of borrowing the existing ingenuity and resources accumulated during the development of modern microelectronics.

In this dissertation we investigate several theoretical aspects of a silicon-based quantum computer in which qubits are represented by the spins of electrons bound to phosphorous donors in silicon. Encoding each qubit in terms of three neighboring donor electron spins, we can realize universal quantum gate operations with only the Heisenberg exchange coupling $J S_1 \cdot S_2$ between neighboring donors. Therefore, studying the exchange coupling for a phosphorous donor pair in silicon is of central importance for providing the experimentalists with qualitative insights and quantitative guidance for building such a silicon quantum computer.

After giving some general considerations on the quantum computer architecture, we develop the necessary theoretical tools. A multi-valley effective mass equation is derived and discussed, to handle impurities in a multi-valley semiconductor. Then we apply it to solve a single Si:P donor embedded in our quantum computer architecture. We show that the width of the silicon quantum well can significantly influence the energy splitting and charge distributions of the ground state. Oscillation of level splitting is observed as the quantum well width or donor position is varied at atomic scale.

Elementary gate operations for 3-donor-spin qubits involve a neighboring pair of donors at each step. The exchange coupling in Heisenberg model
hamiltonian, defined as the energy splitting of the lowest singlet and triplet states, has to be calculated from the realistic two-donor hamiltonian. We discuss several popular methods to solve the two-donor problem and develop an appropriate extended Hartree-Fock method that can give reliable results for a well-separated donor pair subject to tunable coupling. This method is first applied to a Si:P donor pair in the framework of hydrogenic effective mass theory, to study how to tune the exchange coupling with simple gate potentials. A followed study shows that under a parallel electric field the singlet and triplet states exhibit very different polarization behaviors. This difference can be exploited to measure the state of an electron spin. We also show that, a perpendicular electric field cannot tune the exchange coupling efficiently.

Then we apply the realistic multi-valley effective mass equation, coupled with a realistic modelling of the potential generated by gate electrodes, to a pair of phosphorous donors in silicon quantum well. By varying the gate electrode voltages, the exchange coupling can be tuned with exponential efficiency in a wide range. We find that, for best performance, we need to set the quantum well width to be around 10 nm, and the donor separation to be around $10 a_B^* \simeq 24nm$ in the doping plane. We analyze in detail an adiabatic half-swap operation between neighboring donor spins. The gate operation time is estimated to be 0.2 ns, which satisfies the constraints put by the donor spin decoherence time and by the validity of adiabatic approximation.

The interference between different valley components could lead to oscillations of exchange coupling as donor positions are shifted by occasion. We find the exchange oscillation persists even with only two relevant valleys for donors in a strongly-strained silicon quantum well. It is also shown that the oscillation induced by changing donor separation at atomic scale is strongly suppressed as donors approach each other.

Finally, we study the entanglement issue in quantum computing context. We analyze the low-energy Hilbert space for a pair of qubits encoded by localized electron spins and suggest a suitable measure to describe the entanglement between qubits involving indistinguishable electrons and in the presence of leakage errors. The dynamics of inter-qubit entanglement during a gate operation is also studied.
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List of Abbreviations

QC Quantum Computer.
Si:P Phosphorous Doped in Silicon.
CNOT Controlled-NOT.
SET Single Electron Transistor.
QW Quantum Well.
HL Heitler-London.
MO Molecular Orbital.
HF Hartree-Fock.
UHF Unrestricted Hartree-Fock.
EMA Effective Mass Approximation.
EME Effective Mass Equation.
MVEME Multi-Valley Effective Mass Equation.
1 Introduction

1.1 The Physics behind Information

Today is often referred to as 'the Era of Information'. The development of information technology has been playing a more and more significant role in shaping human life\(^1\). We are surrounded by all kinds of information, dealing with information (such as receiving, processing, and sending) everyday to get along with the modern society. Information, the crucial ingredient in everyone’s life, after all, is something that is represented by the state of a physical system (e.g., magnetic discs or tapes, electronic circuits, the human brain, etc). Therefore, we need to explore the underlying physics to process information in a controllable way. Laudauer’s principle \([1]\), stating that the erasure of 1 bit of information necessarily dissipates an energy of \(k_B T \ln 2\), clearly demonstrates how physical laws put constraints on the processing of information.

With the ongoing downsizing of widely-used electronic devices to atomic scale, the underlying physics for information processing changes from classical physics to quantum mechanics. The nature and processing of information encoded by quantum states is quite different from classical information, due to the fundamental difference between quantum and classical physics. For example, quantum information cannot be copied with perfect fidelity \([2]\), as a result of the superposition principle and unitary dynamics. Another example with peculiar quantum nature is that, we cannot measure the unknown state of a quantum system without disturbing it. Both examples mentioned above have very important implications in quantum information processing.

Maybe the most ambitious device in our mind for quantum information processing is the quantum counterpart of a classical computer, i.e., a large-scale quantum computer (QC). The idea of building computers based on principles of quantum mechanics was suggested \([3]\) by Richard Feynman in

\(^1\)For example, without the invention of world-wide internet, it would cost much more time for me to prepare this thesis.
1982, motivated by the observation that there seems to be essential difficulties in simulating quantum mechanical systems on classical computers. The occasional contemplations [4] over quantum computers in the subsequent 10 years, has grown quickly to a very active research field, stimulated by Shor’s discovery [5] of a quantum algorithm for efficiently factoring large integers. The factoring problem (finding the prime factors of a composite number), is of practical importance to the widely used schemes of public key cryptography, which are based on the difficulty of factoring. However, the exponentially increased efficiency of Shor’s quantum algorithm over the best known classical algorithms, would make the current cryptography technology vulnerable, if a large-scale quantum computer can be fabricated and used to attack it. Other quantum algorithms discovered later on, such as Grover’s searching algorithm [6], although less impressive as Shor’s factoring algorithm, have further confirmed the great advantages provided by a quantum computer.

1.2 Quantum Computation

Maybe the most fundamental feature of quantum mechanics is the superposition principle [7]. It has many unexpected consequences on the possible ways to process information quantum mechanically. The elementary unit of quantum information, qubit (which is coined by analogy to classical bit), is represented by the state of a quantum two-level system. For a classical two-state system, its state can only take two discrete values 0 and 1; while for its quantum counterpart, the qubit can be in an arbitrary superposition of the two basis states \(|0\rangle\) and \(|1\rangle\):

\[
|\phi\rangle = \cos \frac{\theta}{2} |0\rangle + e^{i\phi} \sin \frac{\theta}{2} |1\rangle \tag{1.1}
\]

where \(\theta\) and \(\phi\) are real numbers describing the relative amplitude and relative phase of the two basis states, respectively. The spin of an electron, or the polarization of a photon, is a natural quantum two-level system to represent a qubit.

A realistic quantum computer is necessarily composed of lots of (let’s say, \(N\)) qubits to perform nontrivial tasks. The state of the quantum register (memory), or the \(N\)-qubit state in a \(2^N\) Hilbert space, has to be coherently manipulated to keep the track of quantum information. In a quantum com-
puter, information is processed in the following way [8]:

1. The desired initial state is prepared. This can be done either by cooling the system to its ground state, or simply by performing a projective measurement followed by a rotation if necessary. For example, we can polarize all spins with a large global magnetic field to prepare a $|00\cdots0\rangle$ product state (where $|0\rangle = |\uparrow\rangle$ or $|\downarrow\rangle$)

2. Then the desired quantum algorithm achieving certain tasks is performed by controlling the time evolution of the quantum system consisting of N qubits. The evolution has to be unitary to keep the coherent nature of the N-qubit state. It is demonstrated [9] that any unitary operation on N qubits can be constructed from a series of elementary local operations acting on one or two (adjacent) qubits only. Specifically, a single type of two-qubit operation, the Controlled-NOT (CNOT) gate, assisted with single qubit rotation, can realize arbitrary unitary operation in N-qubit space.

3. At the end of the computation, the final state of the quantum register is measured in an appropriate basis. The measurement gives us the desired classical outputs from which we can infer the solution to our problem.

Realistic implementation of a large-scale quantum computer is still far away, mainly because the quantum information carried by physical qubits is easy to be out of track due to decoherence of the register state induced by the inevitable system-environment coupling. The issue of decoherence is still not quite well understood and is attracting intensive research activities. To describe the decoherence of a single qubit (the simplest quantum system), we can write the initially pure state [Eq. (1.1)] in terms of a density matrix

$$\rho = |\psi\rangle\langle\psi| = \begin{bmatrix} \cos^2 \frac{\theta}{2} & \frac{1}{2} \sin \theta e^{-i\phi} \\ \frac{1}{2} \sin \theta e^{i\phi} & \sin^2 \frac{\theta}{2} \end{bmatrix} \tag{1.2}$$

If the qubit is encoded physically by an electron spin in a solid, it is usually coupled with the surrounding nuclear spins, other electron spins, phonons, or even the orbital degrees of freedom of the same electron. Therefore, it can no longer be described by a pure state of a closed system. The imbalanced populations of $|0\rangle$ (or $|\uparrow\rangle$) and $|1\rangle$ (or $|\downarrow\rangle$) can be relaxed to reach thermal equilibrium, via an energy transfer between the qubit system and its surrounding environment. The characterization time for this process is called $T_1$, the (longitudinal) relaxation time. Even without energy transfer
and population change, the phase coherence between the two basis states $|0\rangle$ and $|1\rangle$ can be gradually lost, which can be characterized by $T_2$, the phase decoherence time (also called the transverse relaxation time). Usually $T_2$ is much shorter than $T_1$, so it is the more restrictive and thus more important quantity for quantum information storage and processing. After a time on the order of $T_2$, if we assume no population relaxation has happened, the density matrix of the qubit can be described by

$$\rho = \cos^2\frac{\theta}{2}|0\rangle\langle 0| + \sin^2\frac{\theta}{2}|1\rangle\langle 1|.$$ (1.3)

The above state is an incoherent (classical) mixture of two pure states rather than their coherent (quantum) superposition. The quantum information carried by the phase factor $\phi$ is completely lost. As we go to a correlated multi-qubit system, the issue of decoherence is much more complicated and we usually need many more parameters to characterize it. For a good introduction to the issue of decoherence, see the lecture notes by Leggett [10].

Fortunately, although the unavoidable decoherence is pretty undesirable for performing quantum computation, it is not necessary to be completely reduced to zero. The discovery of quantum error correction codes [11, 12] makes fault-tolerant quantum computation possible, if only we can perform $10^4$ or more\(^2\) gate operations within the decoherence time $T_2$.

For an introduction to the theory of quantum information and computation, we refer the reader to Preskill’s lecture notes [15] or the book by Nielsen and Chuang [8].

### 1.3 DiVincenzo Criteria

There is a set of requirements for the implementation of quantum computation. It is proposed and summarized by DiVincenzo, and often referred to as DiVincenzo criteria [16, 17]. It is widely accepted by the quantum information community as a check-list for scrutinizing implementation proposals. It consists of seven requirements as follows:

\(^2\)There are various estimates about the error tolerance of a quantum computer using error-correction codes. The error threshold is roughly defined as the ratio of an elementary gate operation time $T_g$ to the qubit decoherence time $T_2$. Estimates on $T_g/T_2$ vary from $10^{-6}$ to $10^{-3}$ [13, 14]. The $10^{-4}$ error threshold is most widely accepted by the quantum information community.
1. A scalable physical system with well characterized qubits
2. The ability to initialize the state of the qubit to a simple fiducial state, such as $|00\cdots0\rangle$
3. Long relevant decoherence times, much longer than the gate operation time
4. A "universal" set of quantum gates
5. A qubit-specific measurement capability
6. The ability to interconvert stationary and flying qubits
7. The ability faithfully to transmit flying qubits between specified locations

The first five are the core requirements of quantum computation, while the last two are the requirement for using quantum computation in conjunction with quantum communication\(^3\). The requirement "1" seems pre-satisfied for any reasonable proposal for a scalable quantum computer, but as emphasized by DiVincenzo, this is not true. To declare the achievement of milestone "1", we should be able to assemble an array of two-level systems with the structure of its active Hilbert space clearly verified by spectroscopic means. After having achieved "1" as stated above, the initialization requirement "2" is almost satisfied by definition. The criteria "3" and "4" are mostly studied by theorists, with emphasis on understanding the underlying decoherence mechanisms for the physical system representing qubits and simulating the relevant controllable interaction to perform one- and two-qubit operations. Criteria "5" mainly entails experimental efforts. The measurement apparatus should also be scalable along with qubits. The measurement capability adapted to a realistic computation situation can only be demonstrated after the successful fabrication of a well-defined qubit array.

### 1.4 Exsiting Proposals and Implementations

In the past decade there have been numerous proposals for implementing quantum computation in various physical systems and the number of proposals is still growing (for a review, see Ref. [18]). Among them, the first implementation of a two-qubit state, a CNOT gate, was done with a single $^9Be^+$ ion in an ion trap [19], based on the Cirac-Zoller proposal with

\(^3\)For example, we need quantum communication to realize distributed quantum computation or a quantum network.
qubits encoded by electronic states of cold trapped ions [20]. Later on, other one- and two-ion gates have been demonstrated [21, 22]. However, the first demonstration of an algorithm was done with $^{13}C$ labelled chloroform using nuclear magnetic resonance (NMR) [23], where qubits are encoded by specific nuclear spins of molecules. What’s more, it was reported in 2000 an experimental realization of an algorithmic benchmark using an NMR technique that involves coherent manipulation of seven qubits [24].

Although NMR and ion trap implementations are leading in this early prototype stage, it is not equivalent to say that they are better candidates to realize our ultimate goal: to fabricate a large-scale quantum computer. In fact, the number of qubits in liquid-state NMR proposal is hard to be scaled up and the scalability of the ion trap qubits is yet to be demonstrated.

On the other hand, quantum computer architectures implemented in solids [25], and especially in semiconductors [26], have been extremely attractive for its potential of exploiting the existing enormous amount of ingenuity and resources accumulated during the development of modern microelectronics.

### 1.5 Silicon-based Quantum Computation

The first silicon-based implementation of quantum computation was proposed by Kane [26] in 1998. In Kane’s scheme [26, 27], the nuclear spins of $^{31}P$ dopant atoms embedded in a silicon host, were proposed as the elementary QC units, or qubits. The resonance frequency for a nuclear spin can be tuned by the hyperfine interaction between electron and nuclear spins, which is controlled via a gate electrode, the so-called A-gate, over each qubit. Thus, a globally applied a.c. magnetic field can realize arbitrary rotations on selected nuclear spins. The J-gate (in conjunction with A-gates), placed over the middle of two neighboring donors, allows a controllable qubit-qubit interaction by tuning the exchange coupling between the mediating donor electrons via the change of potential barrier between neighboring qubits. Obviously, this proposal requires a delicate spin transfer between electrons and nuclei for read-in and read-out of quantum data and multi-qubit operations. What’s more, although nuclear spins may be used as a good candidate for memory due to their very long decoherence times, for logic operations
the time required to switch a nuclear spin is always much longer than the switching time for an electron spin, since nuclear spin has a much larger mass.

There also exist variations to the original Kane theme [28, 29, 30, 31, 32], to circumvent the difficulties or simplify the QC implementation. Vrijen et al. [28] suggested utilizing the full power of band-structure engineering and epitaxial heterostructures. The spin of a bound electron in a donor atom is used as the qubit. The qubit can be selectively tuned in and out of resonance under gate-control to realize single-qubit operation, by taking advantage of g-factor variations available in SiGe heterolayers. Larger surface gate biases could be employed to couple neighboring qubits in a controllable way by displacing the bound electrons deep into Ge-rich layers. However, this scheme suffers from the complexity of g-factor engineering and possible qubit loss due to ionization when the bound electron is dragged into the high-g region.

In this thesis, we will focus on a specified variation [32] to the Kane’s implementation proposal. We will describe it and provide general considerations in the next chapter. However, our theoretical studies on Si:P donors, is not only important to this specific QC architecture, but also of importance to different implementation schemes involving donors in silicon.

1.6 Outline

This thesis is organized as follows. In Chapter 2 we describe the Si:P exchange-based quantum computer architecture. We analyze the relevant issues for the architecture to realize quantum computation. We derive and discuss in Chapter 3 the multi-valley effective mass equation that can be employed to calculate phosphorous donors in a silicon host. In Chapter 4 (see Ref. [34]) a two-valley effective mass equation is adapted to the problem of a single P donor embedded in a strained silicon quantum well. The effects of quantum well width to the Si:P ground state energy splitting and charge distributions are studied in detail.

In Chapter 5 different approaches to the two-electron problem are summarized, discussed, and compared with each other. We analyze the advantages

For example, there is a QC proposal [33] with each qubit encoded by a two-donor-ion charge states.
and disadvantages of Hartree-Fock, Heitler-London, Molecular Orbital, and Configuration Interaction methods. We develop an extended Hartree-Fock approach that can synthesize the advantages of Hartree-Fock and Heitler-London approximations. This approach turns out to be good for calculating the two-donor system in our QC architecture.

After building necessary theoretical and computational tools, we simulate in chapter 6 (see Ref. [35]) the effect of a uniform electric field and a parabolic model potential on a pair of P donors in silicon, where a hydrogenic effective mass theory is employed. We analyze the polarizability of the singlet and triplet states for a donor pair and its implications for single-spin measurement.

Chapter 7 (see Ref. [34]) contains by far the most significant numerical results for a pair of phosphorous donors embedded in a silicon quantum well. We study in detail the effect of a realistic gate potential on the exchange coupling. The influence of quantum well width, donor separation, donor position shift are extensively calculated. We discuss the implications of our results to the implementation of the exchange-based Si:P electron spin quantum computer. We also evaluate the exchange oscillation as the donor positions are shifted at atomic scale.

We deal in Chapter 8 (see Ref. [36]) with the issue of entanglement during a gate operation, within a two-site two-electron Hubbard model. With each qubit represented by the spin state of a localized electron, we analyze the correct method to quantize the relevant entanglement during a two-qubit gate operation with double-occupancy leakage errors.

The Appendices A-D contain additional materials related to Chapter 6 and 7.
2 Si:P Donor Spin-based Quantum Computer Architecture

2.1 Introduction

Doping in semiconductors is widely used in modern silicon-based microelectronics technology, and has impacted the traditional information industry significantly. With the size of transistors and integrated circuits keeping decreasing, the physical properties of the devices become more and more sensitive to the detailed configurations of impurities [37]. In the quantum computing context, after Kane’s seminal proposal [26], there have been increased research activities on using donors in silicon as the elementary units to build a naturally scalable quantum computer (QC).

Phosphorous donor in silicon, is one of the most well studied impurities [38]. It is the only impurity in silicon that is both monovalent and isocoric, which makes the impurity potential relatively simple. The single electron bound to a phosphorous donor, is rather stable with a non-degenerate ground state. Silicon crystal has a conduction band with six equivalent indirect minima. A strong impurity potential near the core breaks the 6-valley degeneracy of the silicon conduction band, yielding a sizable energy gap of $\sim 15\text{meV}$ between the ground and the first-excited state [39]. Therefore, the spin state of electron bound to each phosphorous donor in silicon host, is a good and natural candidate for encoding a qubit. As we mentioned in the preceding chapter, electron spins can realize a much fast logic operation than nuclear spins, since an electron has a much smaller effective mass and much larger magnetic moment.

In this chapter we describe our Si:P electron spin-based quantum computer architecture and discuss several issues important for realizing fault-tolerant quantum computation. This chapter is organized as follows. In Sec. 2.2 we address the decoherence problem for Si:P donor electron spin. The QC
architecture studied in this thesis is introduced in Sec. 2.3. We compare it to a similar architecture based on Si/SiGe quantum dots. Sec. 2.4 is dedicated to the discussion on gate operations with exchange coupling. We analyze in Sec. 2.5 the problems of initialization and read-out for our QC architecture. Conclusion is drawn in Sec. 2.6.

2.2 Decoherence of Si:P Donor Electron Spin

Decoherence due to interaction with the environment was thought to be fatal to quantum computation, until the discovery of quantum error correction (QEC) principle. With quantum error correction, the quantum information carried by a qubit is encoded by an entangled state for a composite system consisting of the original qubit and several ancillary qubits nearby. The entangled state is constructed by supplementary gate operations and its carried information on the original qubit is robust against external noise, although the entangled state itself could lose coherence partially. The original qubit state can then be restored by performing rotations conditioned on the results of measurement performed on the ancillary qubits. Obviously, the implementation of QEC requires much more resources (ancillary qubits and additional operations) as the price for realizing fault-tolerant quantum computation. What’s more, QEC is only possible for a sufficiently low ratio of the elementary gate operation time $T_g$ to the phase decoherence time $T_2$. The error threshold for QEC is roughly $T_g/T_2 \sim 10^{-4}$. It is thus of importance to get a realistic estimation of the $T_2$ decoherence time, for a single Si:P electron spin under a magnetic field and temperature appropriate for quantum computation.

Experiments had been performed long time ago on evaluating the relaxation and decoherence time for Si:P electron spins. The relaxation time $T_1$ was first measured by Feher and Gere. Under a magnetic field $B=0.32$ T and at a temperature as low as $T=1.25$ K, the spin-flip rate $T_1^{-1}$ is approximately $4 \times 10^{-4}$ s$^{-1}$, or equivalently, $T_1 \approx 2500$ s [40]. The phase decoherence time, $T_2$, is measured by spin-echo techniques, for isotopically purified Si:P to be roughly $10^{-4}$ s to $10^{-3}$ s with a donor concentration $n = 10^{16}$ cm$^{-3}$ [41, 42].

The recently increased interests toward developing a silicon-based quan-
tum computer have attracted both experimentalists and theorists to re-
examine the decoherence issues in silicon. A very recent measurement by
Tyryshkin et. al. gave an exceptionally long decoherence time, $T_2 \sim 60\,\text{ms}$,
for a P donor electron in isotopically purified $^{28}\text{Si}$ at 7K [43]. An experimental
report by Abe et.al. last year demonstrated that the phase decoherence
time for a P donor electron in $^{29}\text{Si}$ is about an order of magnitude shorter
than that in $^{28}\text{Si}$, the natural abundance Silicon single crystals [44]. They
concluded from the orientation dependence study that the phase decoherence
is caused by spectral diffusion due to flip-flops of the host nuclear spins.

Although the measurements of decoherence time scales has directly con-
firmed the feasibility of using Si:P electron spins as qubits to perform quan-
tum computation, theoretical studies [45, 46, 47, 48, 49, 50] on the relevant
decoherence mechanisms and quantitative calculations are still indispensable.
It is of critical importance to find out the dominant decherence processes,
the effect of decoherence to the QC gate operations [51, 52], the additional
decoherence due to gate electrodes employed in gate operations, and the way
to reduce the decoherence and its induced errors.

For quantum computation at low temperatures, the decoherence of an
electron spin in solids is mainly caused by electron-nuclear interaction, spin-
orbital coupling, or interaction with other electron spins. The explana-
tion for the extraordinary long $T_1$ for Si:P electron spins is rather clear
[53]. The spin flips via spin-orbital coupling and electron-phonon interaction are greatly suppressed for localized electrons [54] due to the constraint
of energy-momentum conservation. The spin-orbital coupling in silicon [50]
is significantly weaker than in other popular semiconductors such as GaAs
for quantum computing. In a completely isotopically purified $^{28}\text{Si}$, where the
nuclear-spin hyperfine interaction are completely suppressed, it is estimated
[53] that the phase decoherence time $T_2$ could be as long as twice of $T_1$.

Within highly isotopically purified $^{28}\text{Si}$, the residual decoherence mech-
anism for a donor spin is dominated by the spin dipolar coupling [48] with
other donor spins. This kind of coupling, can in principle be compensated
by appropriate gate sequence [55] in quantum computation. But the exact
trade-off between reducing the decoherence and increasing the gate operation
complexity is not clear yet.
2.3 Si:P Quantum Computer Architecture

The QC architecture we focus on is a modified version of Kane-type architecture. A detailed discussion of the experimental setup can be found in a recent publication by Tucker and Shen [32]. An array of phosphorous donors (3 donors are shown in Fig. 2.1) is patterned into a $Si_{1-x}Ge_x/Si/Si_{1-x}Ge_x$ quantum well. Efforts are being taken both by Tucker’s group [32, 56] and the Australian Center for Quantum Computer Technology [57, 58, 59] toward positioning of P donors into silicon with atomic accuracy. A microscopic model calculation was performed by Qian et. al [64] in our group on the electronic structure of the phosphorous δ-doping sheet embedded in silicon, taking in account the full band structure effect with an empirical pseudopotential model.

In our design (Fig. 2.1), phosphorous donors are placed at substitutional sites on a plane inside the $Si/Si_{1-x}Ge_x$ quantum well (QW). We use the composition value $x = 0.3$, which yields approximately a quantum well depth of $\Delta E_c = 300meV$ with respect to the barriers. The strained silicon QW not only prevents ionization of the donors during gate operations, but also reduces the valley degeneracy of the donor ground state. The $Si_3N_4$ layer right below the top metallic gates, is introduced to produce the desired gate potential and a tunable exchange coupling. The planar SET shown in Fig. 2.1 can be patterned into the P δ-layer by STM along with the individual P donor qubits, in the same lithographic step.

Our device presented in Fig. 2.1 is somehow similar to that of Friesen et. al. [29], where one uses a Si/SiGe quantum well to confine electrons vertically and uses top gates to confine electrons laterally. Electron spins in such ”quantum dots” act as qubits, with top gate voltages tuning the exchange coupling between qubits. However, the use of phosphorous donor electrons in our device provides a much smaller qubit size and a more densely integrated QC as we scale up the number of qubits. Furthermore, as we shall see in this paper, the available strong gate-assisted exchange coupling allows a much faster gate operation than that in the Friesen et. al. proposal, which would enable faster computation and more easily satisfy the condition for gate operation duration v.s. qubit decoherence time required by quantum error correction principle. By using naturally bound donor electrons as qubits, we avoid additional top gates used to provide lateral confinement and the
Figure 2.1: The composite 3-spin "universal exchange" qubit of Si:P donors in a Kane-type architecture with the integrated SET readout. The heterostructure is grown along $z//\{001\}$ direction. From bottom to top, the heterostructure cross section consists of a thick, n-doped ground layer, a 28nm undoped $Si_{0.7}Ge_{0.3}$ tunnel barrier, a 10-nm Si quantum well (with phosphorous donor array embedded in the middle), a 7nm undoped $Si_{0.7}Ge_{0.3}$ tunnel barrier, a 5nm $Si_3N_4$ layer and lithographically-patterned metallic top gates. The logic qubit is represented by the 2-dimensional subspace $|S, S_z\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$ of the three neighboring donor spins, with logic zero $|0_L\rangle = |S\rangle|\uparrow\rangle$ and logic one $|1_L\rangle = \sqrt{2/3}|T_+\rangle|\downarrow\rangle - \sqrt{1/3}|T_0\rangle|\uparrow\rangle$. 
problem of precisely controlling the number of electrons in each quantum dot.

2.4 Exchange-based Gate Operation

The electron spin is a natural two-level system. Electron spins in various materials, such as GaAs quantum dots [25], liquid helium [65], or Si/Ge heterolayers [28] have been proposed as qubits to realize quantum computation. However, the single spin rotation usually requires a time-dependent control on local magnetic field \( H(t) = g \mathbf{S} \cdot \mathbf{B}(t) \), where \( g \) is the g factor in host materials). Local magnetic control is such a formidable task that current technology can hardly fulfill it.

The encoding of one qubit in terms of two or more electron spins was first coming from the idea of creating a decoherence-free qubit subspace [66, 67]. Such kinds of encoding can eliminate certain kinds of collective coupling between the qubit (several spins as a whole) and the surrounding environment [66, 67, 68].

The 3-spin encoding scheme proposed by DiVincenzo et. al. [60, 61], is the simplest one that can implement one- and two-qubit operations (and thus universal quantum computation) without requiring a local magnetic control. In the context of our architecture described in last section, a logic qubit is encoded by the subspace of three neighboring phosphorus donor electron spins. Logic zero is represented by spins 1 and 2 in the singlet state \( S \), and spin 3 up. Logic one is a linear combination of triplet states \( T_+ \) and \( T_0 \) for spins 1 and 2, with spin 3 down and up, respectively, to preserve the overall spin quantum numbers. Explicitly, we have

\[
|0_L\rangle = |S\rangle |\uparrow\rangle; \\
|1_L\rangle = \sqrt{2/3} |T_+\rangle |\downarrow\rangle - \sqrt{1/3} |T_0\rangle |\uparrow\rangle. 
\] (2.1)

It is demonstrated by DiVencenzo et. al. [60] that, with the above encoding, the nearest-neighbor Heisenberg exchange coupling (between donor electrons) can be used to construct arbitrary single qubit rotation and a CNOT two-qubit operation. Therefore, universal multi-qubit quantum computation can be realized. This encoding scheme removes the tough technical requirement for controlling magnetic field at the scale of single donor size, to
perform rotations of a single donor electron spin. The tradeoff is that more complicated encoding of qubits and more complicated implementation of gate operation is needed for all-electrically controlled gate operations. There are two kinds of top gates to control qubit operations, shown in Fig. 2. 1, similar to the A-gates and J-gates in Kane’s proposal.

Explicitly, the time-dependent Hamiltonian is for the 3-donor system (in Born-Oppenheimer approximation as the mass of a donor ion is much heavier than that of a donor electron) is given by

\[
H_{123}(t, r_1, r_2, r_3) = \sum_{i=1,2,3} H_{mo}(r_i) + U_{1,2} + U_{2,3} + U_{3,1} + \sum_{i=1,2,3} V_g(t, r_i) \tag{2.2}
\]

where \( H_{mo} \) is the single-electron Hamiltonian including kinetic energy and impurity potential by the three donor ions, \( U_{i,j} \) is the mutual Coulomb repulsion between the \( i \)- and \( j \)-th electrons, and \( V_g \) is the gate potential generated by the top metallic gate electrodes. Obviously, the only time-dependent (and tunable) part in the Hamiltonian is the gate-potential term.

At low temperature and with large splitting between the lowest two orbital states, we can assume all single-particle levels but the lowest one are frozen (i.e., only the lowest orbital state is involved in the system dynamics). With this approximation, Eq. (2.2) can be expressed in terms of annihilation and creation operators:

\[
H_{1,2,3}(t) = \sum_{j,\sigma=\uparrow,\downarrow} \epsilon_j(t) c_{j\sigma}^\dagger c_{j\sigma} \\
+ t_{1,2}(t) \sum_{\sigma=\uparrow,\downarrow} [c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma}] \\
+ t_{2,3}(t) \sum_{\sigma=\uparrow,\downarrow} [c_{2\sigma}^\dagger c_{3\sigma} + c_{3\sigma}^\dagger c_{2\sigma}] \\
+ U \sum_{i=1,2,3} c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow}. \tag{2.3}
\]

where \( \epsilon_j(t) \) is the lowest energy level for the \( j \)-th donor, which is time-dependent due to the modulation of gate potentials (controlled by A-gates and J-gates). \( U \) describes the on-site coulomb interaction and is assumed to be the same for each donor. \( t_{1,2} \) is the tunnelling amplitude between donors 1 and 2, and similar for \( t_{2,3} \). The tunnelling amplitude is mostly influenced by the barrier height between the corresponding donors, which can be tuned via the voltages of the relevant J-gate (and A-gates). It should be pointed out that, we have neglected the direct tunnelling between donors 1 and 3, due
to their large separation and screening by donor 2 in the middle. For similar reason, and for the mutual screening of the donor ion and its corresponding donor electron, we also neglected the direct Coulomb interaction between different donors.

The model Hamiltonian Eq. (2.3) is called Hubbard model. It is widely used in studying correlated electronic properties (e.g., superconductivity) and in preliminary calculations of gate operations in a quantum computer based on localized electron spins [69].

At the limit of small tunnelling strength and large on-site repulsion (i.e., max\(t_{1,2}, t_{2,3} \ll U\)), double-occupancy at each site is strongly suppressed and the coupling between neighboring donors can be approximated by the spin coupling between the corresponding localized electrons. The Hubbard model Hamiltonian Eq. (2.3) can then be mapped to the Heisenberg spin model:

\[
H_{1,2,3}(t) = J_{12}(t)\mathbf{S}_1 \cdot \mathbf{S}_2 + J_{23}(t)\mathbf{S}_2 \cdot \mathbf{S}_3
\]  

(2.4)

where \(J_{ij}\) is called exchange coupling between the \(i\)th and \(j\)th electron. To the second order of \(t_{i,j}/U\), we approximately have \(J_{ij} \sim 4t_{i,j}^2/U\).

The effective Heisenberg Hamiltonian Eq. (2.4), is often used to discuss spin chains and quantum gate operations with spins. It is demonstrated within this model that the electrically controlled exchange coupling can realize universal quantum computation with each logic qubit encoded by three electron spins [60].

Since we can switch on and off the exchange couplings \(J_{1,2}\) and \(J_{2,3}\) independently in our design, we may write the available unitary operations for a pair of spins as

\[
U_{12} = \exp\left[i/\hbar \int J_{12}(t)\mathbf{S}_1 \cdot \mathbf{S}_2 dt\right];
\]

\[
U_{23} = \exp\left[i/\hbar \int J_{23}(t)\mathbf{S}_2 \cdot \mathbf{S}_3 dt\right]
\]

(2.5)

We note that the effect of \(U_{12}\) is to perform a coherent rotation of the logic qubit (Eq. (2.1)) along z-axis, while \(U_{23}\) produces a rotation about an axis in the x-z plane, at an angle of 120°. It is numerically verified that a gate sequence \(U_{23} - U_{12} - U_{23} - U_{12}\) (with appropriate exchange coupling and switching time) is able to realize arbitrary rotations (e.g., flip \(|0\rangle_L\) into \(|1\rangle_L\)) on a logic qubit encoded by Eq. (2.1).
The implementation of a two-qubit (each encoded by three electron spins) CNOT gate is much more complicated. There involve five kinds of exchange coupling for a series of six spins. It was found that the two-qubit CNOT operation can also be performed in 19 steps [60], each step involving only a neighboring pair of spins.

Therefore, any multi-qubit operation involving an array of electron spins can be performed by combining single-qubit rotations and the two-qubit CNOT gate, with electric control on neighboring exchange. However, one must pay a price for circumventing the local magnetic control requirement for the single-spin encoding scheme, since the composite 3-spin encoding would cost much longer time to realize the same qubit operation. The corresponding error-correction scheme would also cost many more ancillary qubits and require more complicated circuits.

2.5 Initialization and Read-out

To prepare the initial state $|00 \cdots 0\rangle$ in logic qubit space, we can first cool the system in a large magnetic field ($\mu_B B >> k_B T$) to get a fully polarized state for all donor electron spins. Then we turn on the J-gate between donors 1 and 2 to increase their electron wave function overlap, so that the exchange coupling between spins 1 and 2 is even larger than $2 \mu_B B$. With such a setup, the ground state of the system will be our desired initial qubit state.

Typical parameters for $10^{-6}$ initialization error at $T=100$ mK are $B \sim 1T$ and $J_{\text{initial}} \sim 200 \mu eV$. The hyperfine interaction between donor electron and $^{31}P$ nuclei is suppressed by the large magnetic field; it adds a rapidly oscillating spin-flip component at the order of $10^{-3}$ to electron spin wave functions and only causes a negligible leakage (out of the encoded subspace) [62].

The practical read-out of each qubit is one of the five core requirements in DiVincenzo criteria. For optimal performance, the read-out device should be integrated with the qubit architecture, and should be equipped with single-shot measurement capacity, fast response and robustness against noise [59]. For our qubit encoded with the three donor spins, labelled by 1, 2 and 3, all that needed to determine the qubit state ($|0\rangle_L$ and $|1\rangle_L$) is to distinguish the singlet/triplet states for the electron pair 1 and 2. Electron 3 will be isolated
by gate potential barriers. The singlet/triplet readout can be realized by the nearby integrated single electron transistor (SET), with the help of spin-charge transduction [63]. The charge transfer between electrons 1 and 2 can be realized by applying a potential difference with the adjusting of gate voltages, if the electron pair is in the singlet state. Full charge transfer from donor 2 to 1 happens at a certain potential difference of $V_D$, forming a double-occupied $D^-$ singlet state. On the other hand, the spin-triplet state remains unpolarized until ionization takes place at a potential difference about 20% higher than $V_D$. The presence/absence of $D^-$ state, corresponding to singlet/triplet, can be sensed by the nearby SET. Our simulation has shown a well-defined window for singlet/triplet readout (cf. Sec. 6.3 of Chap. 6, or Ref. [35]). It is worth emphasizing that the readout should be accomplished within the electron spin lifetime, to make the measurement result reliable.

### 2.6 Conclusion

We have described our quantum computer architecture, which is based on the P donor spins doped in a strained silicon quantum well. With each qubit encoded by three neighboring P donor spins in a line, universal quantum computation can be realized via exchange interaction only. Arbitrary single-qubit and CNOT two-qubit operations can be performed with tunable nearest-neighbor exchange coupling assisted by gate electrode voltages.

The decoherence time for Si:P donor spin is discussed. It is significantly longer than that of other popular semiconductors such as GaAs, providing an important advantage of our architecture.

The implementation procedures of initialization and qubit readout are addressed. It is demonstrated that the desired initial qubit state can be prepared by a large magnetic field and a gate-induced even larger exchange coupling between specified donor pairs. The principle of measuring a qubit is based on the different polarizabilities of singlet and triplet states, with the presence/absence of charge transfer sensed by the integrated SET.
Theory of Phosphorous Donors in Silicon

3.1 Introduction

The incorporation of small amounts of impurities or defects into semiconductors can significantly modify their electronic and optical properties, which has been proven of great usefulness for device applications during the development of semiconductor industry in the past fifty years. The quantity of impurities necessary to change the properties of a semiconductor is often considerably less than one impurity per million host atoms [70]. A given impurity, could introduce localized levels in the otherwise forbidden band gap of the host semiconductor, change the charge carrier density, and influence the nature of other impurities present in the host. The understanding (qualitatively) and characterization (quantitatively) of the change of semiconductor properties due to impurities is important for us to control them as so to engineer the desired (and remove/suppress the undesired) functions (such as conductivity) of semiconductor devices.

The quantum computing device shown in Fig. 2.1 employs the electron spins bound to phosphorous atoms embedded in silicon crystal. At certain locations, silicon host atoms are replaced by phosphorous (P) atoms. Such a P impurity is called a substitutional impurity as compared to an interstitial impurity who occupies an interstitial site. In the periodic table of the elements, phosphorous (P) belongs to group-V, while silicon (Si) belongs to group-IV. Therefore, each P impurity can contribute an extra valence electron to the silicon lattice. For this reason P impurities in silicon are also called donors. The electronic level of this extra electron is close to but lower than the minimum energy of conduction electrons, due to the attractive potential between it and the P nucleus (which has an extra positive charge compared to the Si nucleus). Since the electronic energies of P donors are close to the Si conduction band minimum and can be calculated by means
of the "effective mass approximation", the P donors are also called "shallow donors".

The attractive potential binding the extra valence electron (also called donor electron) to P nucleus, is no longer a simple Coulomb potential, because it depends on the many-body interactions between the electrons in the P atom and the valence electrons of neighboring Si atoms. For simplicity, we can approximate it by the Coulomb potential of a proton screened by the valence electrons of the Si host. With the screening effect approximated by a single dielectric constant of the host crystal, the attractive impurity potential experienced by the donor electron can be expressed as

\[ U(r) \approx U_H(r) \equiv -\frac{e^2}{\epsilon_0 |r|} \]

(3.1)

where \( \epsilon_0 \) is the dielectric constant of the host crystal. The subscript "H" denotes a similarity to the Coulombic potential of a hydrogenic atom. If we assume further that the donor electron is not too localized near the donor ion, we can then use the static (zero-frequency) dielectric constant (which is roughly 12 for silicon) in the above equation.

In addition to the impurity potential Eq. (3.1), the motion of the donor electron is also affected by the crystal potential, since it is moving inside a semiconductor. The Schrödinger equation of the donor electron can be written as

\[ (H_0 + U)\Psi(r) = E\Psi(r) \]

(3.2)

where \( H_0 \) is the one-electron Hamiltonian of the perfect host crystal, \( U \) is the impurity potential with Eq. (3.1) an approximate description of it.

The impurity potential breaks the translation symmetry of the perfect crystal lattice. Therefore, extensive numerical calculations have to be taken for solving Eq. (3.2) directly. However, we can use various approximations to simplify our calculation. The most commonly used method to solve Eq. (3.2) is called effective mass approximation. This approach utilizes the known electronic band structure parameters, such as effective masses, of the perfect host crystal. It is not only useful for calculating impurity energy levels, but also for studying properties of electrons in solids under any weak external perturbations. We will discuss its formulism in the following section.

The chapter is organized as follows. In Sec. 3.2 we derive a single-valley effective mass equation with the help of Bloch functions. Then the
importance of intervalley coupling to Si:P donor is discussed in Sec. 3.3 and a multi-valley effective mass equation (MVEME) is formulated. We discuss in Sec. 3.4 various criticisms and modifications to the proposed MVEME and make concluding remarks.

3.2 Effective Mass Approximation

There are two equivalent approaches to derive the effective mass equation. One approach involves Wannier functions [71], while the other approach utilizes Bloch functions [72]. Here we follow the derivation by Pantelides [38].

Since the Bloch functions $\psi_{n_k}^0$ form a complete orthonormal basis set, we can expand the wave function $\Psi$ in terms of them. Explicitly, we write

\[ \Psi(r) = \sum_{n_k} F_{n_k} \psi_{n_k}^0 \]  

(3.3)

with the Bloch functions $\psi_{n_k}^0$ satisfying the Schrödinger equation for the perfect host lattice

\[ H_0 \psi_{n_k}^0 = E_{n_k}^0 \psi_{n_k}^0 \]  

(3.4)

where the solutions are characterized by the wave vector $k$ in the first Brillouin zone and the index $n$ is introduced to enumerate the various solutions at the same $k$. This is called the reduce-zone representation. However, with the extended-zone representation, $k$ is allowed to take any value in the whole three-dimensional reciprocal vector space, and the index $n$ would not be necessary. Due to the periodicity of $H_0$, the Bloch functions can be written in the form

\[ \psi_{n_k}^0 = e^{ik \cdot r} u_{n_k}^0(r) \]  

(3.5)

where $u_{n_k}^0(r)$ is a periodic function.

By plugging Eq. (3.3) into Eq. (3.2), making use of Eq. (3.4), multiplying on the left by $\psi_{n_k'}^0$, and employing the orthonormal nature of Bloch functions, we obtain

\[ E_{n_k}^0 F_{n_k} + \sum_{n_k'} \langle \psi_{n_k}^0 | U | \psi_{n_k'}^0 \rangle F_{n_k'} = E F_{n_k} \]  

(3.6)

Equation (3.6) may be developed further by using Eq. (3.5) for Bloch functions. Since $u_{n_k}^0(r + R_j) = u_{n_k}^0(r)$ holds for any lattice vector $R_j$, the product $u_{n_k}^0(r) u_{n_k}^0(r)$ can be expanded in term of certain plane waves. We
have

\[ u^{0*}_{nk}(r)u^{0}_{n'k'}(r) = \sum_{p} C^{nn'}_{kk'}(K_p)e^{iK_pr} \]  \( (3.7) \)

with \( K_p \) a set of reciprocal lattice vectors.

Defining \( U(q) \) to be the Fourier transform of \( U(r) \)

\[ U(q) = \int d^3r U(r)e^{-iqr} \]  \( (3.8) \)

and employing Eq. (3.7), we finally get

\[ E^0_{nk}F_{nk} + \sum_{n'k'} \sum_{p} C^{nn'}_{kk'}(K_p)U(k - k' - K_p)F_{n'k'} = EF_{nk} \]  \( (3.9) \)

Equation (3.9) is exact. Approximations have to be made to proceed further. The energy band structure of the host crystal has to be specified and the impurity potential should be given explicitly.

We consider the silicon host, whose conduction band has \( L=6 \) equivalent minima located at \( k^0(\pm 1, 0, 0), k^0(0, \pm 1, 0) \) and \( k^0(0, 0, \pm 1) \) with \( k^0 \simeq 0.86 \times 2\pi/a_0 \). And \( a_0 = 5.43 \text{Å} \) is the lattice constant for silicon. Dropping the index \( n \), we can write

\[ F_k = \sum_{i=1}^{L} \alpha_i F^{(i)}_k \]  \( (3.10) \)

where \( F^{(i)}_k \) is assumed localized around the i-th minimum and the \( \alpha_i \)'s are constants satisfying the requirement of tetrahedral symmetry of silicon lattice. The silicon conduction band is said to have a multi-valley structure, with each valley indexed by its energy minimum.

Inserting Eq. (3.10) into Eq. (3.9), we obtain

\[ E^0_k \sum_i \alpha_i F^{(i)}_k + \sum_{k'} \sum_{p} C_{kk'}(K_p)U(k - k' - K_p) \sum_i \alpha_i F^{(i)}_k = EF_k \]  \( (3.11) \)

In the early stage of effective mass theory, the matrix elements involving different valleys (the so-called intervalley terms) were neglected. In this case, we get an independent equation for each valley,

\[ E^0_k F^i_k + \sum_{k'} \sum_{p} C_{kk'}(K_p)U(k - k' - K_p)F^i_{k} = EF^i_k \]  \( (3.12) \)
To further simplify the above equation, the impurity potential $U$ is replaced by its hydrogenic approximation $U_H$ as shown in Eq. (3.1). Furthermore, it is anticipated that $F^j_k$ is strongly localized around the $j$-th minimum, so we have

$$|k - k'| \ll K_p.$$

(3.13)

Based on this assumption, we can make the following approximations [38]:

1. The $K_p \neq 0$ terms can be dropped, due to the observation that

$$|U_H(k - k' - K_p)| \ll |U_H(k - k')|$$

(3.14)

This can be easily confirmed from the Fourier transform of a Coulomb-type potential.

2. $C_{kk'}(0)$ is approximated by

$$C_{kk'}(0) \simeq C_{kk}(0) \equiv 1.$$  

(3.15)

3. $E_0^j$ is expanded about the band minimum $k_0^j$ to order of $|k - k_0^j|^2$. For silicon who has anisotropic energy band, the $E_0^j$ for a valley centered at $k_0^j = k_0(0, 0, 1)$ can be expanded in the form

$$E_0^j = E_0^0 + \frac{\hbar^2}{2} \left[ \left( \frac{k_x^2 + k_y^2}{m_t^*} \right) + \left( k_z - k_0^2 \right) / m_l^* \right]$$

(3.16)

where $m_t^*$ and $m_l^*$ are the transverse and longitudinal effective masses, respectively.

With the above approximations, Eq. (3.12) can be written as

$$\frac{\hbar^2}{2} \left[ \left( \frac{k_x^2 + k_y^2}{m_t^*} \right) + \left( k_z - k_0^2 \right) / m_l^* \right] F^j_k + \int d^3k U(k - k') F^j_k(k') = (E - E_0^0) F^j(k).$$

(3.17)

where the $F^j_k$ in Eq. (3.10) is replaced by $F^j(k)$ and the sum over $k$ is replaced by an integral.

By defining $F^j(r)$ with

$$F^j(r) = \int d^3k F^j(k) e^{i(k - k_j) \cdot r}$$

(3.18)
and integrating over $k$, we can immediately reach a real space equation:

$$\frac{-\hbar^2}{2} \left[ \frac{1}{m^*_x} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{m^*_z} \frac{\partial^2}{\partial z^2} \right] F^j(r) + U(r) F^j(r) = (E - E^0_j) F^j(r). \quad (3.19)$$

Eq. (3.19) is called single-valley effective mass equation. The real-space function $F^j(r)$ is called the envelope function for the $j$-th valley. The total wave function is now given to first order of $k$ by

$$\Psi(r) = \sum_j \alpha_j F^j(r) u_{k^0_j}(r) e^{i k^0_j \cdot r} \quad (3.20)$$

### 3.3 Multi-valley Effective Mass Equation

The calculation of donor states in silicon was first performed by Kohn and Luttinger [73, 75] and later on elaborated by Faulkner [88] via the single-valley effective mass equation derived in the preceding section. It had been proven to be a great success for most donors, especially for excited states (for a review, see [98]). According to the Kohn-Luttinger theory, the total electron wave function has the form as Eq. (3.20), with the valley-dependent envelope function given by [73, 98, 76], e. g.,

$$F_{\pm z}(r) = \frac{1}{\sqrt{\pi a^2 b}} \exp\left[-\sqrt{(x^2 + y^2)/a^2 + z^2/b^2}\right] \quad (3.21)$$

where the variational parameters, $a$ and $b$, are called effective Bohr radii, due to the formal similarity of the above wave function to the $1s$ state of a hydrogenic atom. The anisotropy of the wave function originates from the effective mass anisotropy. Since the longitudinal effective mass is nearly four times larger than the transverse effective mass, correspondingly, $b$ is significantly smaller than $a$. The estimate in Ref. [77] gives $a = 25.09\,\text{Å}$, $b = 14.43\,\text{Å}$, with the latest experimental values of effective masses, lattice constant and dielectric constant for silicon. It is noted that although the bohr radius scales like $\sim \hbar^2/m_e c^2$, the large effective mass anisotropy results in a much smaller anisotropy in effective bohr radii. That explains the closeness of the result in Ref. [77] to those obtained 50 years ago [73] with significantly different longitudinal effective mass (0.916 v.s. 0.98 in units of free electron mass).

Due to neglecting of intervalley mixing terms, the single-valley calcula-
tion necessarily gives a six-fold degeneracy for the ground state of donors in silicon. What’s more, such a theory has nothing to do with the impurity species: it only dependents on the band parameters of the host crystal. All these turned out not true according to experiments [80, 81].

Experimentally [39], for phosphorous donors in bulk silicon, the zero-field binding energies are $E_b + \Delta_0 = 45.59 \text{ meV}$ (the nondegenerate ground state with A symmetry), $E_b + \Delta_0 - \Delta_E = 33.89 \text{ meV}$ (two-fold degenerate state with E symmetry), and $E_b + \Delta_0 - \Delta_T = 32.58 \text{ meV}$ (three-fold degenerate state with $T_2$ symmetry). Here $E_b$ is the binding energy of six-fold degenerate ground states obtained by single-valley EMA. Kohn and Luttinger’s theory [74, 75] yield $E_b \approx 29 \text{ meV}$, while the more elaborate work by Faulkner [88] gives $E_b \approx 31.27 \text{ meV}$. $\Delta_0$, $\Delta_E$, $\Delta_T$, known as central-cell corrections, are positive, and in contrast to $E_b$, depend on the particular impurity species. For Si:P donors, $\Delta_0 \approx 16.6 \text{ meV}$ according to Kohn and Luttinger (or $14.3 \text{ meV}$ according to Faulkner), $\Delta_E \approx 13.0 \text{ meV}$ and $\Delta_T = 11.7 \text{ meV}$.

Such a large discrepancy between theory and experiment motivated modifications to the single-valley hydrogenic effective mass theory. The deviation mentioned in the preceding paragraph is known as the chemical shift, since the particular chemical nature of the impurity atom was thought to be responsible for its presence. It is also called ”central-cell corrections”, as the chemical details of the impurity should only be important near the central-cell (core) region. The earlier theoretical efforts focused on corrections to the hydrogenic impurity potential [38]. Various relevant effects were taken into account to describe the correct dielectric screening. However, all these early efforts on explaining the chemical shift effect were performed in the framework of single-valley effective mass theory; the intervalley coupling were ignored. The first demonstration of the importance of intervalley mixing appeared in 1970, where Baldereschi used an effective-mass-type perturbation method to estimate the energy level splitting due to intervalley (or valley-orbit) coupling [82]. His calculation revealed that, the so-called ”chemical shift” measured from single-valley theory, is in fact due to the intervalley mixing missed in single-valley theory. The impurity-species-dependent reduction of screening near the impurity nucleus, makes the most important contribution to the intervalley coupling.

Later on Ning and Sah [83, 84] confirmed the importance of intervalley coupling by using a phenomenological two-parameter impurity potential. It
was pointed out and emphasized by Pantelides and Sah [30] that the concept of chemical shifts or central-cell corrections are ill-defined in the one-valley EMA framework, except for isocoric impurities (where impurity and host have the same number of core electrons, e.g., Si:P donor), and the "chemical shift" must arise almost entirely from intervalley mixing, which causes the splitting of the six-fold degenerate ground state of donors embedded in silicon as observed experimentally. Therefore, a multi-valley effective mass equation (MVEME) is needed to correctly solve the impurity problem in a host with multi-valleyed conduction band.

It is a little surprising that the first multi-valley effective mass equation appeared much earlier than the discovery of importance of intervalley coupling. As reported by Fritzsche [85], the first effective-mass equation for a multi-valley band was obtained by Twose [86]. The assumption underlying Twose’s derivation is that the same approximation used for intra-valley terms (corresponding to single-valley case in last section) can also be used for treating the intervalley matrix elements even though the key assumption Eq. (3.13) is no longer true.

For a single substitutional donor situated at \( \mathbf{R} \) in silicon, whose band structure has six equivalent valleys, the electron wave function in real space can be written as:

\[
\Phi(\mathbf{r} - \mathbf{R}) = \sum_i F_i(\mathbf{r} - \mathbf{R})e^{i\mathbf{k}_0^i.(\mathbf{r} - \mathbf{R})}u_i(\mathbf{r}) \tag{3.22}
\]

where \( u_i(\mathbf{r}) \) is the periodic part of the Bloch functions for the i-th valley band minimum at \( \mathbf{k}_0^i \). \( F_i \) is the envelope function for the i-th valley, with \( i = \pm x, \pm y, \pm z \) corresponding to six valleys centered at the band minima \( \pm k_0^i \hat{x}, \pm k_0^i \hat{y}, \) and \( \pm k_0^i \hat{z}, \) respectively. The Twose’s multi-valley effective mass equation (MVEME) reads:

\[
\sum_i \alpha_i e^{i(\mathbf{k}_i - \mathbf{k}_j) \cdot \mathbf{r}}[T_i(\mathbf{r}) (-i\nabla) + U(\mathbf{r}) - E]F_i(\mathbf{r}) = 0 \tag{3.23}
\]

where \( T_i(\mathbf{k}) \) is the expansion of the silicon band structure \( E^0(\mathbf{k}) \) at the i-th minimum.

The MVEME [Eq. (3.23)] is essentially a set of coupled equations for the envelope functions associated with different valleys (\( j = \pm x, \pm y, \pm z \)). If the
intervalley mixing, also called valley-orbital interaction, is negligibly small, the envelope functions for different valleys nearly coincide (up to a coordinate rotation) and the set of MVEME equations reduce to one single-valley EME. That’s the origin of the six-fold degenerate ground state for donors in silicon obtained by Kohn and Luttinger [74, 75]. Only by taking into account the coupling between different valleys we can obtain correct splittings of the ground state. For a substitutional donor in silicon, the system has tetrahedral symmetry. Valley-orbit coupling mixes the six Bloch functions belonging to different valleys to form states with three kinds of symmetries according to the irreducible representations of the $T_d$ group. The linear combinations of them form a singlet with $A_1$ symmetry, a doublet with $E$ symmetry, and a triplet with $T_2$ symmetry. The appropriate linear combinations are

$$A_1 : (X + \bar{X} + Y + \bar{Y} + Z + \bar{Z})/\sqrt{6};$$

$$E : (X + \bar{X} - Y - \bar{Y})/2, (2Z + 2\bar{Z} - X - \bar{X} - Y - \bar{Y})/\sqrt{12};$$

$$T_2 : (X - \bar{X})/\sqrt{2}, (Y - \bar{Y})/\sqrt{2}, (Z - \bar{Z})/\sqrt{2}.$$  \hspace{1cm} (3.24)

Here $X$, $\bar{X}$, $Y$, $\bar{Y}$, $Z$ and $\bar{Z}$ are the labels for the six Bloch functions, according to the directions of conduction band minima.

Eq. (3.23) can be solved once we know the form of the impurity potential $U(r)$. For substitutional donors, such as phosphorous donors in silicon, the impurity potential, $U(r)$, consists of two parts: $U_b(r)$ and $U_s(r)$, where $U_b(r)$ is essentially the difference between the potential of an impurity ion and a host ion, and $U_s(r)$ arises from the redistribution of valence electrons in the crystal, caused by the presence of $U_b(r)$. For phosphorous donors in silicon, the point-charge model is reliable and linear response theory can be validly applied to solve the impurity potential [38, 87]. The resulting impurity potential in k space can be written as

$$U(q) = U_b(q)/\epsilon(q)$$  \hspace{1cm} (3.25)

with $U_b(q)$ given by the Fourier transform of

$$U_b(r) = -ne^2/r + W_b(r)$$  \hspace{1cm} (3.26)

where the first term is the Coulomb potential of one point charge and $W_b(r)$
denotes the short-range contribution. The q-dependent dielectric screening function, instead of simply the constant $\epsilon_0$ in the hydrogenic impurity potential, is used to take care of the correct screening effect both near and far away from the core. A set of exponential functions may be used to simulate the dielectric screening function \[87\].

For Si:P donors, $W_b$ is very small and localized within about one lattice constant. Similar to the short-range behavior of the dielectric screening function, it’s difficult to calculate. Therefore we include all of the short range effects in the modelled dielectric screening function. For convenience we will approximate the dielectric screening effect by a set of isotropic Gaussian functions,

$$\frac{1}{\epsilon(r)} = \frac{1}{\epsilon_0} [1 + A\epsilon_0 \exp(-\alpha_1 r^2) + (1 - A)\epsilon_0 \exp(-\alpha_2 r^2) - \exp(-\alpha_3 r^2)] \quad (3.27)$$

where $\alpha_1, \alpha_2, \alpha_3$ and $A$ are a set of adjustable parameters. The right side of Eq. (3.27) is constructed to give the correct long-range limit.

It turns out that, a single-parameter Gaussian function is adequate for simulating the (inverse of) dielectric screening function calculated in Ref. \[89\] within several lattice constants ($a_0 = 5.43\text{Å}$) and yield the correct long-range limit. Explicitly, the dielectric function used in this paper has the following form:

$$\frac{1}{\epsilon(r)} = \frac{1}{\epsilon_0} [1 + (\epsilon_0 - 1) \exp(-\alpha_c r^2)] \quad (3.28)$$

where $\alpha_c$ is treated as an empirical parameter. We find that $\alpha_c = 1.13$ a.u. gives reasonable agreement with the dielectric function in the range of more than two lattice constants and it yields the correct intervalley splitting of the ground state for a P donor in a silicon quantum well with a large in-plane strain. It is important to note that, larger value of $\alpha_c$ corresponds to smaller modification to the hydrogenic impurity potential.

The impurity potential Eq. (3.28) adopted by us is somehow a mixture of pseudopotential and model potential \[38\]. The form of the potential is assumed to be the same as the screened point-charge potential, with the dielectric function yielding the correct long-range limit and agreeing on average with the realistic screening function at short range. It is similar to the treatment in Ref. \[87\]. On the other hand, the parameter in Eq. (3.28) is adjusted to give a reasonable splitting of the ground state. This is similar to
the model potential calculation in Refs. [83, 84]. However, we do not require our model potential to give the same eigenvalue spectrum as the true potential over a certain energy range, although the energies we obtained for the lowest two states is reasonable. We emphasize that, the splitting value of the lowest states due to intervalley coupling is physically more important than the absolute values of energy levels, because it reflects the buildup of electron probability in the central-cell region. Our model potential is good for studying the relevant levels which may be active during quantum computation, i.e., the two lowest states (which are far separated from the higher-lying levels due to the effect of a large in-plane strain).

3.4 Concluding Remarks

The application of the Twose’s multi-valley effective mass equation by Pantelides and Sah to calculating the ground-state energies of donors in Si and Ge has proven to be in very good agreement [87] with experimental data. However, the derivation of the multi-valley effective mass equation is based on assumptions that has caused various criticisms (e.g., [91, 94, 96, 97]). The key assumption good for single-valley case, Eq. (3.13), no longer holds for multi-valleyed semiconductors. As a consequence, the Umklapp process (which is described by the intervalley scattering involving momentum transfer to the host lattice) can not be dispensed [91, 97].

It is also pointed out by Shindo and Nara [90] that the Twose’s multi-valley EME is inappropriate due to the inclusion of spurious intervalley kinetic energy terms and the neglecting of the overlap effects from Bloch functions in different valleys. By totally excluding the intervalley kinetic energy terms and retaining the Bloch functions, they proposed a different multi-valley equation. Soon after that, Altareli et al. [97] modified this new equation by taking into account the Umklapp effect with a renormalization factor for the impurity potential terms. They obtained satisfactory results for P donors in silicon and Ge donors on arsenium. However, this kind of equation has also been subjected to criticism. It was shown by Herbert and Inkson [95] that, the absence of intervalley kinetic energy terms could lead to instability of the effective-mass donor states in silicon. They argued that, the proper treatment of kinetic energy terms, involves different expressions.
for the region around each valley minimum and the overlapped region of different valleys. Later on, Resca and Resta [92, 93] also proposed a different method to deal with the Umklapp process.

Although much has been done during the development of a correct multi-valley effective mass equation, there exists no theory that can handle all the relevant effects and yield accurate results with few adjusting parameters and without highly demanding calculations. The use of model Hamiltonian can simplify the necessary calculations [99] to yield the correct energy spectrum, as far as only a certain energy range is concerned.

In quantum computing context, the hydrogenic Kohn-Luttinger-type variational envelope functions are often used to calculate various effects, such as the hyperfine interaction [100], the strain effect [104] and the exchange coupling [78, 77]. Such a method can give some qualitative insights to the physics relevant for quantum computation, but quantitatively accurate calculations are highly desired to provide significant help to the realistic design of a quantum computer. Very recently Wellard and Hollenberg [79] worked out a method to go beyond the simple Kohn-Luttinger effective mass theory. They calculated the electronic wave function for a Si:P donor by numerically diagonalizing the donor Hamiltonian within the basis consisting of a discrete set of crystal Bloch functions. The reported results with this method agree well with experiments.

We adopt in this thesis the Twose’s multi-valley effective mass equation to study phosphorous donors in silicon, for two reasons. First, it has been proven to be a success in calculating Si:P donors [87]. Second, it is partially justified by the following observation. Palaniyandi and Malliga have shown that, when the Twose’s equation is used to calculate donor binding energies, the resulting error due to the omission of higher-order Fourier components of the impurity potential (Umklapp process) exactly compensates the error due to overestimate of the no-Umklapp part of the intervalley potential-energy term [96].
4 Single Phosphorous Donor in Strained Silicon Quantum Well

4.1 Introduction

The physics of a particle moving in a quantum well is a classic prototype widely used in textbooks on quantum mechanics. The restriction of movement in one direction changes the energy spectrum in one of its quantum numbers from continuous to discrete. Such a kind of reduction of degrees of freedom has often produced new physics (e.g., the Quantum Hall effect) and obtained extensive applications in material engineering. In solids, realistic quantum wells are constructed mostly via the growth of heterostructures. The band lineups at the interfaces of different materials can result in a confinement potential. Initially, quantum wells were produced by choosing a pair of layers with practically equal lattice constants, for example, the GaAs/GaAlAs pair. Such a heterostructure is called lattice-matched. With modern superlattice growth technology it is also possible to obtain heterostructures with significantly different lattice constants, which results in a compression of one layer and a tension of its adjacent layer [101].

For our specific QC architecture shown in Fig 2.1, phosphorous donors are confined in a quantum well grown along [001] axis where the strained silicon layer is sandwiched by $\text{Si}_{1-x}\text{Ge}_x$ layers. The most popular value of composition $x$ is 0.2 or 0.3. The conduction band minimum for the strained silicon is considerably lower than that of the unstrained $\text{Si}_{1-x}\text{Ge}_x$ layers, which forms a square-well type potential and confines electrons in the silicon layer. The actual values of band discontinuities for a pseudomorphic interface like $\text{Si}/\text{Si}_{1-x}\text{Ge}_x$ are very sensitive to the particular strain situation of the layers [102]. We assume the quantum well height (conduction band offset) to be $U_s = 300$ meV.¹ A high enough barrier is needed to keep the donor

¹Y. Suda and H. Koyama estimated [103] a conduction band offset of 170 meV and a strain-induced band splitting of 200 meV for the strained Si/unstrained $\text{Si}_{0.7}\text{Ge}_{0.3}$ interface.
electrons from leaking out in the presence of gate potentials. As long as the barrier is high enough (and the quantum well width is large enough, i. e., larger than the effective Bohr radius along the confinement direction), the actual value of $U_s$ does not influence the donor ground state much. What’s more, the fraction of Ge can be engineered to modify the actual value of $U_s$.

The large in-plane strain presented in the quantum well reduces the crystal symmetry and splits the six-fold degenerate silicon conduction band into a two-fold-degenerated band and a four-fold-degenerated band. The valley-orbit coupling further removes the remaining degeneracies. As discussed recently in Ref. [104] and Ref. [105] within perturbation theory, the interplay of strain and valley-orbit effect makes only two valleys relevant for the low-lying states [106]. For the quantum well shown in Fig. 2.1, the minima of the two lowest energy valleys are at $k_x = k_y = 0$ and $k_z = \pm k_0$. Their energies are well separated from those at the minima of the other four higher energy valleys by more than 100 meV [103]. Thus, only the $+z$ and $-z$ valleys contribute to the ground state. Explicitly, we are left with two types of linear combinations of Bloch wave functions,

\begin{align}
T^+_z : \text{symmetric : } & (Z + \bar{Z})/\sqrt{2}; \\
T^-_z : \text{antisymmetric : } & (Z - \bar{Z})/\sqrt{2}. \tag{4.1}
\end{align}

The symmetric $T^+_z$ state is the ground state for a single donor at the center of a strained silicon quantum well.

Analogous to Eq. (3.22), for a single donor located at $R = 0$, the two-valley wave function can be written as

\begin{align}
\Phi(r) = F_{+z}(r)e^{+ik_0z}u_{+z}(r) + F_{-z}(r)e^{-ik_0z}u_{-z}(r) \tag{4.2}
\end{align}

The corresponding two-valley effective mass equation with external field is given by

\begin{align}
[T_{+z}(-i\nabla)+U(r)+V_{\text{ext}}-E]F_{+z}(r)+e^{+2ik_0z}[T_{-z}(-i\nabla)+U(r)+V_{\text{ext}}-E]F_{-z}(r) = 0; \\
e^{-2ik_0z}[T_{+z}(-i\nabla)+U(r)+V_{\text{ext}}-E]F_{+z}(r)+[T_{-z}(-i\nabla)+U(r)+V_{\text{ext}}-E]F_{-z}(r) = 0 \tag{4.3}
\end{align}
where \( T_{+z} = T_{-z} \equiv T_z \) has an operator form as follows:

\[
T_z(-i\nabla) = -\frac{\hbar^2}{2m_{\parallel}} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2m_{\perp}} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right).
\]

(4.4)

The envelope functions for the two valleys, \( F_{+z}(r) \) and \( F_{-z}(r) \), are coupled together, as shown in Eq. (4.3). We do not assume the equivalence of \( F_{+z}(r) \) and \( F_{-z}(r) \) as, e.g., in Ref. [29] and Ref. [104], since we shall consider the situation where the external potential or the donor position shift relative to the quantum well breaks the reflection symmetry about \( z = 0 \).

The remaining part of this chapter is organized as follows. In Sec. 4.2 we introduce an appropriate basis set to expand the envelope function of a P donor in strained silicon quantum well. We then transform the two-valley effective mass equation to a matrix equation. Then the single-donor problem is solved in Sec. 4.3. We analyze the influence of quantum well width and donor position to the valley splitting and charge distributions. Concluding remarks are given in Sec. 4.4.

### 4.2 Basis and Matrix Equation

To solve the electron wave functions and energies, we need to choose some well-behaved basis functions to expand the two envelope functions. We modify the set of bases used in our previous paper [35] (in which we study Si:P donors within spherically averaged EMA) to take into account the anisotropy of the silicon band structure and the broken symmetry brought by the external field.

We use a set of two-dimensional (2D) anisotropic Gaussian functions \( \{\beta_j(y, z)\} \) to describe the freedoms in \( y \) and \( z \) directions. Two different kinds of Gaussian functions, \( \{\exp[-\alpha_i(y^2 + z^2/\xi^2)]; i = 1, ..., n_e\} \) and \( \{z \exp[-\alpha_i(y^2 + z^2/\xi^2)]; i = n_e + 1, ..., n_r = n_e + n_o\} \), are used to expand the envelope functions with even and odd symmetry (with respect to \( z \)). The optimum value \( \xi = 0.57 \) for the anisotropy factor is obtained by minimizing the ground state energy. We note that both even and odd symmetric bases are necessary when the external potential lacks reflection symmetry with respect to the doping plane \( (z=0) \). The set of Gaussian parameters \( \{\alpha_i\} \) are optimized such that a linear combination of the 3D Gaussian functions \( \{\exp(-\alpha_i r^2)\} \) best resem-
bles the 1s wave function of a hydrogen atom, while a linear combination of \( \{ z \exp(-\alpha r^2) \} \) best resembles the 2p\(_{z}\) orbital [107].

In our multi-qubit QC architecture, a line of substitutional donors are arranged along the [100] axis, and neighboring qubits can be coupled together mainly by the wave function overlaps along the x axis. To facilitate our calculation and to better describe the inter-donor coupling, we place the system in an artificial 1D box with infinite potential barriers. The center of the box is at \( x = 0 \) and the box size \( L \) is chosen to be large enough (at least 10 nm from the donor ion to either side wall) so that it has negligible effect on the donor binding energy and charge distribution. With the introduction of the box, we can use a set of orthogonal sine functions, \( \{ \sqrt{2/L} \sin[\frac{m\pi}{L}(x + L/2)] , m = 1, ..., n_x \} \), to describe the electron freedom along the x direction. Again, such a set of functions includes both odd (even \( m \)) and even (odd \( m \)) functions of \( x \). This is needed when the donor ion is shifted from the box center (which is the case when more than one donor are present) and/or a nonsymmetric external potential is introduced. Combining the set of sine functions and \( \{ \beta_j(y, z) , j = 1, ..., n_r \} \), we get a set of bases:

\[
B_{jm} = \sqrt{2/L} \sin[\frac{m\pi}{L}(x + L/2)] \beta_j(y, z) 
\]  

(4.5)

where \( jm = (j - 1) \times n_x + m \) and \( N = n_r \times n_x \) is the total number of our basis functions.

The suitability of this basis set was discussed and verified in a previous publication [35] by comparing our numerical results to exact results in various limits.

Now we can expand the two valley-dependent envelope functions as a linear combination of our bases. We write:

\[
F_{+z} = \sum_{jm=1}^{N} c_{jm} B_{jm};
\]

\[
F_{-z} = \sum_{jm=1}^{N} c_{jm+N} B_{jm}. 
\]  

(4.6)

Substituting Eq. (4.6) to Eq. (4.3), we obtain a matrix equation for the
2N-dimensional vector \( \{ c_j, j = 1, \ldots, 2N \} \):

\[
\sum_{n=1}^{2N} H_{mn} c_n = E \sum_{n=1}^{2N} O_{mn} c_n
\]  
(4.7)

where \( \{ H_{mn} \} \) and \( \{ O_{mn} \} \) are \( 2N \times 2N \) Hermitian matrixes, which can be written as \( 2 \times 2 \) block forms in terms of four \( N \times N \) matrixes:

\[
H_{2N \times 2N} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}
\]  
(4.8)

where \( H_{11} \) and \( H_{22} \) are the intra-valley Hamiltonian matrixes for +z and -z valley, respectively, while \( H_{12} \) and \( H_{21} \) describe the intervalley coupling. Obviously, \( H_{21}^* = H_{12} \equiv H^{DV} \), since \( H_{2N \times 2N} \) is Hermitian. We also have \( H_{11} = H_{22} \equiv H^{SV} \) since we have chosen the same set of basis functions to expand the envelope functions for the two valleys. The decomposition of \( O_{2N \times 2N} \) has similar properties (\( O_{21}^* = O_{12} \equiv O^{DV} \) and \( O_{11} = O_{22} \equiv O^{SV} \)). Explicitly, the matrix elements of \( H^{SV} \) and \( H^{DV} \) are written as

\[
H_{ij}^{SV} = \int dr B_i(r) [\hat{T}z(-i \nabla) + U(r) + V_{ext}] B_j(r);
\]

\[
H_{ij}^{DV} = \int dr B_i(r) [\hat{T}z(-i \nabla) + U(r) + V_{ext}] B_j(r) e^{i2k_0z}.
\]  
(4.9)

where it is understood that the operators inside the square brackets only act on the envelope basis functions but not on the valley phase factor. \( O^{SV} \) and \( O^{DV} \) can be obtained by replacing \([ \cdots ]\) in Eq. (4.9) by 1.

Our main equation, Eq. (4.7), is a generalized eigenvalue equation composed of a \( 2N \times 2N \) hamiltonian matrix \( H \) and a \( 2N \times 2N \) overlap matrix. Since the sine functions in \( x \) are already orthogonal, we only need to perform the Gram-Schmidt orthogonalization process on the set of \( y, z \) dependent gaussian functions to convert the generalized eigenvalue equation into a standard eigenvalue equation. We have

\[
\tilde{H}^* \tilde{\mathbf{C}} = E \tilde{\mathbf{C}}
\]  
(4.10)

where \( \tilde{H}^* \) is a \( 2N \times 2N \) Hermitian matrix and \( \tilde{\mathbf{C}} \) denote a 2N-dimensional eigenvector. The full single donor electron wave function can be constructed
from $\tilde{C}$ according to Eqs. (4.2) and (4.6), once the Bloch functions $u_{\pm z}(r)$ are known.

To calculate the charge distribution for the donor electron, we apply Eq. (3.7) [keeping only the $K_p = 0$ component in Eq. (3.7) and using the approximation Eq. (3.15)] to Eq. (4.2), then the following expression is obtained:

$$\rho(r) = \Phi(r)^* \Phi(r) \simeq \left[ F_{+z}(r)^2 + F_{-z}(r)^2 + 2F_{+z}(r)F_{-z}(r) \cos(2k_0 z) \right].$$  (4.11)

where the envelope functions $F_{+z}$ and $F_{-z}$ are assumed to be real functions.

We clearly see that the charge density exhibits strong oscillation along $z$ axis at the scale of $\pi/k_0 \simeq a_0/1.7$, due to the interference of two valleys.

For convenience we define the effective Bohr radius

$$a_{B^*} = \frac{\epsilon_s \hbar^2}{m^* e^2} = 0.529 \AA \frac{\epsilon_s}{m^*/m_0} \simeq 23.4 \AA$$  (4.12)

and the effective Rydberg (donor binding energy)

$$Ry^* = \frac{e^4 m^*}{2 \hbar^2 e_s^2} = 13.59 \text{ eV} \frac{m^*/m_0}{\epsilon_s^2} \simeq 27 \text{ meV}.$$  (4.13)

where $m_0$ is the free electron mass, $m^*$ is the spherically averaged effective mass, $m^* = (\frac{1}{3} m_l^{-1} + \frac{2}{3} m_t^{-1})^{-1} = 0.258 m_0$ with $m_l = 0.911 m_0$ and $m_t = 0.190 m_0$ for silicon.

Throughout this thesis, if not specified, we will use the effective atomic units (a.u.*) in which distance is measured in $a_{B^*}$ and energy measured in $Ry^*$.

### 4.3 Valley Splitting of Si:P donor in Quantum Well

In this section we will study the single Si:P donor confined in a Si/SiGe quantum well with the method we developed in Sec. 4.2. Although there have been in the past enormous publications on the theory of isolated donors in silicon [38], only in recent years have silicon donors been studied in a gen-
eral, inhomogeneous environment due to its relevance to gate control of the bounded electrons in quantum computing context. We have studied \[35\] the effects of a uniform electric field and a one-dimensional parabolic external potential on a pair of Si:P donors, within one-valley spherical EMA. Martins et. al. \[108\] addressed the behavior of shallow donors in silicon under a uniform electric field, using a tight-binding model. Smit et. al. analyzed the effect of a small nearby gate on a hydrogenlike impurity in a semiconductor up to ionization field \[109\]. They also studied the small electric field dependence of the lowest energy states in donors and acceptors, beyond the single-valley EMA, by applying symmetry arguments and perturbation theory \[110\]. Blom et. al. \[105\] used a one-valley hydrogenic effective-mass model with central-cell corrections for calculating the properties of shallow donors inside or outside heterostructure quantum wells. Very recently, Friesen \[111\] developed a multi-valley effective mass theory to study the Stark effect of substitutional donors in bulk silicon, but with valley-orbit coupling treated perturbatively.

For shallow donors in a stressed Si/SiGe quantum well, the strain due to the lattice-constant mismatch lifts the degeneracy of silicon conduction band and only the two lowest-energy (+z and -z) valleys are needed to describe the low-lying donor states. The strain also causes an energy shift for the two valleys (by the same amount). We assume such an effect is completely absorbed in the band offset $U_s$.

The external field potential in Eq. (4.3) is thus composed of two parts: the square QW potential $V_{QW}$ and the gate potential. Details for calculating the gate potential profile can be found in Appendix A.

The quantum well potential has the following form:

$$V_{QW}(z) = \begin{cases} 
U_s & \text{if } |z - z_m| > W/2 \\
0 & \text{otherwise}
\end{cases}$$

\hspace{1cm} (4.14)

where $W$ is the width of the quantum well and $z_m$ the position of the QW central plane.

First we study the case where only $V_{QW}$ is present (without the gate potential). We solved the two-valley EME for a single donor placed in the middle of the well, with the QW width varied from 4 nm to 16 nm. The single donor atom is also at the center of the artificial box. To study the
lowest energy states, we only need to consider bases with even symmetry with respect to both \(x\) and \(z\). Ten Gaussian functions and 120 plane wave functions are used to construct the single-particle bases. The single parameter in the dielectric function, \(\alpha_c\), if taken as 1.13 a.u., yields an intervalley splitting of 3.2 meV between the ground state and the first excited-state, when the QW width is as large as 16 nm. Note that the ground state energy in wide well limit is approximately -34.21 meV, close to the experimental value of the 1s states with \(T_2\) symmetry for a phosphorous donor in bulk silicon. The value of intervalley splitting for a single P donor in a strained Si quantum well, although not available experimentally, was estimated to be 3.3 meV in large strain limit by Koilter et. al. [104] within perturbation theory, while Blom et. al. [105] estimated the central-cell shifts by relating it to the bulk shifts with symmetry consideration. The shift of the lowest two states from the QW one-valley effective-mass value is given by [105]:

\[
\frac{|\Psi_{QW}(r_0)|^2}{|\Psi_{1s}(r_0)|^2} \left[-\Delta_0 + \left\{ \frac{2\Delta_E}{3\Delta_T} \right\} \right].
\]  

(4.15)

where \(|\Psi_{QW}(r_0)|^2\) and \(|\Psi_{1s}(r_0)|^2\) are the QW and bulk envelope function amplitudes near the impurity center, respectively. The values of \(\Delta_0\), \(\Delta_E\), and \(\Delta_T\) are given in Chapter 3, for phosphorous donors in bulk silicon.

In the large QW width limit, the QW-bulk ratio for envelope function amplitudes should be of the order of unity, which gives a valley splitting of about 3 meV, consistent with our calculation. Figure 4.1 shows our calculation of the Si:P ground-state and first-excited-state energies and their splitting as a function of QW width in large scale. We see that both the ground and excited state energies increase as we decrease the QW width, as a consequence of larger kinetic energy for stronger confinement. The intervalley splitting also increases in a similar way. With Eq. (4.15), Blom et. al. predicted the same behavior for the valley splitting as the QW width is varied. They argued that, the ratio in Eq. (4.15) is expected to increase as the QW is narrowed, due to additional confinement. Therefore, the intervalley splitting should also increase.

This can be verified by inspecting the charge distribution. We plot in Fig. 4.2 (a) and (b) the 1D averaged charge distribution (which is obtained by integrating out the other two coordinates in the 3D charge density) along z-
Figure 4.1: The energies of two lowest states of a single Si:P donor and their splitting as a function of quantum well width. For convenience, the valley splitting is plotted in negative values.

axis and x-axis, respectively. The inset of Fig 4.2 (b) shows the 1D averaged charge distribution along y-axis. First we note that, the curves of $\rho_x$ and $\rho_y$ are very similar to each other, although $\rho_x$ is slightly more spread out, due to different basis functions we use for x and y directions (by symmetry they should coincide with each other). The charge distribution along z axis oscillates with a period $2\pi/\Delta k \equiv \pi/k_0 \approx 3\text{Å}$, resulting from the full wave function construction in Eq. (4.2). Due to the influence of QW barriers, the charge distribution is more concentrated around the donor nucleus for narrower confinement, as can be seen from the comparison of $\rho_z$ for the QW width at 6nm and 10nm.

To our surprise, the charge distribution in the direction parallel to the QW plane, shown in Figure 4.2 (b), also shrinks toward the impurity center as the QW is narrowed. This behavior is counterintuitive since we would have expected the shrinking of wave function in one direction would accompany dispersing in other directions. The synchronization of charge redistribution in all the 3 dimensions upon the change of 1D confinement, is due to the cooperative efforts to maintain the 3D shape of 1s orbital so as to lower the
Figure 4.2: The comparison of the averaged 1D charge distribution of Si:P ground state in a quantum well with width 6nm and 10nm. (a) and (b) shows the charge distribution along z and x axis, respectively. The inset of (b) shows the charge distribution along y axis.

ground state energy. We expect that the QW confinement should also have a significant effect on the exchange coupling of two neighboring donor electrons inside the quantum well, as we shall discuss in Chap. 7, since the dispersion of charge distribution would enhance the electron wave function overlap as the QW confinement is reduced.
Figure 4.3: The valley splitting of (a) Si:P donor ground state and (b) lowest quantum well state, as a function of quantum well width. The dotted lines connect points with a spacing of $a_0/2$. The inset of (a) shows the valley splitting of Si:P ground state as a function of donor position shift from the quantum well central plane, for a QW width fixed at 9nm.

We plot in Figure 4.3 (a) the valley splitting $\Delta E_P$ of the Si:P ground state as the QW width varies in small scale. The calculated points cover QW width range from about 8nm to 10nm, with a spacing of $a_0/4 \approx 1.36Å$. It clearly shows an oscillatory behavior and the oscillation magnitude decays
as the QW width increases, while the oscillation period is approximately one lattice constant ($a_0$).

For comparison, we also calculate the valley splitting of the lowest QW states, $\Delta E_W$. Such a valley splitting has been re-examined recently for Si/SiGe heterostructures within a 2-band tight-binding model [112, 113]. Here it is done by solving the two-valley EME without the impurity potential. The boundary conditions at the QW interfaces are neglected, since the lowest QW states are mostly confined inside the silicon quantum well for a QW width more than 8nm and a barrier height of 300 meV. We use the products of 20 (2D) Gaussian functions and 100 sine functions to expand the 3D wave functions of the lowest QW states. Fig. 4.3 (b) shows the QW valley splitting for the QW width varying from 50 to 80, in units of $a_0/4$. First we note that the magnitude of $\Delta E_W$ is approximately several tenths of meV for the QW width range shown, consistent with the tight-binding calculation of Ref. [113]. Compared to the valley splitting of impurity states $\Delta E_P$, $\Delta E_W$ is about 6 times smaller. This significant difference between the magnitude of $\Delta E_W$ and $\Delta E_P$ is due to the presence of central-cell correction brought by the impurity potential. Second, similar to $\Delta E_P$, $\Delta E_W$ also oscillates and decays as the QW width increases. Comparing the pattern of Fig. 4.3 (b) with Fig. 4.3 (a), we see that the oscillation of $\Delta E_W$ is much more frequent than $\Delta E_P$ on this smallest scale. However, if we view the oscillations at a larger scale (as in Ref. [113]), say, in units of $a_0/2$, $\Delta E_W$ will oscillate less frequent than $\Delta E_P$, as shown by the dotted lines in Fig. 4.3 (a) and (b). Note that the oscillation period on the $a_0/2$ scale is about 3.5$a_0$, nearly the same as the oscillation shown in Fig. 3 of Ref. [113].

Compared to the sophisticated microscopic tight-binding calculation, we conclude that, our simple calculation, although it has overlooked the delicate boundary conditions for finite-height barriers, is able to produce similar results. The oscillatory behavior shown in Fig. 4.3 (a) and (b), is due to the presence of multiple propagating states in the well, which is inherently included in our two-valley effective mass approximation, as shown in the composition of the full wave function in Eq. (4.2) and the charge distribution described approximately by Eq. (4.11).

We also study the intervalley splitting for the Si:P donor states as the donor atom is moved away from the center plane of the quantum well (but still kept in the center of the artificial box).
symmetry of the QW potential is broken and we need to include both even and odd basis functions with respect to \( z \). We use 10 Gaussian functions in the form of \( \{ \exp[-\alpha_i(y^2 + z^2/\xi^2)] \} \) (with \( \alpha_i \) optimized to resemble the 1s orbital of the hydrogen atom [107]) and 6 Gaussian functions in the form of \( \{ z \exp[-\beta_j(y^2 + z^2/\xi^2)] \} \) (with \( \beta_j \) optimized to resemble the 2p\(_z\) orbital of the hydrogen atom [107]) to take care of the mixed symmetry. Eighty sine functions with even parity is used for the description of freedom along x axis.

We plot in the inset of Fig 4.3 (a) the valley splitting as a function of donor position inside the silicon quantum well, with the QW width fixed at 9 nm. The valley splitting also shows an oscillatory behavior as the donor position is shifted. The magnitude of oscillation increases as the donor is moved away from the QW center, while the oscillation shows a double-period structure, with periods \( \sim 0.5a_0 \) and \( \sim 0.75a_0 \). The increase of the valley splitting as the donor is moved away from the QW center can be explained with the help of Eq. (4.15). The QW envelope function amplitude \( |\Psi_{QW}(r_0)|^2 \) is expected to increase as one of the barrier is more easily sensed by the donor bound electron (similar to the case when the quantum well is narrowed).

The effect of gate potential on a single donor will not be presented here, since here we focus on the gate control of exchange coupling for a donor pair, as we shall address in Chap. 6 and Chap. 7. It is worth mentioning that although a spectrum narrowing due to gate potential is observed (the intervalley splitting decreases as the gate-induced electric field pulls the donor electron away from the central cell), the ground state energy is lowered, in contrast to the result obtained in Ref. [111] for donors in bulk silicon where the Stark effect of a phosphorous donor in bulk silicon was studied with a perturbative multi-valley effective mass theory.

### 4.4 Concluding Remarks

Following the multi-valley effective mass approach, we have developed a two-valley equation for a single P donor in silicon quantum well. By turning the valley-coupled Schrödinger equation into a single matrix eigenvalue problem, we are able to solve the donor electron ground state energies and wave functions. The central cell correction is consistently incorporated by our model.

\footnote{This difference could result from the difference of the valley-orbital coupling of a two-valley model and a six-valley bulk model.}
potential, yielding the correct valley splitting of donor ground state.

We have studied the effects of quantum well confinement and donor position shift on the valley splitting and charge distribution for the single-donor ground state. We find that, as the quantum well is narrowed, the electron wave function shrinks and larger valley splitting is obtained. The shrinking of wave function happens in all the three dimensions, although only the confinement along z-axis is changed. This is caused by the correlated nature of the three-dimensional electronic wave function.

For a QW with fixed width, the valley splitting also increases as the donor approaches either of the QW edges. We have examined the effects of atomic-scale variations of QW width and donor position. The oscillation of valley splitting for donor electron ground state is observed for both cases. The valley splitting of the lowest QW states is also calculated as a function of QW width and oscillation behavior is confirmed. We have analyzed these results and compared them to relevant publications by other authors.
5 Approaches to Two-electron Problem

5.1 Introduction

It is usually much harder to implement a two-qubit gate than a single-qubit operation. The tunable coupling between a pair of qubits is crucial for proposals on implementation of quantum computers. One of the most popular physical systems for representing a qubit is the spin of an electron bound to an impurity or confined by a quantum dot. The overlapping of electron wave functions produces the desired effective spin coupling, which can be approximately described by the Heisenberg exchange model [114]. However, the applicability of Heisenberg model will depend on various system parameters, like the single-particle level spacing, the spreading of electron wave function, etc. What’s more, the exchange coupling strength presented in the effective Heisenberg model has to be calculated from first principles.

It is thus of importance to study the dynamics of the coupled two-electron system from the original exact Hamiltonian. In the absence of a magnetic field and without including the negligible spin-orbital coupling, spin variables are irrelevant in the system Hamiltonian. The two-electron Hamiltonian is given by

\[ H(r_1, r_2) = H_s(r_1) + H_s(r_2) + V_{ee}(r_1, r_2) \]  \hspace{1cm} (5.1)

where \( H_s(r) \) is the single-particle Hamiltonian for one electron after removing the other electron and \( V_{ee} \) is the mutual electron-electron Coulomb interaction. \( H_s(r_1) \) is usually composed of three parts: the single-electron kinetic energy term \( T \), the potential energy term \( V_{con} \) arising from the confinement potential which localizes electrons, and the external potential term \( W_{ext} \). The confining potential, such as the impurity potential or the potential in quantum dots, is usually determined by the system geometry and material properties, and thus unable to be tuned. On the other hand, the external potential, usually resulting from the effects of external fields or integrated
gate electrodes, is tunable with external control parameters.

In many problems of a single-particle Schrödinger equation, the ground state wave function turns out to be a nodeless function. Similarly, there is also a theorem [115] on the ground state of a two-electron system: the ground-state eigenfunction for the Hamiltonian Eq. (5.1) is nodeless, and the total angular momentum (including the contributions of orbital angular momentum and spin) is zero. If the Hamiltonian is invariant under the rotation of the coordinate axes, both the total orbital angular momentum and total spin for the ground state should be zero. Furthermore, the ground state has to be nondegenerate, as a consequence of the fact that, the eigenfunctions of a Hamiltonian are orthogonal and two nodeless functions cannot be orthogonal. As an example, the ground state of helium atom is a (nonmagnetic) singlet state. For heavier atoms (with more than two electrons), the ground state has a certain number of nodes, so as to satisfy Hund’s rules.

For the two-electron problem associated with a pair of well-separated donors, of course, it also has a singlet ground state in the absence of magnetic field. The antiparallel spins can take the spatial orbital hybridization and reduce their kinetic energy via one-electron hopping (to the neighboring site occupied by the other electron).

In the past decade the two-electron system (with each electron bounded to a distinct center) has been extensively studied due to its theoretical importance in quantum computing context [61, 116, 117, 118, 119]. Hartree-Fock (HF), Heitler-London (HL), or Hund-Mulliken molecular-orbital (MO) methods were most often used to evaluate the low-energy spectrum. Qualitatively speaking, the reliability of these methods is limited by the assumption that only one rigid single-particle level (for each binding center) is involved in the construction of two-electron wave functions. Such methods are only applicable at certain limits of the realistic system. Hartree-Fock method is only good when the electrons can be regarded as moving independently. HL approximation works for a weakly-coupled two-electron system, with the lowest single-particle level well separated from upper excited levels. One the other hand, MO method is only good for weakly-coupled or strongly-coupled cases where only a few single-particle molecular orbitals are active. These methods cannot describe the intermediate-coupling region with adequate accuracy.

We have tried to go beyond these simple approximations to obtain quantitatively reliable results on a pair of Si:P donors [34, 35], with an unrestricted
Hatree-Fock approach (UHF) with flexible single-particle levels characterized by Generalized-Valence-Bond-type (GVB) wave functions.

This chapter is organized as follows. In Sec. 5.2 we describe and discuss the restricted and unrestricted Hartree-Fock approximation. The Heitler-London method is analyzed in Sec. 5.3. Then we discuss in Sec. 5.4 the Hund-Mulliken molecular-orbital approach. In Sec. 5.5 we formulate the process of projected UHF approach and describe in detail the extended unrestricted Hatree-Fock method. We show that the extended UHF method has the advantages over other methods. For simplicity we discuss all the above mentioned methods in the framework of a two-electron system, although they can be easily generalized to a many-electron system. Concluding remarks are given in Sec. 5.6.

5.2 Hartree-Fock Method

In the Hartree-Fock (HF) approximation, each electron is supposed to move independently in the self-consistent mean field produced by all other electrons. The N-electron wave function is a simple product of N single-electron wave functions, or a single Slater determinant. The construction of the total wave function has to obey the Pauli exclusion principle.

There are various versions of Hartree-Fock approaches to a many-electron system. If the systems that one studies are closed shell systems (no unpaired electrons), one can perform a restricted Hartree-Fock (RHF) calculation where each orbital is occupied by two electrons with antiparallel spins. However, it is not appropriate to our two-electron system, where electrons are bound to well-separated donors, with a very small probability of double occupation (on the same spatial orbital). The unrestricted Hartree-Fock (UHF) removes the restriction on spins and could significantly improve the calculated ground state energy. On the other hand, the UHF method has a shortcoming that the ground state is not necessary to be a pure singlet state.

The HF equation for two electrons is given by

\[
[H_s(r_1) + (J_2 - K_2)]\psi_1(r_1) = E_1\psi_1(r_1)
\]  

(5.2)
where the operators $J_1$ and $K_1$ are defined by

$$J_2 \psi_1(r_1) = \int d r_2 \psi_2^*(r_2) \psi_2(r_2) V_{ee}(r_1, r_2) \cdot \psi_1(r_1)$$

$$K_2 \psi_1(r_1) = \int d r_2 \psi_2^*(r_2) \psi_1(r_2) V_{ee}(r_1, r_2) \cdot \psi_2(r_1).$$ \hspace{1cm} (5.3)

where all the integrals include sums over spin indices. It is clear that $J_2$ is the mean field created by the second electron via direct Coulomb repulsion, while $K_2$ describes the effect of exchange between the two electrons. The exchange term $K_2$ vanishes if the spin indices of two orbitals $\psi_1$ and $\psi_2$ are different.

The parallel equation for $\psi_2$ can be obtained similarly. Therefore, $\psi_1$ and $\psi_2$ can be solved by iterative techniques. We can first guess a trial wave function for $\psi_2$ and solve the effective single-electron equation for $\psi_1$. Then the obtained $\psi_1$ is used to get a new $\psi_2$. We do it iteratively until the solutions converge. The unpolarized UHF two-electron wave function has the following form,

$$|\Psi\rangle = \frac{1}{\sqrt{2}} [ |\psi_1 \uparrow\rangle_1 |\psi_2 \downarrow\rangle_2 - |\psi_2 \downarrow\rangle_1 |\psi_1 \uparrow\rangle_2]$$ \hspace{1cm} (5.4)

where the arabic subscripts for "\rangle" are used to specify electrons. Such a Slater determinant is always antisymmetric with respect to the interchange of particle labels. We note that the above expression can not be factored out as a product of the spatial part and the spin part. Therefore, such a state do not have definite total spin ($S$), which is in conflict with the two-electron theorem mentioned in Sec. 5.1 on the ground state property.

The main shortcoming of HF approximation is due to the underlying oversimplified physical picture where electrons only "see" an average background produced by other charges. Hence, electron correlation is only partially taken into account by the consideration of Pauli’s exclusion principle and by the iterative algorithm to elaborate the single-electron levels and minimize their energies. In addition, it is illustrated in Ref. [119] that in numerically solving the HF equations in the presence of magnetic field, the results would depend significantly on specific choice of gauges. It is argued that the breakdown of the gauge invariance is due to the one-Slater-determinant nature of the HF wave function, while a true two-electron wave function should be a
superposition of an infinite number of Slater determinants.

5.3 Heitler-London method

The Heitler-London (HL) method is an approximation in which the lowest two-electron state is constructed in a specific way from only two single-particle levels. Let \( \phi_L \) and \( \phi_R \) denote the fixed one-particle wave function localized at the left and right donor site, respectively. Then according to HL approximation, the two-electron spatial wave function is a symmetric (singlet) or antisymmetric (triplet) combination of one-electron wave function products

\[
\Psi_{\pm}(r_1, r_2) = \frac{1}{\sqrt{2(1 \pm s^2)}}[\phi_L(r_1)\phi_R(r_2) \pm \phi_R(r_1)\phi_L(r_2)],
\]  

(5.5)

where the subscript + (−) denotes singlet (triplet) states, and \( s \equiv \langle \phi_L | \phi_R \rangle \) is the overlap integral.

In the Heitler-London construction, the relevant lowest two-electron wave functions are always factorized into a spatial part and a spin part. The spatial wave function for the singlet state is symmetric with the interchange of electrons’ spatial labels, so the corresponding spin wave function should be antisymmetric with the interchange of spin labels, to keep the total wave function antisymmetric. Similar argument applies to the triplet state. Explicitly, the singlet and triplet spin states are given by

\[
|S^0\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle];
\]

\[
|T^{+1}\rangle = |\uparrow\uparrow\rangle;
\]

\[
|T^{-1}\rangle = |\downarrow\downarrow\rangle;
\]

\[
|T^0\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle].
\]  

(5.6)

with “S” and “T” denotes singlet and triplet, respectively. The superscript on “S” or “T” specifies the total spin number projected along z-axis. We can use \( |S, S_z\rangle \) to represent these four states, with the correspondence \( |S^0\rangle = |0, 0\rangle \) and \( |T^\mu\rangle = |1, \mu\rangle \) (\( \mu = +1, 0, -1 \)).

Because the Heitler-London method is essentially a two-level model (with
the triplet state 3-fold degenerate in spin space), it can be mapped to an effective Heisenberg exchange Hamiltonian in spin space:

\[ H_J = J \mathbf{S}_1 \cdot \mathbf{S}_2 \]  

(5.7)

where J is the energy difference between the singlet and triplet states and can be calculated from the original spatial Hamiltonian via

\[ J = \frac{\langle \Psi_- | H_{12} | \Psi_- \rangle}{\langle \Psi_- | \Psi_- \rangle} - \frac{\langle \Psi_+ | H_{12} | \Psi_+ \rangle}{\langle \Psi_+ | \Psi_+ \rangle} \]  

(5.8)

J is often called exchange splitting or exchange coupling. To get a simpler expression for J, we assume the single-particle Hamiltonian is comprised of

\[ H_s(r) = T(-i\nabla) + V(|r - r_L|) + V(|r - r_R|) \]  

(5.9)

with the single-particle orbitals \( \phi_L \) and \( \phi_R \) satisfying the following equations:

\[ [T(-i\nabla) + V(|r - r_L|)]\phi_L = e_0 \phi_L; \]
\[ [T(-i\nabla) + V(|r - r_R|)]\phi_R = e_0 \phi_R. \]  

(5.10)

where we have assumed the two donor at \( r_L \) and \( r_R \) to be identical.

Now we can proceed to calculate J by defining the relevant integrals

\[ V \equiv \int d^3r_1 d^3r_2 |\phi_L(r_1)|^2 |\phi_R(r_2)|^2 [V_{ee}(r_{12}) + V(|r_1 - r_R|) + V(|r_2 - r_L|)] \]
\[ = \int d^3r_1 d^3r_2 |\phi_L(r_1)|^2 |\phi_R(r_1)|^2 [V_{ee}(r_{12}) + V(|r_1 - r_L|) + V(|r_2 - r_R|)]. \]  

(5.11)

and

\[ U \equiv \int d^3r_1 d^3r_2 \phi_L^*(r_1) \phi_R^*(r_2) \phi_R(r_1) \phi_L(r_2) [V_{ee}(r_{12}) + V(|r_1 - r_R|) + V(|r_2 - r_L|)] \]  

(5.12)

where the last integral, U, is often called exchange integral.

Applying Eqs. (5.10), (5.11) and (5.12) to Eq. (5.8), we can get an ex-
pression of $J$ in terms of $V$, $U$, and the overlap $s$:

$$J = 2 \frac{V s^2 - U}{1 - s^4}$$  \hspace{1cm} (5.13)$$

We see from the above equation that, for far-separated donors, $s \simeq 0$, and $J$ only depends on the exchange integral, $J \simeq -2 \cdot U$. The sign of $U$ is not obvious, although it should be negative to give a singlet ground state (antimagnetic exchange coupling), according to the general two-electron theorem. The asymptotic limit of the exchange energy between two hydrogenic systems separated by a distance $R$ is calculated long time ago with Heitler-London approximation. It is given by [121]

$$J = 1.64 \frac{e^2}{\epsilon a_B} \left( \frac{R}{a_B} \right)^{5/2} \exp\left( -\frac{2R}{a_B} \right),$$  \hspace{1cm} (5.14)$$

where $a_B$ is the Bohr radius. This kind of analytic evaluation was generalized to donors in semiconductors in a recent publication [122].

However, Heitler-London method would yield a ferromagnetic exchange coupling (negative $J$) for hydrogenic systems separated by very large distance ($\geq 60a_B$) [120]. This reflects the qualitative limitation of the Heitler-London approximation. Since the two doubly-occupied configurations are completely neglected in HL calculation, it could overestimate the energy of the singlet state, especially for donors relatively strongly coupled during gate operation. As a consequence, the exchange coupling in the corresponding Heisenberg spin Hamiltonian might be underestimated.

5.4 Molecular Orbital Method

The molecular orbital method, also called Hund-Mulliken approach, extends the Heitler-London approximation by including the two doubly-occupied states [61, 115]. The two-electron Hamiltonian can be transformed to a $4 \times 4$ Hermitian matrix with the basis set

$$\{ \phi_u(r_1)\phi_g(r_2), \phi_g(r_1)\phi_u(r_2), \phi_u(r_1)\phi_g(r_2), \phi_g(r_1)\phi_g(r_2) \}$$
where the new single-particle levels (called molecular orbitals) can be expressed as a linear combination of the original atomic orbitals:

\[ \phi_g = \frac{\phi_L - \eta \phi_R}{\sqrt{1 - 2s\eta + \eta^2}}; \]

\[ \phi_u = \frac{\phi_R - \eta \phi_L}{\sqrt{1 - 2s\eta + \eta^2}} \]

(5.15)

with \( \eta = (1 - \sqrt{1 - s^2})/s \).

The above molecular orbitals are constructed so that they are mutually orthogonal. We can further antisymmetrize or symmetrize the basis functions with corresponding spin wave functions. There are six relevant basis functions in the whole (spin and spatial) Hilbert space. In the absence of a magnetic field, the states with different \( S_z \) are decoupled with each other. The polarized spin states \( T^+ \) and \( T^- \) are irrelevant for dynamics. The exchange coupling is only determined by the four states with \( S_z = 0 \), i.e., the two doubly-occupied singlet states, the delocalized singlet state and the \( |T^0\rangle \) state (the last two are considered in Heitler-London approximation). Therefore, the molecular orbital Hamiltonian can be mapped to a two-site two-electron Hubbard model Hamiltonian similar to the mapping of Heitler-London model to the Heisenberg spin model. It gives a better description than the HL approximation by definition. However, its reliability also depends on how much the fixed single-particle levels (\( \phi_L \) and \( \phi_R \)) are separated from the excited levels and whether or not they are changed significantly during the dynamical process controlled by gate potentials.

### 5.5 Projected and Extended Unrestricted Hartree-Fock Approach

The unrestricted Hartree-Fock method has the advantage of providing accurate single-particle levels, with the disadvantage of yielding wrong spin configuration and failing to grasp the full effect of electron correlations. On the other hand, the Heitler-London approximation can construct the spatial and spin states consistently and largely take care of electron correlations for well-separated donors, but the use of rigid single-particle levels has limited its flexibility and accuracy to handle the effect of external controls.
There have been efforts to combine the advantages and avoid the disadvantages of the above two approximations. Yannouleas and Landman [124, 125, 126, 127] proposed using the spin-and-space unrestricted Hartree-Fock method in conjunction with the companion step of the restoration of spin and space symmetries via Projection Techniques. In the first step an UHF approach is applied to the two-electron Hamiltonian, after which we get a set of single-particle levels. Suppose two of such levels are $|\phi_L\rangle$ and $|\phi_R\rangle$. An UHF two-electron state with total spin zero along $z$-axis can be constructed as Eq. (5.4),

$$|\Phi_{UHF}\rangle = |L \uparrow, R \downarrow\rangle = \frac{1}{\sqrt{2}}[|\psi_L \uparrow\rangle_1 |\psi_R \downarrow\rangle_2 - |\psi_L \downarrow\rangle_1 |\psi_R \uparrow\rangle_2]$$

(5.16)

which turns out to be a single Slater determinant.

The above state is an eigenstate of the $z$-projection of the total spin, $S_z = S_1 + S_2$, with $S_z = 0$. However, it is not an eigenstate of the square, $S^2$, of the total spin. To generate an eigenstate of $S^2$, a projection operator can be applied to $|\Phi_{UHF}\rangle$ to get a two-electron wave function with desired spin and spatial symmetry. For example, one can use a projector operator $P_- = 1 - \bar{\omega}_{12}$ (where $\bar{\omega}_{12}$ interchange the spins of two HF orbitals) to obtain the singlet state of the two-electron system [127]

$$|\Psi_s\rangle = P_- |L \uparrow, R \downarrow\rangle \propto [|L \uparrow, R \downarrow\rangle - |L \downarrow, R \uparrow\rangle]$$

(5.17)

In terms of the spatial and spin variables for each electron, it is found that the above singlet state can be factorized,

$$|\Psi_s\rangle \propto [|\phi_L(1)\phi_R(2)] + |\phi_R(1)\phi_L(2)] \otimes [|\uparrow_1\downarrow_2 - |\downarrow_1\uparrow_2]]$$

(5.18)

where it should be emphasized that the arabic numbers are labels for specifying electrons. Similarly, we can obtain the wave function of a triplet state with $|S, S_z\rangle = |1, 0\rangle$ by applying the projection operator $P_+ = 1 + \bar{\omega}_{12}$ to Eq. (5.16).

Eq. (5.18) turns out to have the form of a Helter-London (HL) wave function. However, unlike the original HL scheme which uses fixed atomic orbitals, expression (5.18) employs the UHF orbitals that are self-consistently optimized for any coupling range and in the presence of external potentials.
Therefore, that type of wave function[Eq. (5.18)] can be characterized as a generalized Heitler-London (GHL) wave function. The corresponding energy is then calculated by estimating the expectation value of the original two-electron Hamiltonian.

The above method has been applied by Yannouleas and Landman to quantum dot atoms and molecules [124, 125, 126, 127] and better results are obtained as compared to naively applying Hatree-Fock or Heitler-London approximations. This approach is also known in quantum chemistry as the projected unrestricted Hartree-Fock method [123].

We have applied a different method to deal with the two-electron system in quantum computing context [35]. The method is known as the extended unrestricted Hartree-Fock method [128], where the projection is made before performing the iterative procedure. As we are only concerned with the two lowest two-electron energy states with the well-known spin configurations, it is much more convenient for us to use the extended UHF method. We first construct a two-electron spatial wave function in the form of Eq. (5.5).

The wave function is supposed to be an eigenfunction of the two-electron Hamiltonian[Eq. (5.1)],

$$ H(r_1, r_2)\Psi_\pm(r_1, r_2) = E\Psi_\pm(r_1, r_2). \quad (5.19) $$

We choose an appropriate set of orthonormal basis functions, $b_n(r)$; $n = 1, \cdots N$ to describe the one-electron wave functions $\phi_R(r)$ and $\phi_L(r)$. Let the expansion coefficients for $\phi_R$ and $\phi_L$ be $R_n$ and $L_n$, respectively. Assume that in a given iteration, we already know the expansion coefficients $R_n$ for $\phi_R(r)$. The above two-electron eigenvalue equation can then be reduced to a single-electron eigenvalue problem by projecting it into the state $\phi_R$. The projected eigenvalue equation within the basis now reads

$$ \sum_n [\langle n' | H_1 | n \rangle + \langle \phi_R | H_1 | \phi_R \rangle \delta_{n',n} \pm \langle n' | H_1 | \phi_R \rangle R_n \pm R_n' \langle \phi_R | H_1 | n \rangle \rangle L_n = E \sum_n (\delta_{n',n} \pm R_n R_n)n L_n. \quad (5.20) $$

where "+" and "-" correspond to the singlet and triplet states, respectively.

The equations[Eq. (5.20)] are processed independently for singlet and triplet states. The unknown single-particle orbital $\phi_L(r)$ can be solved via
the standard diagonalization procedure within the one-electron basis. The newly obtained \( \phi_L(r) \) is then used to solve \( \phi_R(r) \), and we do it iteratively until the singlet or triplet ground state energies and wave functions converge.

For large donor (dot) separation (weak coupling), we may use the ground state wave function for single donor as our initial guess for either \( \phi_R(r) \) or \( \phi_L(r) \). For small donor (dot) separation (strong coupling), using molecular orbital as our initial guess will work better. Since in typical QC architectures the donor ions are always well separated and the external potential is usually weak so as not to disturb the system spectrum too much, we will always use the atomic orbital as the starting point of our calculation.

Like the projected UHF method, the extended UHF method has combined the advantages of Hartree-Fock approach and Heitler-London approximation. The common point of the two methods is that, they use a generalized-Heitler-London-type two-electron wave function to approximate the exact wave function with correct spin configurations. The single-particle levels used to construct the two-electron wave functions are self-consistently determined. Either of these two methods can successfully deal with both weakly and strongly coupled two-electron systems.

It should be emphasized that the projected wave function in the projected UHF method is not an eigenfunction of the original two-electron Hamiltonian, while in the extended UHF method, the two-electron function is required to satisfy the eigenvalue equation Eq. (5.19) during each iteration. The advantage of molecular orbital method is also integrated into our calculation. The contributions from doubly-occupied configurations are included self-consistently.

As compared to the single-determinant wave functions of restricted or unrestricted HF methods, our wave function [Eq. (5.5)] is a linear combination of two Slater determinants; thus, it represents a more accurate modelling of the real wave function beyond regular mean-field approximations. We have numerically verified that if we use the atomic orbital (molecular orbital) as the starting point for our extended UHF calculation, we get after one iteration a lower energy (both for singlet and triplet) than that obtained by either the HL or MO approach.
We note that for the triplet states
\[
\phi_L(r_1)[\phi_R(r_2)+C\phi_L(r_2)]-\phi_R(r_1)+C\phi_L(r_1)]\phi_L(r_2) = \phi_L(r_1)\phi_R(r_2)-\phi_R(r_1)\phi_L(r_2).
\]
(5.21)

where \(C\) is an arbitrary constant. This means that if \(\phi_L\) is linearly dependent on \(\phi_R\), we can always choose a new \(\phi_L\) which is orthogonal to \(\phi_R\) without altering the results. Numerically, since we use a finite set of basis functions, imposing such a constraint means we need to expand \(\phi_L\) in terms of \(N-1\) independent basis functions. Failure to do this will lead to a singular overlap matrix and the generalized eigenvalue problem will collapse. To avoid this problem, we use one less basis function for the expansion of \(\phi_L(r)\) and require all basis functions to be orthogonal to \(\phi_R(r)\) during each iteration.

5.6 Concluding Remarks

The continuing use of various approximate approaches originates from the numerical difficulties inherent in the more rigorous and advanced configuration interaction (CI) method (also known as direct or exact diagonalization method). In the CI approach [123], a number of Slater determinants are used to construct the correlated many-electron wave functions. For example, the spatial wave function for a two-electron singlet state (with a fixed spin wave function \(|S^0\rangle\) separated from the spatial part) can be expanded as

\[
\Psi(r_1, r_2) = \sum_{i,j=1}^{N} [\phi_i(r_1)\phi_j(r_2) + \phi_j(r_1)\phi_i(r_2)]
\]
(5.22)

where \(N\) is the total number of basis functions used in describing the involved single-particle levels. The wave function can then be solved by directly diagonalizing the two-electron Hamiltonian within two-electron basis functions shown in the square brackets. There are \(N(N+1)/2\) two-electron bases constructed from \(N\) single-particle levels.

The single-particle basis \(\phi_j\) can be either atomic or molecular orbitals, or generalized valence bond orbitals. The advantage of the CI method is that it can approach the exact correlated many-electron wave function with increased accuracy by increasing the number of basis functions. However, in realistic calculation, we have to take into account the demanding computa-
tional resources (time and memory).

We adopt the extended UHF method instead of the CI method because it can handle the well-separated two-donor problem with adequate flexibility and good accuracy, and it requires much less computational resources, while the large number of bases needed in the CI method makes it currently unpractical.

The floating-phase Heitler-London approach, proposed recently by Koiller et. al. [23], corresponds to a special case of our method. A single parameter describing the relative phase of $\phi_L$ and $\phi_R$ is allowed to vary to improve the naive application of the usual HL approximation with rigid atomic orbitals and zero relative phase. As can be seen by definition, this method is much less flexible and less accurate than our method for studying the two-electron problem in a wide range of coupling strength and under inhomogeneous external controls.
6 Coupled Si:P Donors in Uniform Electric Field

6.1 Introduction

As illustrated in Chapter 2, the exchange coupling between a neighboring pair of donor electrons can realize universal quantum computation, with each qubit represented by the two-dimension subspace of 3 neighboring donor-electron spins. Both an arbitrary single-qubit rotation and the two-qubit controlled-NOT gate require only two-donor dynamics (in Heisenberg model) during each step. In other words, universal gate operation for multiple logic qubits can be performed via a series of simple operations between a neighboring pair of donor electron spins (physical qubits) with tunable exchange interaction.

To perform a desired nontrivial operation between two electron spins we need to be capable of switching on and off the exchange coupling efficiently at specified moments. Suppose we want to swap the spin states of two neighboring donor electrons. If the two spin states are the same, we need to do nothing. If the two spins are in different states, for example, \( | \uparrow_1 \downarrow_2 \rangle \), we then need to get a final state \( | \downarrow_1 \uparrow_2 \rangle \) after some duration. For simplicity, we consider the two-spin dynamics in the framework of Heisenberg model

\[
H_{12}(t) = J(t)S_1 \cdot S_2
\]

(6.1)

where \( J(t) \) is the time-dependent exchange coupling that can be tuned by some external controls such as the gate electrodes shown in Fig. 2.1. The involved two-spin Hilbert space is four-dimensional, with a possible choice of basis \( \{ | \uparrow_1 \downarrow_2 \rangle, | \downarrow_1 \uparrow_2 \rangle, | \uparrow_1 \uparrow_2 \rangle, | \downarrow_1 \downarrow_2 \rangle \} \).

Let us tune the exchange coupling \( J(t) \) adiabatically. Suppose \( \{|c_j(t)\} \) is the complete set of eigenvectors for the instantaneous Hamiltonian \( H(t) \) with corresponding energies \( E_j(t) \). Any initial state can be expressed as a superposition of the initial energy basis, \( |\Psi(0)\rangle = \sum_j c_j |c_j(0)\rangle \). Then, ac-
According to adiabatic approximation [129], at any later moment \( t \), the system evolves into 
\[
|\Psi(t)\rangle = \sum_j c_j \exp[-i/\hbar \int_0^t E_j(t)dt]|e_j(t)\rangle.
\]

Now we consider the Heisenberg Hamiltonian Eq. (6.1). Obviously, the instantaneous eigenstates of \( H_{12}(t) \) are given by
\[
|S_0\rangle = \frac{1}{\sqrt{2}}[|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle]
\]
\[
|T_0\rangle = \frac{1}{\sqrt{2}}[|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle]
\]
\[
|T^{+}\rangle = |\uparrow_1\uparrow_2\rangle
\]
\[
|T^{-}\rangle = |\downarrow_1\downarrow_2\rangle
\]
(6.2)

where \( |S_0\rangle \) is the ground state with an energy of \( E_{S_0}(t) = -J(t)/4 \), while the other three states are degenerate, with an energy of \( E_{T_0}(t) = 3J(t)/4 \). Note that the eigenstates are remaining the same at any instant; only their corresponding energies change with time.

So an initial state \( |\Psi(0)\rangle = |\uparrow_1\downarrow_2\rangle = \frac{1}{\sqrt{2}}[|S_0\rangle + |T_0\rangle] \) will evolve at a later moment \( \tau \) to
\[
|\Psi(\tau)\rangle = \frac{1}{\sqrt{2}}[\exp(i/\hbar \cdot \frac{1}{4} \int_0^\tau J(t)dt)|S_0\rangle + \exp(-i/\hbar \cdot \frac{3}{4} \int_0^\tau J(t)dt)|T_0\rangle].
\]
(6.3)

The realization of spin swapping the initial state at moment \( t = \tau \) requires \( |\Psi(\tau)\rangle = |\downarrow_1\uparrow_2\rangle = \frac{1}{\sqrt{2}}[-|S_0\rangle + |T_0\rangle] \). Or equivalently, up to a trivial global phase factor, we have
\[
\int_0^\tau J(t)dt/\hbar = n \times 2\pi + \pi.
\]
(6.4)

where \( n \) can be any integer, although we usually choose \( n=0 \) to complete our desired operation as soon as possible.

Therefore, to swap (interchange) two spins with different polarizations, we only need to tune the exchange coupling \( J(t) \) for a duration of \( \tau \) so that the exchange pulse satisfies the accumulated phase relation, Eq. (6.4). Another important example of gate operations is the half swap operation between two spins. Analogous to Eq. (6.4), it requires the phase accumulated by the exchange coupling to be
\[
\int_0^\tau J(t)dt/\hbar = n \times 2\pi + \frac{\pi}{2}.
\]
(6.5)
to realize a unitary operation

\[ U_{\sqrt{SW}} = \exp(-i\frac{\pi}{2}S_1 \cdot S_2) \quad (6.6) \]

with which (and assisted by certain single-spin rotations) the important
controlled-NOT (CNOT) two-spin gate can be constructed.

The above example of gate operation has demonstrated the central im-
portance of the exchange coupling in realizing electron-spin-based quantum
computation. In a realistic two-electron system (e.g., a diatomic molecule
or a double quantum dot), the exchange coupling can only be calculated by
solving the original spatial Hamiltonian

\[ H(r_1, r_2, t) = \sum_{j=1,2} [T_j + U(r_j)] + V_{ee}(|r_1 - r_2|) + \sum_{j=1,2} W_{ext}(r_j, t) \quad (6.7) \]

where \( T_j \) is the kinetic energy term for the j-th electron, and \( U \) is the potential
specified by the system. For a couple of donors, \( U \) is composed of the impurity
potential of the two donor ions. \( V_{ee} \) is the mutual interaction of two electrons.
\( W_{ext} \) is the external potential term, which is the only tunable part.

We have to solve the Hamiltonian Eq. (6.7) at any fixed moment to learn
how to adapt the exchange coupling via external controls. We first do it
in this chapter for a pair of P donors in silicon, assuming simple external
potentials and in the framework of hydrogenic effective mass approximation.
Then in next chapter we will do it with a more sophisticated and rigorous
model and with a realistic gate potential calculated from first principles.

In the hydrogenic effective mass approximation, we simplify the realistic
Hamiltonian to a hydrogen-molecule-like Hamiltonian for the envelope func-
tion by ignoring the intervalley mixing and central cell effect while assuming
the effects of the periodic crystal potential are captured by the effective mass
tensor and the background dielectric constant (\( \epsilon_0 = 11.4 \)). We further as-
sume the silicon effective mass is isotropic, characterized by its spherically
averaged value, \( m^* = (\frac{1}{3}m_l^{*\text{m}} + \frac{2}{3}m_t^{*\text{m}})^{-1} = 0.3m_0. \)

Under such approximations a single Si:P donor at \( R_0 \) can be by described
by the simple one-band single-valley effective-mass equation in real space [cf.
Eq. (3.19) and Ref. [98]:

$$\left[ -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{\epsilon_0|\mathbf{r} - \mathbf{R}_0|} \right] F(\mathbf{r}) = (E - E_0) F(\mathbf{r}) \quad (6.8)$$

where $E_0$ is the energy at the conduction band minimum.

Thus the effective single-electron Hamiltonian (in the field of two donor ions) can be written as

$$H^s(\mathbf{r}) = -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{\epsilon_0|\mathbf{r} - \mathbf{R}_1|} - \frac{e^2}{\epsilon_0|\mathbf{r} - \mathbf{R}_2|} \quad (6.9)$$

with the two donor placed at $R_1$ and $R_2$.

The full wave function for a donor electron can be expressed as the product of an envelope function and the Bloch function at the band minimum $k_0$:

$$\phi(\mathbf{r}) = F(\mathbf{r}) u_{k_0}(\mathbf{r}) e^{i k_0 \cdot (\mathbf{r} - \mathbf{R}_0)} \quad (6.10)$$

The two-electron envelope function is given by

$$G_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2(1 \pm s^2)}} [F_L(\mathbf{r}_1) F_R(\mathbf{r}_2) \pm F_R(\mathbf{r}_1) F_L(\mathbf{r}_2)], \quad (6.11)$$

with "+" ("-") corresponds to a singlet (triplet) and $s = \langle F_L | F_R \rangle$. The two-electron envelope function satisfies the following effective mass equation

$$\left\{ \sum_{i=1,2} [H^s(\mathbf{r}_i) + W_{ext}(\mathbf{r}_i)] + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} G_\pm = E_\pm G_\pm \quad (6.12)$$

for a weak and smooth external potential $W_{ext}$.

The exchange coupling is defined as the splitting of the lowest singlet and triplet states,

$$J = E_- - E_+ \quad (6.13)$$

This chapter is organized as follows. In Sec. 6.2 we study the effect of a one-dimensional parabolic potential, which models the J-gate by a single control parameter. The dependence of exchange coupling and charge distributions on the control parameter are examined. Then we analyze in Sec. 6.3 the effect of a uniform electric field parallel to the inter-donor axis. We calculate the exchange coupling in the presence of such an electric field and
compare the electric-field-induced charge transfer behaviors for the lowest singlet and triplet states. The implications for realizing spin readout is analyzed. Finally, in Sec. 6.4 we study how a uniform electric field perpendicular to the inter-donor axis can influence the exchange coupling and we give an estimate on the field strength to ionize donor electrons. We make concluding remarks in Sec. 6.5.

### 6.2 Effect of J-gate Model Potential

The potential imposed by a realistic J-gate depends on the detailed experimental settings and may be very complicate (cf. Appendix A for a realistic calculation of the gate potential generated by electrodes in the architecture shown in Fig. 2.1). However, a simple model potential can grasp certain important features of the system. For example, earlier studies on quantum dots often assumed a simple 2D parabolic confining potential. In a calculation performed by Hu and Das Sarma on a double quantum dot molecule, they modelled the central barrier (similar to the J-gate modulated barrier between two donors) of a quantum dot molecule by a 2D Gaussian function [119].

Here, we model the J-gate qualitatively by a one-dimensional parabolic potential with its minimum located in the middle of the two donor ions, which acts like an attractor and could strongly enhance the wave function overlap of the two donor electrons. Let the $x$ axis passes through the two donor ions and their midpoint is at $x = 0$. Explicitly, the J-gate potential takes the form

$$V_J(x) = \mu \frac{(x - R/2)(x + R/2)}{(R/2)^2}.$$  \[6.14\]

where the two donor ions are placed at $(\pm R/2, 0, 0)$ and $\mu$ is the energy difference (in units of $Ry^*$) between the potential minimum $(x = 0)$ and donor sites $(x = \pm R/2)$. Therefore, such a J-gate potential with positive $\mu$ can attract the donor electrons toward each other, increasing their wave function overlap.

For convenience in choosing a finite set of flexible basis functions along the $x$ axis, we place the system in a well with infinite potential barrier for $|x| > L/2$. The size of $L$ is chosen to be large enough (at least $5 \ a_B^1$ from

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1We in this chapter omit the “*” in $a_B^*$ without causing confusions. "$a_B$" always means...
either box boundary to its nearest donor ion), so it has a negligible effect on the donor binding energy. We expand the spatial part of the single-particle wave function in terms of a linear combination of basis functions defined as

\[ b_{m,i}(r) = \sqrt{2/L} \sin[k_m(x + L/2)]\beta_n(y^2 + z^2) \]  

(6.15)

where \( k_m = m\pi/L \) and \( \beta_n(y, z) \) is set of orthogonal functions constructed from the 2D Gaussian functions \( \exp[-\alpha_i(y^2 + z^2)] \). The set of Gaussian parameters \( \{ \alpha_i \} \) are optimized such that a linear combination of the 3D Gaussian functions \( \exp[-\alpha_i r^2] \) best resembles the 1s wave function of a Hydrogen atom [107]. Since the donors are well separated and their electron wave function mixing happens mainly along the \( x \) direction, the wave function in the \( y \) and \( z \) directions should remain close to the 1s orbital of isolated donors; thus, several Gaussian functions should be good enough to describe them. In the \( x \) direction, there would exist several kinds of mixing of single-particle orbitals, such as the \( s-p \) hybridized state (one electron in the \( s \) orbital of donor 1 while the other in the \( p \) orbital of donor 2), \( p-p \) hybridized state, and doubly occupied states (both electrons bound to the same donor ions), which may become significant when a gate potential or a parallel electric field is applied. The set of plane wave functions in the \( x \) direction are flexible and convenient enough to characterize all possible state mixings. The suitability of the basis functions used here is examined by comparing our numerical results to the exact results in various limits. For example, with five 2D Gaussian functions and 50 sine functions we obtain a single-donor ground-state energy of -0.998 Ry and the \( H_2 \) molecule ground state energy of -2.282 Ry, which is better than the results obtained with the Heitler-London approximation (-2.231 Ry) [130] or Hartree-Fock approximation (-2.267 Ry) [131].

We first consider the case with an inter-donor separation \( R = 10a_B \). The box size used to define the plane wave basis in the \( x \) direction is set to be \( L = 20a_B \), and 5 × 50 basis functions (five Gaussian functions in the plane and 50 plane waves along the \( x \) axis) are used for solving Eq. (6.12). Using the extended Hartree-Fock method described in Chapter 5, we calculate the energies and wave functions for the lowest singlet and triplet states as functions of the J-gate potential strength (\( \mu \)). We are only interested in cases \( a_B^* \) (the effective bohr radius defined in Chap. 4) if not specified.
where $\mu$ is below some critical value $\mu_c$, beyond which the electrons can be delocalized from its donor ions and trapped by the J-gate potential well. In that case, the electrons will lose their identities during a gate operation and extra levels can be activated to cause leakage errors and open additional decoherence channels. Another restraint may come from the validity of adiabatic approximation. The low-energy spectrum of the two-electron system should maintain the same structure (i.e., no level crossing) if we perform gate operations adiabatically.

To find the critical value $\mu_c$, we define an averaged one-dimensional charge distribution along the inter-donor axis as

$$\rho(x) = \frac{\int dy \int dz \int d\mathbf{r}_2 |\Psi(\mathbf{r}, \mathbf{r}_2)|^2}{\int d\mathbf{r} \int d\mathbf{r}_2 |\Psi(\mathbf{r}, \mathbf{r}_2)|^2}. \quad (6.16)$$

The charge distribution $\rho(x)$ has a significant change when $\mu$ exceeds $\mu_c$. It is found that $\mu_c$ depends strongly on the inter-donor separation. Large separation allows a relatively deep gate potential to enhance the exchange splitting while keeping the qualitative shape of charge distribution unchanged.

Fig. 6.1 shows the exchange splitting, $J$, as a function of the J-gate potential strength $\mu$ for various inter-donor separations, $R = 8$ and $R = 10$. At $\mu = 0$ and $R = 10$, we obtain an exchange splitting of $1.07 \times 10^{-6}$, which is about half of the asymptotic result estimated by Eq. (5.14). The exchange splitting increases exponentially as we increase the depth of the gate potential $\mu$. The exponential dependence of $J$ on $\mu$ enables such a J-gate to switch on and off the spin-exchange coupling between neighboring qubits efficiently. At $\mu = 0.8$ the exchange splitting is $J = 0.00234 \text{ Ry}^*$ (approximately 70 $\mu$eV if we use $\text{Ry}^* = 30 \text{ meV}$). Such a value of exchange splitting yields an adiabatic half-swap gate operation time of $\sim 15\text{ps}$ with a flattop pulse. However, it doesn’t satisfy the large exchange requirement for initializing the 3-donor-spin-encoded qubit array (cf. Chap. 2). We note that, at $R = 15$, the exchange splitting is about $10^{-10} \text{ Ry}^*$ when the J-gate potential is off (also consistent with the asymptotic result) while a gate potential with $\mu = 1.0$ can only push the exchange energy to the order of $10^{-5}$. This means that, to complete the same operation, a quantum computer with a donor spacing of $R = 15$ will need about 1000 times longer than what is needed for $R = 10a_B^*$. 

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Figure 6.1: Exchange splitting, $J$ as a function of the strength of J-gate potential, $\mu$ for $R = 8$ and 10 $a_B$.

We do not perform more analysis on quantum gate operation here, as we will address it in detail with a more realistic model in the next chapter.

Fig. 6.2 shows the averaged charge distribution $\rho(x)$ for various strengths of the J-gate potential for $R=10$ $a_B$. We see that up to $\mu = 0.8$, in either singlet or triplet state, both electrons are still localized mainly around their donor ions, while there is a significantly charge distribution buildup near $x = 0$ as $\mu$ goes up to 1.0. We note that $\rho(x)$ at $x = 0$ in the singlet state is higher than its counterpart in the triplet state. It is especially evident in Fig. 6.2 for the $\mu = 1.0$ case. This can be understood based on the Pauli exclusion principle, as electrons tend to avoid each other in the triplet configuration.
Figure 6.2: Averaged charge distribution along the inter-donor axis, $\rho(x)$ [as defined by Eq. (6.16)] for various strengths of the J-gate potential: $\mu = 0$ (dotted), 0.6 (dashed), 0.8 (solid), and 1.0 $Ry^{*}$ (dash-dotted). (a) Singlet; (b) triplet. The inter-donor separation is fixed to be $R = 10a_B$.

6.3 Effect of a Parallell Electric Field

To model the effect of a uniform electric field, we add an electrostatic potential term $V_F = -eFx \ ( -eFz )$ for parallel (perpendicular) field to the
Hamiltonian $H^*$, which leads to a Stark shift and finite lifetime for the (quasi-) bound states. For parallel field, the single-electron basis functions used are the same as those defined in the previous section [Eq. (6.15)]. With the wave functions confined in the region $|x| < L/2$, the problem of electric-field-induced finite lifetime can be avoided. At a finite electric field, the size of the confining box (L) must be chosen small enough so that the quantum confined energy level associated with the triangular potential (induced by the artificial confining walls and the electric field) is well above the the ground singlet and triplet state composed from a finite set of basis functions. Otherwise, the variational calculation may lead to an incorrect ground-state wave function. On the other hand, the confining walls should be far enough away from donor ions (the nearest distance between walls and donors is at least 5 $a_B^*$) in order to avoid an artificial confinement effect on the exchange splitting or charge distribution. This consideration puts an upper limit on the strength of the parallel field above which the variational calculation (with a finite basis) breaks down. However, this constraint can be relaxed if a finite J gate potential (such as the one used in Sec. 6.2) is also present, since such an attractive potential can lower the system levels compared to field-induced levels.

The Stark effect on the energies of the lowest singlet and triplet states is illustrated in Table 6.1 for $R = 10a_B$ and $\mu = 0$, where the width of the confining well is chosen to be ($L = 20a_B$). The electric field lowers the energies of both singlet and triplet states, but the triplet state energy is much less affected due to the Pauli exclusion principle. We note that at $F = 0.1Ry^*/a_B$, the singlet state becomes a doubly-occupied donor state and the energy of the ground singlet state experiences an abrupt lowering compared to the energy at $F = 0.08Ry^*/a_B$. If we further increase the electric field, the variational calculation will break down.

Next, we study the evolution of charge distributions of both singlet and triplet states at a fixed donor separation $R=10$ $a_B$ in the presence of a fixed J-gate potential with strength $\mu = 0.2$ $Ry^*$ as we vary the parallel electric field. The confinement width is set to $L=30$ $a_B$ and our basis consists of five radial Gaussian functions (in the y-z plane) and 80 sine functions of x (along the interdonor axis). We find that the singlet state changes abruptly to a doubly occupied state at a critical field due to the interplay of Stark
Table 6.1: Energies for the lowest singlet ($E_s$) and triplet ($E_t$) states of a donor-pair separated by $R = 10a_B$ under a uniform electric field $F$ along the inter-donor axis. The exchange coupling is defined as the singlet-triplet splitting, $J = E_t - E_s$. All energies are in units of $Ry^*$ and the fields in units of $Ry^*/a_B$. Note that the single donor ground state energy without applying electric field obtained in our variational calculation is $-0.99787087Ry^*$.

<table>
<thead>
<tr>
<th>$F$</th>
<th>$E_s$</th>
<th>$E_t$</th>
<th>$J$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-1.99574172</td>
<td>0.00000107</td>
</tr>
<tr>
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<td>0.10</td>
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<td>-2.01838976</td>
<td>0.17627862</td>
</tr>
</tbody>
</table>

shift and electron-electron interaction. Figure 6.3 (a) shows the charge distribution of the ground singlet state along the x axis at zero field and in the neighborhood of the critical field. We see clearly that at an electric field less than $0.085 \, Ry^*/a_B (~12.6 \text{ kV/cm})$, the charge density displays two distinct peaks centered around the two donor ions. The degree of distortion (polarization) is rather small, which indicates that the electric field is not large enough to conquer the Coulomb blockade. At $F=0.09 \, Ry^*/a_B$, the singlet charge density displays a single enhanced peak (cf. the long-dashed curve) around the left donor ion, revealing an almost complete charge transfer from the right donor to the left.

As shown in Fig. 6.3 (b), the charge distribution of the triplet state as a function of the electric field is remarkably different from the singlet state. At $F=0.11 \, Ry^*/a_B$, the charge distribution still displays two peaks similar to the $F=0$ case (other than a weak polarization indicating a slight charge transfer from the right donor ion to the region between two donor ions). This behavior again can be explained by the Pauli exclusion principle, which prevents the two electrons of parallel spin to reside on the same site. As we further increase the electric field to $F=0.115 \, Ry^*/a_B$, the right donor is mostly ionized by the electric field and a new peak appears in the left region of the left donor, while the previous peak centered around the left donor remains unchanged. The appearance of the new peak indicates single-electron ionization of the two-donor molecule, which may be named "Pauli-enhanced ionization". Compared to the triplet state, the doubly occupied
Figure 6.3: The averaged charge distribution along the inter-donor axis, \( \rho(x) \), for various strengths of the parallel electric field with a fixed donor separation \( R = 10a_B \) and J-gate strength \( \mu = 0.2Ry^* \). (a) Singlet; (b) triplet.

The singlet state is rather stable even under a large electric field with strength up to \( F = 0.2 \, Ry^*/a_B \).

The polarizations (defined as the absolute expectation value of \( x_1 + x_2 \),
in units of $a_B$) for the lowest singlet and triplet states are plotted in Fig. 6.4 as functions of electric field for $R=10$ and $\mu = 0.2$. There clearly exists a window between two critical electric fields, $F_{cS}^S$ (the field at which the singlet donor state abruptly changes to a doubly occupied donor state) and $F_{cT}^T$ (the field above which the lowest triplet state abruptly becomes ionized). Table 6.2 lists the values of critical electric fields for the singlet ($F_{cS}^S$) and the triplet ($F_{cT}^T$) for various donor separations and at different strengths of J gate. We found that the critical fields are insensitive to the strength of J gate, but sensitive to the donor separation. We note that the polarization behavior for the case with $R=8\ a_B$ and $m = 0.4\ Ry^*$ is qualitatively different and we find no abrupt change of the charge distribution. In this case, the potential barrier between donor ions is significantly lowered and a new molecular orbital can be formed. The molecular orbital is a linear combination of atomic orbitals on the donor site and the localized orbitals centered at the bottom of the J-gate potential. This localized orbital acts like a bridge or relaxation channel.
for the charge transfer. As a result, the charge transfer occurs gradually as we increase the electric field. There is a high probability for one electron to stay on the bridge due to the interplay of the electric field and Coulomb blockade (or Pauli exclusion for the triplet state). It is pushed by the electric field from one side and blocked by Coulomb interaction (or Pauli exclusion) from the other side.

At a fixed donor separation, the critical electric field is different for singlet ($F^S_c$) and triplet ($F^T_c$) states, with $F^S_c < F^T_c$. Therefore, at an electric field with strength between $F^S_c$ and $F^T_c$, where the singlet state is in a doubly occupied configuration while the triplet has not yet become ionized, the difference of their electron charge density on the left half space is approximately 1. This fact can be used as an efficient means (assisted with a single-electron transistor as we discuss in Chap. 2) to distinct a triplet state from a singlet state. Since the width of the window between the two critical fields for $R=10 \ a_B$ is approximately $0.02 \ R^*_{\text{AB}}/a_B \approx 3 \ kV/cm$, an accuracy of 1 kV/cm for the applied electric field is required for a readout scheme.

As shown in Table 6.2, both $F^S_c$ and $F^T_c$ become smaller for larger donor separation. This can be understood as follows. For the singlet state, the potential-energy difference between the left and right donor sites due to the electric field is larger for the more widely separated donor pair, which makes it easier for the electron bound to the right donor to hop to the left donor site. For the triplet state, since the doubly occupied configuration is forbidden, one of the electrons tends to be more easily ionized at larger donor separation in order to keep the energy of the system lower. Burdov [132] derived an equation for the critical field of the singlet state of the two-electron double quantum dot based on a Hund-Mulliken ansatz:

$$\frac{1.786e^2}{\epsilon_s R} - \frac{e^2}{2\epsilon_s L} = 2e|E|L$$

(6.17)

where $\epsilon_s$ is the static dielectric constant, $R$ is the dot radius, and $2L$ the interdot distance. The left-hand side of the equation is the energy difference between electron-electron interaction in the same and different quantum dots, and the righthand side is the work done by the electric field on a charge to move it from one quantum dot to the other quantum dot. So, to do the same amount of work to overcome the Coulomb blockade (the left-hand side changes very little for a fairly large separation), the required field is smaller
Table 6.2: Strength of the critical electric fields (in $Ry^*/a_B$) for the ground singlet state ($F^{S}_c$) at which the ground state becomes a doubly occupied state or the lowest triplet state ($F^{T}_c$) beyond which one donor electron is ionized. The values of critical electric fields are listed for various donor separations and at different strengths of J-gate.

<table>
<thead>
<tr>
<th>$R$</th>
<th>$\mu = 0.2$</th>
<th>$\mu = 0.4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>$F^{S}_c$</td>
<td>$F^{T}_c$</td>
</tr>
<tr>
<td>8</td>
<td>0.105</td>
<td>0.150</td>
</tr>
<tr>
<td>10</td>
<td>0.090</td>
<td>0.110</td>
</tr>
<tr>
<td>15</td>
<td>0.065</td>
<td>0.070</td>
</tr>
</tbody>
</table>

It has been proposed that the different polarization behavior of singlet and triplet states can be used as a means for measuring a single-electron spin state [27, 63]. At the first step, the to-be-measured electron will be coupled to a second electron in a known spin state. Then a distinction of singlet or triplet of the two-electron system can be used to infer the spin state of the first electron. To measure whether the electrons are in a singlet or triplet state, the two-electron system will be put in the vicinity of the small island of a single-electron transistor (SET), whose conductance peaks (as a function of the chemical potential of the central island) will experience different shifts for singlet and triplet states, since their remarkably different polarizability will affect the island potential differently.

### 6.4 Effect of a Perpendicular Electric Field

Using an electric field perpendicular to the inter-qubit axis to control the exchange coupling has also been considered. By using the Heitler-London ansatz and evaluating the difference of the Stark shift of mean positions of the two electrons, Burkard and co-workers [117] have shown that, in the case where dots of different sizes are coupled, such an electric field can switch the spin coupling on and off with exponential sensitivity. This semi-quantitative argument cannot be applied to the case with bound electrons in Si:P acting as qubits, since such a perpendicular electric field will induce the same Stark shift for bound electrons which have the same Bohr radius.
Here we numerically calculate the dependence of the lowest-lying singlet and triplet energies on the strength of a uniform perpendicular electric field (taken to be along the z axis in our coordinate system). In this case, we expand the single-particle wave functions, $\phi_R(r)$ and $\phi_L(r)$, in terms of linear combinations of basis functions defined as

$$b_{m,\alpha,L}(r) = \sqrt{2/L} \sin[k_m(z + L/2)] e^{-\alpha_i[y^2 + (x + R/2)^2]},$$

(6.18)

and

$$b_{m,\alpha,R}(r) = \sqrt{2/L} \sin[k_m(z + L/2)] e^{-\alpha_i[y^2 + (x - R/2)^2]},$$

(6.19)

respectively. The width of the confining well along the z direction is set to be $L = 10a_B$. Six radial Gaussian functions (with optimized exponents) and 20 plane waves \{\sqrt{2/L} \sin[k_m(z + L/2)]\} are used for the expansion of the single-particle wave functions.

Figure 6.5 (a) shows how the exchange splitting varies as we increase the strength of the perpendicular electric field. For $R=10a_B$, the exchange splitting at $F=0.15$ Ry/$a_B$ is about 2.3 times the exchange splitting without the electric field. Figure 6.5 (b) illustrates the dependence of electron wave function overlap ($\langle \phi_L|\phi_R \rangle$) on the strength of perpendicular electric field. The electron wave function overlaps for the singlet and triplet states almost coincide, with the overlap for the singlet state slightly larger. As we increase the field, the wave function overlap between the two electrons is enhanced. This is caused by the electric-field-induced s-p$_z$ hybridization. Since the 2p$_z$ orbital has a larger radius than the 1s orbital, the increased hybridization leads to a larger overlap. It is for this reason that the exchange splitting increases as the magnitude of the perpendicular electric field increases.

Although the exchange splitting does increase gradually with the increase of the field strength, we cannot use such a perpendicular electric field alone to switch on and off the spin coupling in a donor-spin-based quantum computer since the electric field needed to produce the desired exchange splitting would be so large that the electrons would be well ionized from their donor sites. The electric-field-induced ionization probability of the ground state hydrogen atom can be estimated according to the analytic formula [133]

$$\Gamma = (4/F)e^{-2/3F}.$$ 

(6.20)
Figure 6.5: (a) Exchange splitting and (b) electron wave function overlap $|\langle \phi_L | \phi_R \rangle|$ as functions of the perpendicular electric field for R=10 $a_B$ and R=8 $a_B$.

where $F$ is the field strength. The above expression is scaled with atomic units, and is only valid for an electric field $F \ll Ry^*/a_B$.

At a field of $0.04 Ry^*/a_B$, the probability for ionization during a switching time of 30 ps is around $2.6 \times 10^{-4}$, which already exceeds the criterion for
the error-correction scheme to work properly. At a field of $0.1 \, \text{Ry}^* / a_B$, the probability for ionization is already close to 100%. However, the above estimation is obtained for a hydrogen atom in free space. For phosphorous donors in silicon, the presence of strong central-cell attractive potential can greatly reduce the ionization rate. What’s more, it could be further reduced by a quantum confinement such as the SiGe/Si/SiGe quantum well (cf. Chap. 4).

Anyway, it is of practical technical difficulty to implement a uniform electric field in realistic semiconductors. A more suitable and realistic scheme to manipulate the spin coupling in the coupled-donor system is to use the J-gate potential modelled in Appendix A. The effect of such a realistic external potential will be studied systematically in the next chapter.

6.5 Concluding Remarks

In summary, we have calculated the exchange splitting for electrons bounded to a donor pair in Si:P within a spherical effective mass approximation. We find by numerical calculation that the approximate donor separation relevant for Si:P spin-based quantum computing is around $R = 10 \, a_B (\sim 30\text{nm})$, which is nearly on the reach of today’s fabrication technology.

We have applied an extended Hartree-Fock method to obtain the energies and wave functions for the lowest-lying singlet and triplet states of the coupled-donor system. Our method provides an efficient and reliable means to study two-center two-electron systems such as the double quantum dot and coupled-donor pair under external fields. It is numerically confirmed that our method is better than the Heilter-London, Hund- Mulliken molecular-orbital, or regular Hartree-Fock approach.

Using a one-dimensional parabolic potential to simulate the effect of the J gate, we have studied the sensitivity of the exchange splitting to the gate potential. Our study confirms the feasibility of using such a J gate to switch on and off the spin-exchange interaction in a Si:P electron-spin-based quantum computer. Furthermore, we have analyzed the different polarizability of singlet and triplet states by numerically calculating the evolution of their charge distributions under a uniform electric field along the inter-donor axis. We find that for a fixed donor separation there exists a window between two critical
electric fields, within which the singlet state transforms to a doubly occupied configuration, while the triplet state remains in a bound coupled-donor state, thus displaying distinctly different polarizability. Such a finding provides a guide for the design of experiments for measuring the single-electron spin via the use of an SET, which senses the different polarizability in the singlet and triplet states.

We have also studied the influence of a perpendicular electric field on the exchange splitting. We find that, although such an electric field does enhance the exchange splitting slowly by increasing the electron wave function overlap, it cannot act as an efficient means by which to switch on and off the spin coupling.

Finally, we note that the current study has neglected the multi-valley effect of the silicon conduction band and the central-cell correction to the donor impurity potential. To give a more quantitatively accurate calculation of the exchange splitting for coupled donors in Si, one needs to apply a more realistic Hamiltonian (such a Hamiltonian for a single donor in silicon quantum well has been developed in Chapter 4) and a more realistic modelling (see Appendix A) of the J-gate potential to study relevant issues that we have missed in this paper. That will be fully addressed in the next chapter.
7 Voltage Control on Exchange Coupling

7.1 Introduction

The simple model calculation presented in Chap. 6 has qualitatively provided us with some important insights into the exchange coupling and polarizabilities for a coupled of P donors in silicon. However, they are not capable of giving quantitatively reliable results. The most important feature lost in such a simple model is the intervalley interference, as a natural consequence of silicon’s multi-valleyed conduction band structure. The second one, which makes the valley-orbital coupling significant, is the central cell correction to the constantly-screened impurity potential \( \frac{1}{\epsilon_0} | \mathbf{r} - \mathbf{r}_0 | \). The third one, is due to the oversimplified modelling of the realistic potential generated by gate electrodes.

In this chapter we will perform a realistic simulation on a pair of P donors embedded in a SiGe/Si/SiGe quantum well. For this purpose, we use the two-valley effective mass equation developed in Chap. IV, which has given quantitatively reliable results for a single P donor in a silicon quantum well. To take care of the correct spin-and-space symmetry for the two-electron wave function and the electron correlations, we adopt the extended Hartree-Fock approach, which was introduced in Chap. 5 and successfully applied to a pair of well-separated hydrogenic impurities in Chap. 6.

As the matrix elements for single-donor Hamiltonian has been evaluated in Chap. 4, we are left with the calculation on gate-induced potential and the mutual electron-electron interaction. The voltage-tunable gate potential is calculated by Poisson-Schrödinger equation, with appropriate boundary conditions for the realistic experimental setup shown in Fig 2.1. It can be explicitly expanded as

\[
V_{\text{gat}}(x, z) = \sum_n \cos(k_n x) A_n [e^{k_n z} - e^{-k_n (z+2b)}] + A_0 (z+b) + \phi_1.
\]

(7.1)
where the coefficients $A_n$, $A_0$ and $\phi_1$ in the above expansion are determined numerically from boundary conditions. $\hat{b}$ is the total thickness of the heterostructure layers (below gate electrodes) we described in Chap. 2. The set of $k_n$ satisfies $k_n = n\pi/d$, with $d$ the unit cell length of our system composed of a line of donors (and correspondingly, a line of top gate electrodes) along $x//[100]$ direction.

The two-valley mutual e-e calculation is given by

$$
\langle i_1\nu_1, j_2\nu_2 | V_{ee} | i'_1\nu'_1, j'_2\nu'_2 \rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \frac{e^2}{\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \phi_{i'}(\mathbf{r}_1) \phi_{j'}(\mathbf{r}_2) \\
\times e^{i(\nu'_1 - \nu_1)k_0z_1} e^{i(\nu'_2 - \nu_2)k_0z_2}.
$$

(7.2)

where $\phi_j$ is a set of basis for a single-donor envelope function, $\nu_1, \nu_2, \nu'_1$ and $\nu'_2$ are valley index. Since only the +z and -z valley are relevant for donors in strained silicon quantum well, the index can only take values of $\pm 1$. Note that we have assumed the e-e mutual interaction is a Coulomb potential screened by a uniform dielectric constant, $\epsilon_0$. This can be justified by the following observation. In contrast to the attractive impurity potential who has a central cell region, the e-e interaction is repulsive and the two electrons tend to avoid each other so that $V_{ee}$ can be described by the long-range Coulomb-type potential screened by a uniform dielectric background of silicon host. The complicated e-e interaction integral can be simplified to a series of fast Fourier transforms (FFT), and for each FFT there are only one-dimensional integrals to be calculated numerically.

This chapter is organized as follows. In Sec. 7.2 we present a systematic simulation on the two-donor system in the presence of realistic gate potentials. The exchange coupling as a function of gate-electrode voltages are calculated, for several typical donor separations in quantum computer design and for various quantum well widths. An exchange-based gate operation is analyzed in Sec.7.3, with the help of the voltage-exchange relation built in Sec. 7.2. We study in Sec. 7.4 the oscillation of exchange coupling (as donor positions are shifted at atomic scale), due to the intervalley interference effect. In Sec. 7.5 we summarize our work and present relevant remarks on the Si:P based QC architecture.
7.2 Exchange Coupling for Si:P Donor Pair

The Heisenberg exchange interaction, defined as the splitting of the lowest singlet and triplet states, plays a central role in most solid state QC architectures. As a result, exchange coupling has been frequently revisited for a pair of localized electrons ever since the first quantum dot QC proposal. Heitler-London approximation is most frequently used, where single-particle orbitals are first variationally determined and two-particle wave function is constructed as in Eq. (5.6). This kind of approximation, although does fairly well for well separated impurities (or quantum dots), it does not provide enough flexibility to handle the strong-coupling case where electron wave function becomes significant in the presence of a gate potential. As a better alternative, we suggested in [35] applying the extended UHF method to solve the two-electron system.

To develop a silicon quantum computer, it is of great importance to quantitatively understand the effect of external controls on the exchange coupling for a pair of donors in silicon. The complicated silicon band structure makes this a formidable task. Our simple-model calculation presented in Chap. 6 (cf. [35]) is the first effort to quantitatively characterize the effect of external controls on donor pair exchange coupling.

This study was followed by the calculations of Wellard et. al. [78, 134, 135] at the Australian Center for Quantum Computer Technology. They first calculated the potential created by a simple J-gate voltage bias, using a commercial software package designed for the modelling of semiconductor devices. The wave function for a singlet donor at \( R_0 \) is expanded as [78],

\[
\Phi(r - R_0, V_J) = \sum_{n,l,m} c_{n,l,m}(V_J) \sum_{\mu} F_{\mu}^{n,l,m}(r - R_0)e^{i k_{\mu} \cdot (r - R_0)} \tag{7.3}
\]

where the \( F_{\mu}^{n,l,m}(r - R_0) \) are a set of anisotropic hydrogenic envelope functions defined by Faulkner [88]. The \( \mu \) labels the six valleys of silicon conduction band and determines the anisotropy of the corresponding envelope function. They calculated the expansion coefficients of the single-donor wave function by directly diagonalizing a single-donor Hamiltonian consisting of the hydrogenic Hamiltonian used by us in Chapter 6 and a J-gate potential dependent on \( V_J \).

It should be pointed out that, their calculations ignored the interfer-
ence of different valleys, i. e., the matrix elements involving different $\mu$ were neglected. As a consequence, the effects of J-gate on different valley-components are assumed to be independent, with their difference caused only by the anisotropy of the J-gate potential and valley-dependent envelope functions. Then the exchange coupling for a pair of Si:P donors was calculated by the Heitler-London approximation, with the gate-potential-adapted single-donor wave function Eq. (7.3). They compared their result with our calculation where the J-gate potential is modelled by a one-dimensional parabolic potential (cf. [35]or section 6.2). It was found that the two models agree well at some parameter zone, but the one-dimension modelling of J-gate is not sufficient. A more realistic gate potential should be at least two-dimensional, due to the inherent inhomogeneity along the growth direction (perpendicular to the inter-donor axis) induced by top metallic gates and interfaces between different layers.

In this section we present a more realistic and systematic study on a phosphorous donor pair embedded in a strained silicon quantum well, as shown in the QC architecture sketch (Fig. 2.1). To solve the lowest singlet and triplet states, we combine the extended Hartree-Fock method for a two-electron system (cf. Chap. 5 for a general discussion and Chap. 6 for an application) and the two-valley effective mass equation for a single donor (cf. Chap. 4). The gate potential, which has the form of Eq. (7.1), is a smooth and weak potential and can be safely incorporated into the effective mass equation.

We consider a pair of coupled donors, labelled by 1 and 2 in Fig. 2.1. The gate potential to control the exchange coupling is tunable via two gate voltages, $V_c \equiv V_{12}$ and $V_g \equiv V_{01} \equiv V_{23}$. The gate electrodes right above donor atoms, $V_1$ and $V_2$ (known as A-gates) are disabled in this study, since they are not necessary for tuning the exchange coupling for a donor pair (but they will be needed for the cooperation of 3 neighboring donors). The modelling of the electrostatic potential distribution due to applied voltages on the gates is presented in the Appendix A. The potential distribution in the QW region is given by Eq. (7.1). We plot in Fig. 7.1 (a)-(d) to show several gate potential profiles for different values of $V_c$ and $V_g$. We see that these two gate voltages are indeed capable of tuning the barrier height between two P donors in the silicon QW.

The width of the artificial 1D box is set to be the same as the size of the
Figure 7.1: The gate potential (measured in units of $R_y^*$) profile at different gate voltages: (a) $V_c = −2.1 V$; (b) $V_c = −0.8 V$; (c) $V_c = −0.6 V$ and (d) $V_c = −3.2 V$. $V_g = −1.8$ for all these four cases. In each figure, the potential shape is plotted along x axis, with three different distances (15, 17, 19 nm) from the top gates. The doping plane in our QC device (cf. Fig. 2.1) is 17 nm below the top gates. The two P donors are placed at $±5 \ a_B^*$.
2-donor unit cell, $L_x = 4p$, for the donor array with a spacing of $2p$. Since the electrons are bound to the donors mainly within $1a_{B^*}$ and dispersed a little in the presence of gate potential, the box boundaries will not affect the charge distribution when $p$ is larger than $4a_{B^*}$. The box boundaries pass through the centers of gate electrode $V_{01}$ on the left and $V_{23}$ on the right, respectively. $V_{01}$ and $V_{23}$ (cooperating with other gate electrodes) are typically set to produce potential barriers high enough to suppress the coupling between the specific donor pair (1 and 2) with neighboring donors (labelled 0 and 3, respectively) during each step of gate operations. In this sense, our 1D box is no longer artificial. The central J-gate, $V_{12}$, is right above the middle point ($x=0$) of the two donors. Note that, as we mentioned in Chap. 4, the sine functions with both even and odd parities are needed to expand the donor electron wave functions, because the donor locations now have no simple symmetries with respect to the 1D box.

First we calculate the exchange coupling when the gate potential is absent ($V_c = V_g = 0$). The donor separation, is first set to $R \equiv 2p = 10a_{B^*}$, a generally accepted value for Si:P spin-based QC architecture and within the access of current nano-fabrication technology [57]. We vary the QW width from 4nm to 16nm and plot the corresponding exchange splitting in Fig. 7.2. In the wide-well limit, the exchange splitting converges to about $1.4 \times 10^{-6}\text{Ry}^*$, on the same order of magnitude but a little smaller, compared to the exchange coupling for two hydrogenic impurities in bulk silicon estimated via the asymptotic formulae [121]. However, it is about 40 percent larger than the numerically calculated value by our single-valley hydrogenic effective mass approximation in Ref. [35]. Our current two-valley calculation is more reliable, since we take into account the effective-mass anisotropy, central-cell correction to the impurity potential, and intervalley coupling.

We see clearly from Fig. 7.2 that the exchange splitting $J$ depends strongly on the QW width. It decreases as the quantum well is narrowed. The exchange splitting at $W_d = 6\text{nm}$ is about one order smaller than that at $W_d = 16\text{nm}$. Comparing their single-particle overlaps, $S \equiv |\langle \Phi_L | \Phi_R \rangle|$ for singlet states (the overlaps are always zero for triplets according to our construction of two-particle wave functions) with each other, we have $S = 5.8 \times 10^{-4}$ for $W_d = 6\text{nm}$ and $S = 1.7 \times 10^{-3}$ for $W_d = 16\text{nm}$, respectively. As we narrow the quantum well from 6nm to 4nm (slightly less than 2 $a_{B^*}$), the exchange splitting is reduced further by one order of magnitude and the
overlap $S$ decreases to $2.0 \times 10^{-4}$. This is just what we expected, since from Chap. 4 (Fig. 4.2) we know that the charge distribution is shrinking toward the impurity centers in all three dimensions with the increasing of QW confinement. This confinement-induced shrinking effect decreases the overlap between neighboring donor electrons, and therefore, reduces their exchange coupling.

The inset of Fig. 7.2 illustrates the effect of QW-width variation at atomic scale on the exchange splitting, where the QW width is varied from 58 to 74 monolayers (approximately from 8 to 10 nm) and the spacing of width variation is one monolayer (1 monolayer=$a_0/4 \simeq 1.36\text{Å}$). Different from the oscillatory behavior of the valley splitting for single donor ground state shown in Fig. 4.3 (a), the exchange splitting varies with the QW width monotonously even at the atomic scale.

Now we switch on the gate voltages $V_g$ and $V_c$. The QW width is fixed at 10nm, the appropriate value for producing the desired range of the exchange
Figure 7.3: (a) The exchange coupling of a donor pair separated by 10 $a_B^*$ as a function of central gate voltages. The three curves correspond to three different values of side gate voltages $V_g = -1.4, -1.8$ and $-2.0$ V, respectively. The isolated point (filled square) on the $V_c = 0$ axis corresponds to the exchange coupling without any gate potential ($V_c = V_g = 0$). (b) The dependence of exchange coupling on central gate voltages, with $V_g$ fixed at 1.8 V. The three curves correspond to three different donor separations $R = 8, 10$, and $12a_B^*$, respectively. Both (a) and (b) are plotted in logarithmic scale for the exchange coupling. The quantum well width is fixed at 10 nm.
coupling for our QC architecture. We shall fix the value of $V_g$ and vary $V_c$ (the central gate voltage), since the potential barrier height between the coupled donors is mainly influenced by voltage difference of the central gate and side gates. Fig. 7.3 (a) shows the influence of the central gate voltage ($V_c$) on the exchange coupling for donors separated by $10 \, a_B^*$, with $V_g$ fixed at -2.0, -1.8 and -1.4 V, respectively. We notice that voltage dependence of the exchange splitting can be approximately fitted by an exponential curve (shown as straight line in logarithm-scale plot), similar to our previous simulation where single-valley hydrogenic EMA is employed and the gate potential is modelled by a one-parameter one-dimensional parabolic function. The three lines corresponding to three different values of side gate voltages, are nearly parallel to each other, which means that the logarithmic slope is independent of the gate voltages and it only depends on the intrinsic geometry settings of the QC architecture, such as the donor separation, QW width, and distance of doping plane from the top gates. Therefore, we may define the logarithmic slope as a measure of the gate voltage tunability (with respect to the exchange coupling) as

$$\eta = \frac{\partial \log J}{\partial V},$$

where we have omitted the subscript of $V_c$ and obviously, $\eta$ has the dimension of $V^{-1}$. Note that in Ref. [136], $\partial J/\partial V$ is similarly defined as the susceptibility of a device to voltage errors. Here, our gate voltage tunability is better defined since it is constant throughout the appropriate working voltage range and it characterizes the intrinsic device properties.

In Fig. 7.3 (b), we compare the gate voltage dependence of J-coupling for a pair of donors separated by $R=8, 10, \text{ and } 12 \, a_B^*$, respectively. First, we notice that for $R=8$ and $12 \, a_B^*$, both the corresponding curves deviate (but not significantly) from straight lines on logarithmic scale. The three lines are crossed with each other near $V_c = -0.7 V$. The logarithmic slopes, indicting the gate voltage tunability on the exchange coupling, are remarkably different. As the central gate voltage is tuned from -2.2 to -0.6 V, the variation range of exchange coupling is 2, 5, and 9 orders, for $R=8, 10 \text{ and } 12a_B^*$, correspondingly. Obviously, larger donor separation corresponds to large gate tunability on exchange coupling. However, as we will see in next section, larger gate tunability also leads to more stringent requirement for voltage control accuracy.
Since $\eta$ is independent of $V_g$, we may focus on the case with side gate voltages fixed at $V_g = -1.8V$. By tuning the central gate voltage $V_c$, we are able to vary the exchange coupling by more than eight orders of magnitude. The full range is not shown in Fig. 7.3 (a), but we can further reduce the exchange splitting to as low as $10^{-11}Ry^*$ by lowering $V_c$ to $-3.0 V$ for $V_g = -1.8V$. The exchange splitting at $V_g = -2.1V$ approximately equals the value of $\approx 10^{-6}Ry^*$ in the absence of gate potential ($V_c = V_g = 0$). Reliable quantum computation requires a much smaller J-coupling than the gate-off value for qubit isolation. In Ref. [32], it is argued that the ‘off-state’ coupling will need to be $J_{off} \approx 10^{-12}eV$ or less. We see that the J-coupling at $V_c = -3.0V$ can fulfill this requirement.

Furthermore, the large initialization requirement $J_{on} \approx 200\mu eV$ (required to initialize the logic 0 state of the 3-donor qubit) [32] is also within our tunability. At $V_c = -0.6(-0.8)$, we can reach a J-coupling of approximately $400(93)\mu eV$.

However, as discussed in Refs. [35] and [78], we can not arbitrarily enhance the exchange coupling by lowering the potential barrier between donors. To illustrate this, we plot in Fig. 7.4 the 1D averaged charge distribution along x axis for the lowest singlet and triplet states at different gate voltages. Each plot shows a two-peak structure with peaks near the donor nuclei. Except for Fig. 7.4 (a) and (d) where the coupling and overlap is weak and the charge distributions for singlet and triplet almost coincide, singlet state has a larger probability than the corresponding triplet state in the central region between donors, due to the Pauli exclusion principle (cf. the discussion in Chap. 6 or Ref. [35]). In Fig. 7.4 (a), although the gate-off exchange coupling is nearly equal to that at $V_c = -2.1V$ and $V_g = -1.8V$, their charge distributions are different. For the gate-off case, the two charge distribution peaks are symmetrically centered at the donor sites, while for the case of $V_c = -2.1V$ and $V_g = -1.8V$, they are more spread out and become nonsymmetric with respect to the donor locations. However, the averaged donor electron distances for these two cases, are nearly the same, which is the reason that they have close magnitudes in exchange coupling. Fig. 7.4 (d) shows the charge distribution for the ‘off-state’ configuration. The peak centers are shifted significantly away from each other with a negligible overlap, and are more dispersed than those in Fig. 7.4 (a). For the case of $V_c = -0.8$ shown in Fig. 7.4 (b), the singlet is only slightly different from
Figure 7.4: The averaged 1D two-electron charge distribution of singlet (solid) and triplet (dotted) states along the inter-donor axis, for different gate voltages. The side gate voltage is $V_g = -1.8V$ for (b), (c) and (d). The charge distributions for singlet and triplet almost coincide for weakly coupled donor pairs, as shown in (a) and (d). The gate-off exchange coupling is very close to the gate-on case with $V_c = -2.1V$ and $V_g = -1.8V$, while their charge distributions are apparently different, as shown in (a). It is clearly demonstrated that the gate voltages can tune the overlap between neighboring donor electron wave functions and consequently, the exchange coupling.
the triplet, with slightly larger (smaller) weight in the central (donor site) region, and the peak centers remain close to the donor locations as in the case of configurations of Fig. 7.4 (a), although they are pulled toward each other to give an enhanced overlap. In Fig. 7.4 (c), when the (attractive) gate potential becomes even stronger, the difference between singlet and triplet charge distributions becomes more significant, and the weights in the central region are comparable to those in the donor regions. For this case, the gate potential is strong compared to the impurity potential, and electrons have a large probability to be trapped in the central region. This situation is undesirable for QC implementation, since it may complicate the spin dynamics for gate operations, and more importantly, produce extra decoherence channels and reduce gate fidelity. The $V_c = -0.8$ configuration is relatively much safer and can nearly produce the desired exchange coupling in the large limit.

### 7.3 Exchange-based Two-Spin Gate Operation

With a time-dependent voltage pulse, the exchange coupling which controls the spin dynamics varies accordingly as the time progresses, and spin states can be manipulated in a controllable way. As a prototype for gate operation, we consider the adiabatic half-swap operation for two neighboring donor electrons, implemented with a voltage pulse $V_s(t)$. In principle, the pulse shape of $V_s(t)$ can be arbitrary, although the accumulated phase by the exchange coupling must satisfy the following relation [see the introduction of Chap. 6]:

$$\int_{\tau_s} dt J(V(t))/\hbar = \pi/2. \quad (7.5)$$

Here $\tau_s$ is the gate operation time.

We now use the voltage-exchange relation [Fig. 7.3] calculated in Sec. 7.2 to design an exchange pulse. Approximately, the exchange coupling is dependent analytically on the central gate voltage via

$$J(t) \simeq \alpha \times \exp(\eta V(t)), \quad (7.6)$$

where $\alpha = 0.224eV$ and $\eta = 6.9V^{-1}$ for $R = 10a_B^*$ and $V_g = -1.8V$.

To get a realistic estimate of the gate operation time, we assume a sym-
metric linear (central gate) voltage pulse, defined by

\[ V(t) = \begin{cases} 
V_0 + 2\Delta V(t/\tau_s + 0.5) & \text{if } -\tau_s/2 \leq t \leq 0; \\
V_0 - 2\Delta V(t/\tau_s - 0.5) & \text{if } 0 \leq t \leq \tau_s/2 
\end{cases} \quad (7.7) \]

where the voltages during the whole gate operation span a range of \([V_0, V_0 + \Delta V]\). We have already shown that \([-3.0, -0.8]\) is an appropriate voltage range for \(R = 10a_B^\ast\), which can give a sufficiently small 'off-state' exchange coupling and large 'on-state' exchange coupling without disturbing the two-electron charge distribution significantly. The maximum exchange coupling is achieved right at the middle of gate operation, corresponding to \(V_0 + \Delta V\).

Plugging Eqs. (29) and (30) into Eq. (28) with \(V_0 = -3.0V\) and \(\Delta V = 2.2V\), the gate operation time is found to be \(t_s \approx 0.2ns\). Compared to the experimental transverse decoherence time of \(T_2 \approx 60ms[11]\), the proposed pulse gives a relative error of \(\sim 10^{-7}\), well satisfying the fault tolerant computation requirement of a relative error less than \(10^{-4}\). On the other hand, the gate operation time is restricted from below by the adiabatic gating requirement[41],

\[ \tau_s > \tau_{\text{min}} := \max\{\hbar/\delta\epsilon_1, \hbar/\delta\epsilon_2\}, \quad (7.8) \]

where \(\delta\epsilon_1\) and \(\delta\epsilon_2\) are the single-particle lowest level spacing and two-particle lowest singlet level spacing, respectively. \(\delta\epsilon_2\) is roughly determined by the difference of the on-site and inter-site Coulomb interaction. As discussed in Ref.[41], for ultra small quantum dots, \(\delta\epsilon_1\) is usually much larger than \(\delta\epsilon_2\). However, this is not the case for multi-valleyed semiconductors such as Si. The presence of gate potential can cause single-particle spectrum narrowing as mentioned in the Chap. 4. \(\delta\epsilon_1\), given by the intervalley splitting of the single donor ground state, is approximately \(3.0meV\) when gate potential is absent, while with gate potentials at \(V_c = -0.8V\) and \(V_g = -1.8V\) we have \(\delta\epsilon_1 \sim 0.43meV\). In comparison, \(\delta\epsilon_2\) is \(\sim 0.78meV\) at the same voltages. We find that when \(V_g\) is fixed at \(-1.8V\) and \(V_g\) varies in the voltage range \([-3.0, -0.8]\), \(V_c = -0.8V\) corresponds to the smallest value for both \(\delta\epsilon_1\) and \(\delta\epsilon_2\). Therefore, according to Eq. (31), we get an estimate of the gate operation time, \(\tau_s > 1.5ps\) on the adiabatic lower restriction. This requirement is also well satisfied by our proposed linear voltage pulse with a gate operation time of 0.2 ns.

This gate-induced narrowing of single-particle level spacing requires an
operating temperature to be about six times lower than the gate-off estimate ($\sim 30K$), to avoid unwanted thermal transition. To improve the operating temperature, we may increase the contribution of the other four valleys by reducing the Ge composition in the SiGe barrier (i.e. reducing the in-plane strain), decrease the quantum well width, or re-design the gate potential profile. On the other hand, the increase of single-particle level spacing or valley splitting, requiring the single-particle wave functions to be more localized around the impurity centers, would unavoidably reduce the available maximum exchange coupling between neighboring donor electrons (if the donor separation keeps unchanged). Thus the temperature requirement further complicates the issue for optimal design of the QC architecture. However, this problem may be circumvented by the recently proposed multilevel encoding scheme, where a logic qubit is encoded by a subspace of multiple physical levels. The full quantum-computational fidelity is maintained in the presence of mixing and decoherence within logical subspaces. For details of multilevel encoding, see Ref. [137].

The gate voltages that control exchange couplings between neighboring donor electrons cannot be produced at arbitrary accuracy. This results in deviation from the desired pulse shape and exchange coupling, causing gate errors. The instantaneous relative error rate can be quantified by $\delta J(t)/J(t)$ and the accumulated error rate $1 - F = \int_{0}^{\tau_s} \delta J(t)dt/(\pi\hbar/2)$ indicates the loss of gate operation fidelity.

Due to the exponential dependence of exchange coupling on the gate voltages, the instant error rate can be simply related to the gate tunability and voltage fluctuation by

$$\delta J(t)/J(t) = \eta \delta V(t).$$

(7.9)

With this relationship we can obtain a lower bound of the gate fidelity:

$$F_\eta = 1 - \eta \delta V_0,$$

(7.10)

where $\delta V_0$ is the maximum magnitude of voltage uncertainty or fluctuation during the switching time, limited from below by the available control electronics. The other parameter affecting the gate fidelity, is the gate tunability $\eta$ intrinsic to the QC architecture. We note that, to reduce the loss of fidelity,
\( \eta \) should not be too large. This restriction, combining with the requirement of enough tunability so as to achieve the desired 'initialization' and 'off-state' exchange coupling, calls for an appropriate parameter zone (such as the donor spacing, the distance of doping plane to the surface gates, and the width of the silicon quantum well) for the realistic quantum computer device design.

For the typical gate tunability \( \eta \sim 7 \) for two donors separated by 10 \( a_B^* \), a voltage control accuracy of at least \( 1.4 \times 10^{-5} V \) is required to meet the error threshold (1 accumulated error in \( 10^4 \) operations) of fault tolerant computation. This voltage accuracy is about the same order as in Ref. [29], where the authors estimated it with a flattop exchange coupling pulse for the SiGe quantum dot QC architecture.

### 7.4 Exchange Oscillation v.s. Donor Position Shift

Earlier studies on the magnetic susceptibility of Si: P were based on the evaluation of the exchange interaction between electrons located at different randomly distributed impurity sites. A calculation of susceptibility by Andres et. al. [138] revealed that, a rapidly varying interference factor appears in the exchange integral calculated with many-valley orbital ground states for the donors. They used the spherical approximation for the envelope functions, and expressed the exchange integral as a product of an interference factor rapidly varying at lattice constant scale and an isotropic factor which can be obtained from variational calculations for the hydrogen molecule.

In the context of quantum computer with donor spins, Koiller et. al. [77] analyzed the effect of donor position shift on exchange splitting for a well-separated donor pair in bulk silicon, with the Kohn-Luttinger envelope wave function and within Heitler-London approximation. They pointed out the importance of precise donor positioning in QC implementation, due to the exchange oscillation caused by the intervalley interference inherent in the silicon band structure. Later on, a few authors confirmed this kind of exchange oscillation under the perturbations due to applied strain [104] or gate fields [78], still within standard HL framework. Recently, a reconfirmation has been done with a floating-phase Heitler-London approach [139]. A similar approach was used for studying Si/SiGe quantum dots in Ref. [140].
In that paper, the authors demonstrated that, with strong confinement potential and large in-plane strain, there is no atomic-level oscillations in the single-electron wave function, and consequently no exchange oscillation, in contrast to donors in bulk silicon. But as we learned, their calculation is spurious [141].

The phosphorous donors in our QC architecture are embedded in a strained Si quantum well with no additional lateral confinement, thus lying between the two extreme cases: donor electron in bulk silicon and electron strongly confined in all 3 dimensions in gated Si/SiGe quantum dots. Furthermore, as we pointed out in Sec. 7.2, our approach to the two-localized-electron problem is more advanced than the Heitler-London approximation or its modified version. Now we examine whether the donor-position dependent exchange oscillation exists with and without the presence of gate potential (and with four valleys suppressed by the in-plane strain).

First we study the case where two donors are shifted along z axis from the QW central plane by the same amount with their separation remaining unchanged. The calculating points are spaced by \(\frac{a_0}{4}\), the smallest atomic spacing along z axis. It is worth mentioning that, in Ref. [77], donor positions are shifted in units of 10\% of the nearest-neighbor distance in silicon lattice, which is nonphysical for substitutional phosphorous donors.

In Fig. 7.5 (a), we plot the exchange coupling versus shift of donor position (up to \(3a_0\)) along the [001] direction. The system is symmetric with respect to the QW central plane in the absence of gate potential, and both donors remain on the [100] axis with their separation fixed at \(10a_B^*\). We see from Fig. 7.5 (a) that, the exchange coupling does oscillate as both donors are shifted along z axis, contrary to the monotonous behavior shown in the inset of Fig. 7.2, where the QW width is varied on atomic scale. The oscillation magnitude is largest as the donors are shifted from the QW center by a single unit (\(a_0/4\)) and it decays as donors are moved away from the center plane. The upper-bound of the \(\Delta J/J\) for the smallest displacement, is about \(5 \sim 6\%\). As can be seen from the trend of Fig. 7.5 (a), the exchange coupling tends to increase as both donors are shifted away. The inset shows the corresponding singlet overlaps, similar to the pattern of exchange coupling.

We plot in Fig. 7.5 (b) the exchange coupling as a function of donor position shift when a gate potential is switched on. We find that, the exchange oscillation (comparing to the gate-induced exponential increasing) still exists,
Figure 7.5: The exchange coupling as a function of donor position shift away from the quantum well central plane: (a) gate off; (b) gate on ($V_c = -1.6\text{V}$ and $V_g = -1.8\text{V}$). The donor pair remains on the [100] axis, with their separation fixed at $10\ \text{a}_B^*$. The inset of (a) plots the overlap of single-particle wave functions (for singlet state) as a function of donor position shift, which shows the same pattern as the exchange coupling. The dotted line in (b) is an exponential fitting curve, illustrating the significant effect of gate potential on the exchange coupling for donors at different distances from top gates.
but the over-all exponentially growing behavior is preserved.

Now we study the exchange coupling as both donors are shifted along their coupling direction, i.e., [100] axis. The smallest possible donor position shift (and donor separation change) is $a_0/2$, to keep both donors in the QW central plane. To better describe the delicate change of the wave function overlap upon position shift along $x$ axis, we use 280 since function (for x-direction freedom and 3 Gaussian functions (for $y$ and $z$) to construct the single-particle basis. The parameters in the 3 Gaussians, are adjusted to take care of the central cell correction so that correct valley splitting is reproduced for the single donor ground state. The 1D box width is set to be $25a_B^* (\sim 60nm)$, to further reduce possible artificial effects of box boundaries.

![Figure 7.6: The exchange coupling (plotted in logarithmic scale) as a function of donor separation. The donor pair remains on the [100] axis, with their separation varied from 70 to 90, in units of half lattice constant, $a_0/2$. The dotted line is an exponential fitting curve, appearing as a straight line in the logarithmic-scale plotting.](image)

We plot in Fig. 7.6 the exchange splitting for donor separation varied from 70 to 90 $a_0/2$ (or 190 to 244 Å). The figure is plotted in logarithmic scale, as the exchange splitting has an exponential dependence on donor sep-
paration. The dotted line is an exponential fitting curve. We find that the fitting works fairly well. Compared to the exchange oscillation in Fig. 7.5 (a), the exchange splitting is almost monotonically increasing as the donor separation is reduced. Only for separation larger than $85a_0/2$, exchange splitting is no longer monotonic and residual oscillation is present. This behavior can be qualitatively understood in the following way. The valley-interference induced exchange oscillation is analogous to noise, which is prominent when the exchange coupling (analogous to signal) is weak. The exponential dependence of exchange splitting on donor separation, tends to suppress the oscillation for small enough separation (strong enough exchange coupling). If we take the exponential fitting curve as a reference, the deviation oscillates strongly from both sides of the reference curve at large separation and decays as separation is decreased.

Based on our calculation, it is worth to make a few remarks on the importance of precise donor positioning to fault tolerant quantum computation. First, the deviation of donors from any host atom site is highly undesirable, since the electronic properties of an interstitial donor is remarkably different from a substitutional donor. Second, a recent report shows that the STM-based lithographic technology can position single P atoms into Si with $\sim 1$ nm accuracy [58]. If unfortunately, a donor atom is shifted away from the desired site, it will result in large computation error (due to the deviation of exchange coupling from desired value) and qubit measurement error (due to the qubit leakage to undesired subspace). However, this should be able to be detected in the calibration process described in Ref. [32], and we can either adjust the gate voltage to reduce error or reject the erroneous qubit.

7.5 Concluding Remarks

In this chapter we have presented a systematic study on coupled phosphorous donors in a strained silicon quantum well, relevant for silicon-based quantum computer design. Following the multi-valley effective mass approach, we have developed a two-valley equation for the single donor. By turning the valley-coupled Schrödinger equation into a single matrix eigenvalue problem, we are able to solve the donor electron ground state energies and wave functions. The central cell correction is consistently incorporated by our model.
potential, yielding the correct valley splitting.

The extended unrestricted Hartree-Fock method is applied to a pair of coupled donors, without losing the delicate nature of single-particle wave functions. Accurate wave functions and energies of the lowest singlet and triplet states can be obtained. The Heisenberg exchange coupling is calculated at different QW widths and we find that a wider quantum well gives rise to larger exchange splitting. The QW width of 10 nm is appropriate for our proposed QC design.

We have calculated the gate potential profile numerically by solving Poisson equation with appropriate boundary conditions. The effect of gate voltages on exchange coupling between neighboring donors is analyzed, for several donor separations. We find the appropriate separation and voltage zones suitable for qubit initialization and gate operation. A gate tunability is defined to characterize the efficiency of gates to alter the exchange coupling. With a linear time-dependent voltage pulse shape, we have evaluated the appropriate gate operation time of 0.2 ns for a spin half-swap operation, considering both the requirements of fault tolerant quantum computation and adiabatic operation. An analytic formulae for the lower bound of the gate operation fidelity is obtained, by relating it to the gate tunability and voltage control accuracy. For a typical gate tunability, and to realize fault tolerant quantum computation, a voltage control accuracy of $1.4 \times 10^{-5}$ V is necessary.

The valley degeneracy of the Si:P donor electron ground state could lead to oscillation of the exchange coupling as donor positions are shifted. With our approach to the two-electron problem, we have calculated the exchange coupling as a function of donor position shift perpendicular to QW plane. Oscillation is observed when gate potential is switched off, and switching-on of gate potential can suppress the exchange oscillation. The exchange coupling as a function of donor position shift along donor coupling axis is also calculated. We find that the exchange oscillation is greatly suppressed at small donor separation and residual oscillation can be observed at large separation. The oscillation behaviors can be explained by analogy to the signal-to-noise ratio.

In conclusion, we have studied in a systematic way the ground state of single Si:P donors and the exchange coupling of a coupled donor pair placed in a strained silicon quantum well. Our calculation is of importance in evaluating the prospects and providing practical guidance for a P-donor
silicon-based quantum computer.
8

Entanglement of Qubits
Involving Identical Particles

8.1 Introduction

In the past decade, companying the increased interests on quantum computation, there have been enormous research activities on the understanding, characterization, and application of quantum entanglement [8]. On one hand, entanglement plays a key role in the fundamental issues of quantum theory ever since the thirties of last century [142]. On the other hand, entanglement is an essential resource in the applications of quantum mechanics to quantum information processing (QIP), such as quantum computing, quantum cryptography, quantum teleportation, and super dense coding [143]. Due to its central significance, the past and ongoing studies on entanglement mainly focus on quantifying entanglement properties of states for composite systems and their various applications to quantum information processing. Except for quantum computing, the involved composite system in QIP is typically partitioned into subsystems separated by macroscopic distance, where the total Hilbert space of the composite system can be written as a tensor product of respective Hilbert spaces of subsystems. In this way, entanglement naturally arises as a consequence of superposition principle in quantum mechanics combined with the tensor product structure of the Hilbert space for the composite system. For such kind of composite system with clearly defined Hilbert space structure, there have been fruitful progress in quantifying entanglement, especially for bipartite systems [144]. However, in quantum computing, there involves encoding of logic qubits into two-dimensional subspaces of physical systems (physical qubits), which usually contain some indistinguishable particles\(^1\), and multi-qubit operations are usually realized through the dynamic evolutions of such particles. Furthermore, physical qubits can be coupled

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\(^1\)For example, with the DiVincenzo encoding scheme [60] applied to our QC architecture described in Chapter 2, each qubit involve three donor electrons.
with environment in an intriguing way. Therefore, quantifying entanglement in such systems requires more careful analysis on the structure of Hilbert space and failure to do so has led to controversies.

Since in quantum computer (QC) architectures qubits are usually encoded by some spatial or spin degrees of freedom of electrons, the entanglement between qubits and quantum electron correlation are intrinsically related to each other. Historically, electron correlation is a very old concept ever since the founding of quantum mechanics. The electron correlation as a consequence of the Coulomb interaction greatly enriches the physics of many-electron systems such as atoms, molecules, and solids. On the other hand, the nontrivial Coulomb interaction requires many more efforts for physicists to deal with the realistic correlated motion beyond its mean-field caricature. Quantifying the electron correlations has thus attracted a lot of efforts from both physicists and chemists. In the past, several measures such as the correlation energy and the exchange and Coulomb hole have been developed to describe electron correlations, while only until recently there are attempts to define quantum-kinematic measures for the correlation strength, which only depends on the one-particle reduced density matrix (1PDM) of the many-electron wave function. The 1PDM for a normalized N-particle wave function \( \Psi(1, 2, ..., N) \) is defined as

\[
\gamma(1; 1') = N \int \Psi(1, 2, ..., N)\Psi^*(1', 2, ..., N)d2...dN \quad (8.1)
\]

where the index denotes a combined spin and spatial coordinate of a particular electron. This quantity is of fundamental importance in quantum chemistry, through which all one-electron properties of the system can be determined. It is worth pointing out that an integration over spin variables of the 1PDM turns out to be the charge-density matrix.

In order to calculate the energy and other two-electron properties, one needs reduced two-particle density matrix (2PDM),

\[
\Gamma(1, 2; 1', 2') = N(N - 1) \times \\
\int \Psi(1, 2, 3, ..., N)\Psi^*(1', 2', 3, ..., N)d3...dN \quad (8.2)
\]

Clearly \( \Gamma \) is related to \( \gamma \) by a simple reduction of variables. In quantum chemistry the Hamiltonian contains at most two-particle interactions and in
this sense the N-particle wave function contains more details than necessary. Formally, 2PDM is sufficient and necessary for computing the energy and other two-electron properties. However, the Hohenberg-Kohn theorem [145], based on which modern density-functional theory has built, states that the energy is a unique functional of the ground-state charge density (the diagonal elements of the charge-density matrix), i.e., knowledge of the charge density is sufficient to completely determine the ground state energy of the system.

Based on the observation that the 1PDM is idempotent both for non-interacting systems and for interacting systems described within the mean field approximation, Ziesche [146] defines the electron correlation strength in terms of natural occupation numbers \( n_\kappa \) (the eigenvalues of the 1PDM with the normalization \( \sum_\kappa n_\kappa = N \))^2:

\[
S_C = -\frac{1}{N} \sum_\kappa n_\kappa \log n_\kappa
\]  

where \( S_C \) is called correlation entropy per particle. \( S_C \) characterizes the correlation-induced deviation from the single Slater determinant wave function (or Hartree-Fock approximation). Any wave function obtained by the configurational mixing of two or more Slater determinants may yield a nonzero correlation entropy.

In this chapter we present a study on the entanglement and correlation measures for composite systems containing indistinguishable particles. In Sec. 8.2 we first analyze the Hilbert space structure of a two-electron two-site system, then review recent studies on entanglement and correlation measures of indistinguishable particles. In Sec. 8.3, we introduce the "correlation of formation" measure and show that it yields the same result as the reduced entropy measure for any two-particle pure state with 4 single-particle modes. We then extend the concept to the two-particle correlation of a many-particle system. Through the analysis of a two-site Hubbard model in Sec. 8.4, we discuss the physical meanings for entanglement between modes and quantum electron correlation. In Sec. 8.5 we introduce a concept, "subspace-restricted entanglement", for systems whose Hilbert space can be decomposed in a spe-

\(^2\)Note that this correlation entropy is different from the so-called Jaynes entropy, which is the von Neumann entropy of the spin-traced (charge density) matrix, \( S_{\text{Jaynes}} = -\text{Tr}[\rho(r; r') \log \rho(r; r')] \). Throughout this chapter, we use base 2 logarithm as usual in information theory.
specific way. With this concept we study in Sec. VI the entanglement issues relevant to the two-qubit process involved in solid state quantum computation. Concluding remarks are made in Sec. 8.6.

8.2 Entanglement v.s. quantum correlation for identical-particle systems

Entanglement is a quantum nonlocal property of composite systems. It is meaningless to discuss entanglement without specifying the way in which the composite system is partitioned into subsystems. Moreover, it is useless if we cannot address the individual subsystems physically, i.e., perform local unitary operations and/or measurements. Locality and nonlocality are relative concepts with respect to a specific partition of the composite system. For distinguishable-particle systems, they usually have well defined partitions into subsystems and the total Hilbert space can be mapped to the tensor product of subsystem Hilbert spaces. However, for indistinguishable-particle systems, their Hilbert spaces cannot be partitioned into physically meaningful subspaces in an obvious way. Therefore, it is necessary to study the relation between the distinguishable-particle representation and indistinguishable-particle representation.

In this paper we will concentrate our study on systems containing genuine particles (such as electrons or atoms), rather than gauge bosons (such as photons) and each specified system contains a fixed number of particles. Specially, for a two-site two-electron system (assuming each site has a single mode excluding spin), we can divide the composite system into two subsystems denoted by site labels A and B.

If we treat the electrons like distinguishable particles, then the local space of A is $H_A = \{|0_A\rangle; \{|\uparrow_A (1)\rangle, |\uparrow_A (2)\rangle\}; \{|\downarrow_A (1)\rangle, |\downarrow_A (2)\rangle\}; \{|\uparrow_A (1) \uparrow_A (2)\rangle, |\downarrow_A (1) \downarrow_A (2)\rangle, |\uparrow_A (1) \downarrow_A (2)\rangle, |\downarrow_A (1) \uparrow_A (2)\rangle\}$. $H_B$ for subsystem B can be similarly defined. Each site subspace has 1 zero-particle state, 4 one-particle states, and 4 two-particle state. Since the electrons are in

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3Zanardi [147] first pointed out, by analyzing the algebraic structure of the set of operationally relevant observables, that the very notion of entanglement is fundamentally ambiguous due to the nonuniqueness of the decomposition of a given system into subsystems.
principle indistinguishable at short distance, the 4 one-particle states reduce to 2 states, and the 4 two-particle states reduce to one \(|↑_A \ (1) \ ↓_A \ (2)) - |↓_A \ (1) \ ↑_A \ (2))\) due to the Pauli exclusion principle for fermions. Hence each subspace labelled by site has dimension 4.

To write the multi-particle wave function concisely and remove all its redundant labels, we introduce creation and annihilation operators. For electrons (fermions) they satisfy anticommuting relations: \([C_{iσ_1}^\dagger, C_{jσ_2}^\dagger]_+ = δ_{ij}δ_{σ_1σ_2}; \ [C_{iσ_1}^\dagger, C_{jσ_2}^\dagger]_- = 0\). We can build a one-to-one correspondence between the vectors obtained by applying creation operators to the vacuum state and the physically distinguishable subsets:

\[
C_{iσ}^\dagger |0\rangle = \{ |σ_i(1)\rangle, |σ_i(2)\rangle \} \equiv |σ_i\rangle
\]

\[
C_{iσ_1}^\dagger C_{jσ_2}^\dagger |0\rangle = \frac{1}{\sqrt{2}}[|σ_{1i}(1)\rangle|σ_{2j}(2)\rangle - |σ_{1i}(2)\rangle|σ_{2j}(1)\rangle] = |σ_{1i};σ_{2j}\rangle
\]

with \(σ_1, σ_2 = ↑, ↓\). Note that the artificial ordering of spin labels of two-electron states is removed naturally as a consequence of anticommuting relationship of \(C_{iσ}^\dagger C_{iσ}^\dagger = 0\) and Pauli exclusion principle is naturally satisfied due to \(C_{iσ}^\dagger C_{iσ}^\dagger = 0\). Thus, the set of physically allowable states for subsystem A can be written as

\[
H^∗_A = \{ |0_A\rangle, C_{A↑}^\dagger |0_A\rangle, C_{A↓}^\dagger |0_A\rangle, C_{A↑}^\dagger C_{A↓}^\dagger |0_A\rangle \}
\]

Next we consider the physically allowable states of the composite system. In general, \(H^∗_{AB}\) is not a subspace of \(H_A \otimes H_B\) but an antisymmetric subspace of \(H_A \otimes H_B\) with fixed particle number, since there is extra symmetry requirement for wave functions constructed from one single-particle state in \(H_A\) and the other single-particle state in \(H_B\). Explicitly, we can write [using the abbreviated notation for the antisymmetric combination as given in (8.4)]

\[
H^∗_{AB} = \{ |T^{+1}\rangle, |T^{-1}\rangle, \{|T^0\rangle, |S^0\rangle \}, |D_A\rangle, |D_B\rangle \}
\]

\[
= \{ |↑_A;↑_B\rangle, |↓_A;↓_B\rangle, \\
|↑_A;↓_B\rangle + |↓_A;↑_B\rangle, |↑_A;↓_B\rangle - |↓_A;↑_B\rangle, \\
|↑_A↓_A\rangle|0_B\rangle, |0_A\rangle|↑_B↓_B\rangle \}
\]

where the six vectors are orthogonal but not normalized. Each state is antisymmetric with respect to particle label (1 and 2) exchange. We can divide
them into subspaces for spin triplets: \( \{ T^{+1}, T^{-1}, T^0 \} \), nonlocal spin singlet: \( \{ S^0 \} \), and doubly occupied spin singlets \( \{ D_A, D_B \} \), which satisfy different symmetry conditions with respect to the spin label exchange. The wave functions of the last two doubly occupied states are clearly in a separable form and in \( H_A^* \otimes H_B^* \), while the other four states need more careful analysis.

By means of the correspondence provided by Eq. (8.4), we can recast states in \( H_{AB}^* \) into the following form:

\[
H_{AB}^* = \{ |T^{+1}\rangle, |T^{-1}\rangle, |T^0\rangle, |S^0\rangle, |D_A\rangle, |D_B\rangle \}
\]

\[
= \{ C_{A1}^\dagger C_{B1}^\dagger |0\rangle, C_{A1}^\dagger C_{B1}^\dagger |0\rangle, \frac{1}{\sqrt{2}} (C_{A1}^\dagger C_{B1}^\dagger + C_{A1}^\dagger C_{B1}^\dagger) |0\rangle, \frac{1}{\sqrt{2}} (C_{A1}^\dagger C_{B1}^\dagger - C_{A1}^\dagger C_{B1}^\dagger) |0\rangle, C_{A1}^\dagger C_{A1}^\dagger |0\rangle, C_{B1}^\dagger C_{B1}^\dagger |0\rangle \}.
\]

(8.6)

To characterize entanglement, the most importance thing we need to do is to analyze the relationship between the physically allowed total state space \( H_{AB}^* \) and the physically allowed subspace, \( H_A^* \) and \( H_B^* \). Since there is a unique antisymmetric combination of any two-electron two-site wave functions, we can assign a one-to-one correspondence between \( C_{A\sigma}^\dagger C_{B\sigma'}^\dagger \otimes C_{B\sigma'}^\dagger |0\rangle \) and \( C_{A\sigma}^\dagger C_{B\sigma'}^\dagger |0\rangle \), or simply write \( C_{A\sigma}^\dagger C_{B\sigma'}^\dagger |0\rangle = C_{A\sigma}^\dagger C_{B\sigma'}^\dagger |0\rangle \). Hence, we have \( H_{AB}^* \subseteq H_A^* \otimes H_B^* \). Note that usually \( \text{dim}(H_{AB}^*) < \text{dim}(H_A^* \otimes H_B^*) \) due to superselection rules.

Accordingly we can apply to our system the routine procedure for distinguishable-particle system to define separability and entanglement measure for \( H_{AB}^* \subseteq H_A^* \otimes H_B^* \). This is essentially the entanglement of modes or entanglement between sites as first studied by Zanardi [148] for fermionic lattices. Namely, for any pure state \( |\Psi\rangle (\in H_{AB}^*) \) shared by subsystems A and B, we define the entanglement between A and B to be the von Neumann entropy for the reduced density matrix, defined by

\[
\rho_B = Tr_A |\Psi\rangle \langle \Psi|,
\]

\[
\rho_A = Tr_B |\Psi\rangle \langle \Psi|.
\]
Thus the entanglement for state $|\Psi\rangle$ is

$$E_{AB}(|\Psi\rangle) = S(\rho_A) = S(\rho_B) = -Tr(\rho_A \log_2 \rho_A).$$

To be consistent, $\rho_A$ ($\rho_B$) should be supported by the physical allowed local Hilbert space, $H^*_A$ ($H^*_B$). This is guaranteed by the above argument that $H^*_{AB} \subseteq H^*_A \otimes H^*_B$.

Based on the above analysis, we conclude that the entanglement between sites or modes for identical particles can be used as a resource for QIP such as teleportation in the same way as for distinguishable-particle system. Therefore, we call such kind of partition as distinguishable partition, whether the composite system contains indistinguishable particles or not. The indistinguishability of particles introduces no mystery to the entanglement between sites or modes.

For example, for a two-site one-photon system, which has been applied experimentally [149] to teleport a vacuum-one-photon qubit between two sites. At first sight, it appears puzzling because there should have no entanglement for a one-particle system. However, we can partition the system into two subsystems A and B according to sites, since we want to know if we can realize teleportation between A and B. With only one photon, we have $H_A = \{|0\rangle_A, |1\rangle_A\}$, and $H_B = \{|0\rangle_B, |1\rangle_B\}$, in particle number basis. The tensor product space $H_A \otimes H_B$ has a dimension of $2 \times 2 = 4$. However, the physically allowed states lie in a one-photon subspace of $H_A \otimes H_B$. Explicitly,

$$H^* = \{|0\rangle_A|1\rangle_B, |1\rangle_A|0\rangle_B\}. \quad (8.7)$$

Any such one-photon state, if not localized (i.e., neither $|0\rangle_A|1\rangle_B$ nor $|1\rangle_A|0\rangle_B$) must be entangled with respect to the two sites A and B. This one-photon entanglement between sites is realized with the help of vacuum states $|0\rangle_A$ and $|0\rangle_B$. Such kind of entangled states can be used to teleport a vacuum-one-photon qubit from A to B, since we can perform local Bell measurements in a similar way as in Ref. [150] and communicate classically between sites A and B. So, there is no mystery at all in “teleportation or entanglement via one particle”. Controversies arise if, instead of partitioning the composite system into subsystems by sites or by modes, we partition the composite system into subsystems based on individual particles. Due to the indistinguishability of
particles, such a partition is in principle unphysical. We cannot address each subsystem individually in an unambiguous way and we cannot implement classical communication between such subsystems. So there is no physical entanglement between indistinguishable particles that can be used for teleportation with information encoded by particles.

The notion of entanglement between indistinguishable particles was first introduced by Schliemann et. al. in Ref. [69]. In their later work [151, 152], it was named quantum correlation for indistinguishable particles, due to the fundamental difference between ordinary entanglement for distinctly-partitioned system and quantum correlation for indistinguishable particles. Below we give a brief review of their work [69, 151] in quantifying quantum correlation between two fermions. For simplicity, we consider a system with two sites (or modes) denoted A and B. Each fermion with spin 1/2 can reside on either site. Using the creation and annihilation operator representation, the single-particle Hilbert space is

\[ H_S = \{ C_A^{\uparrow} |0_A\rangle, C_A^{\downarrow} |0_A\rangle, C_B^{\uparrow} |0_B\rangle, C_B^{\downarrow} |0_B\rangle \}. \]

Any physically allowed two-particle state should lie in the product space \( H_S \otimes H_S \) (with our previously built correspondence) and can be written as

\[ |w\rangle = \sum_{i,j=1}^{4} w_{ij} C_i^{\dagger} C_j^{\dagger} |0\rangle, \]

with \( (1, 2, 3, 4) = (A \uparrow, A \downarrow, B \uparrow, B \downarrow) \). Since \( c_i^{\dagger} c_j^{\dagger} = -c_j^{\dagger} c_i^{\dagger} \), we can build a one-to-one correspondence between \( |w\rangle \) and the matrix \( w_{ij} \) by requiring it to be antisymmetric. The dual matrix of \( w_{ij} \) can be defined by

\[ \tilde{w}_{ij} = \frac{1}{2} \sum_{k,l=1}^{4} \varepsilon^{ijkl} w_{kl}^{*} \] \hspace{1cm} (8.8)

with \( \varepsilon^{ijkl} \) being the usual totally antisymmetric unit tensor. The Schliemann concurrence of quantum correlation for \( |w\rangle \) is defined in a similar way like the concurrence for two-qubit states:

\[ C_S(|w\rangle) = |\langle \tilde{w}|w\rangle| = | \sum_{i,j,k,l=1}^{4} \varepsilon^{ijkl} w_{ij} w_{kl} | \]

\[ = |8(w_{12}w_{34} + w_{13}w_{42} + w_{14}w_{23})| \] \hspace{1cm} (8.9)

Obviously, \( C_S(|w\rangle) \) ranges from zero to one and it vanishes if and only if the state \( |w\rangle \) can be written as a Slater determinant [69, 151]. Moreover, the Schliemann concurrence measure is invariant under any unitary transformations in the single-particle space. Like the concurrence for the
distinctly-partitioned system, there is still lack of successful generalization of Schliemann concurrence to two fermions with arbitrarily high-dimensional single-particle space.

8.3 Correlation of formation

Analogous to the entanglement of two-qubits, we can introduce the following orthogonal magic basis, each being a maximally correlated state, in terms of the basis vectors in $H^*_{AB}$ (note that the two-electron space is six-dimensional): $|e_1⟩ = \frac{i}{\sqrt{2}}(|T^+⟩ + |T^-⟩)$, $|e_2⟩ = \frac{1}{\sqrt{2}}(|T^+⟩ + |T^-⟩)$, $|e_3⟩ = |T^0⟩$, $|e_4⟩ = i|S^0⟩$, $|e_5⟩ = i|D^⟩ ≡ \frac{1}{\sqrt{2}}(|D_A⟩ + |D_B⟩)$, $|e_6⟩ = |D^−⟩ ≡ \frac{1}{\sqrt{2}}(|D_A⟩ − |D_B⟩)$. Using the magic basis we can express any two-electron state as $|Ψ⟩ = ∑_{j=1}^{6} \alpha_j |e_j⟩$ (with $∑_j |\alpha_j|^2 = 1$). It is then easy to verify that $C_S(|Ψ⟩) = |∑_j \alpha_j^2|$ and we have immediately $C_S(|Ψ⟩) ≤ 1$. The Schliemann concurrence reaches its maximum 1 if and only if the expanding coefficients under the magic basis have the same phase factor. By analogy to the entanglement of formation [153], we can define the correlation of formation as

$$C_F = H\left[\frac{1}{2}(1 + \sqrt{1 − C_S^2})\right], \quad (8.10)$$

where $H(x) = −x \log_2(x) − (1 − x) \log_2(1 − x)$ is the binary Shannon entropy function. Since $C_F$ also ranges from 0 to 1 and $C_F$ is a monotonically increasing function of $C_S$, $C_F$ itself is a kind of measure of pair-wise quantum correlation for indistinguishable particles.

As was first shown in Ref. [69] and extended in Ref. [151], a so-called Slater-Schmidt decomposition exists for any two-fermion state $|w⟩$. A unitary operation in single-particle space transforms $C_i = ∑_j U_{ij} f_j$ to new fermionic operators $f_j$ and the state becomes

$$|w⟩ = ∑_{ij=1}^{N} (U_d^† w U^*)_{ij} f_i^† f_j^† |0⟩. \quad (8.11)$$

In the case when the single-particle space has an even integer dimension, $N = 2 \times M$, there exists a matrix U such that the state $|w⟩$ can be cast into

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the Slater canonical form [151]:

$$|w\rangle = 2 \sum_{k=1}^{M} z_k f_{2k-1}^\dagger f_{2k}^\dagger |0\rangle,$$

(8.12)

where $z_k$'s are called Slater coefficients and any state is non-separable if and only the number of nonvanishing Slater coefficients (Slater rank) is larger than 1. Thus any state which can be written as $f^\dagger g^\dagger |0\rangle$ ($f^\dagger |0\rangle$ and $g^\dagger |0\rangle$ lie in the single-particle space) is non-correlated. Specifically, the state $(\frac{c_m^\dagger + c_m^\dagger}{\sqrt{2}})(\frac{c_m^\dagger + c_m^\dagger}{\sqrt{2}}) |0\rangle$, which has a maximal entanglement between sites ($E_M = 2$), has no quantum correlation between particles.

As shown in Eq. (8.12), the maximal Slater rank is $N/2 = M$, the number of single-particle mode for spin-half particles. The normalization condition requires $4 \sum_{k=1}^{M} |z_k|^2 = 1$. Using an analogy to distinguishable bipartite system, Paskauskas and You [154] introduced the reduced single-particle density matrix as: (Note that we have only one reduced single-particle state due to the indistinguishability of particles)

$$\rho^R(|w\rangle) = \frac{1}{2} \sum_{k} c_k |w\rangle \langle c_k^\dagger$$

$$= \sum_{\mu \nu} 2 (w^\dagger w)_{\mu \nu} c^\dagger_{\mu} |0\rangle \langle 0 | c_{\nu}$$

(8.13)

Obviously, the reduced one-particle density matrix is independent of unitary transformations on the single-particle basis. In Slater canonical single-particle basis $f_k^\dagger |0\rangle$, the reduced single-particle density matrix for $|w\rangle$ is simply $\rho^R(|w\rangle) = \sum_{k} 2 |z_k|^2 (f_{2k-1}^\dagger |0\rangle \langle 0 | f_{2k-1} + f_{2k}^\dagger |0\rangle \langle 0 | f_{2k})$, which is diagonal. Also note that for any non-correlated state $f^\dagger g^\dagger |0\rangle$, its reduced single-particle density matrix is $\frac{1}{2} (f^\dagger |0\rangle \langle 0 | f + g^\dagger |0\rangle \langle 0 | g)$, i. e., an equal mixture of $f^\dagger |0\rangle$ and $g^\dagger |0\rangle$. Operationally, this means that performing a projection measurement on a single particle alone will destroy the coherence between different modes of the other particle. Equivalently, we can say that single-particle modes are in fact artifacts for describing indistinguishable multi-particle wave functions (as in the configuration interaction method in quantum chemistry). In contrast, for any separable (product) bipartite pure state of distinctly-partitioned system, the reduced one-party state is also a pure state.

Paskauskas and You [154] quantify the quantum correlation between two
fermions by using the relative entropy, i.e., the von Neumann entropy of the reduced single-particle density matrix (which has two-fold degenerate eigenvalues, \(2|z_k|^2\)):

\[
C_{RE}(|w\rangle) = S(\rho^R(|w\rangle)) - 1 \equiv -Tr[\rho^R \log_2 \rho^R] - 1
= -2 \sum_k^M (2|z_k|^2 \log_2 (2|z_k|^2)) - 1.
\] (8.14)

where the -1 term is introduced so that \(C_{RE} = 0\) for non-correlated states.

Since \(C_{RE}\) is invariant under single-particle unitary transformations, it also provides a smooth measure from the non-correlated state (with \(C_{RE} = 0\)) to the maximally correlated state (with \(C_{RE} = \log_2 M = \log_2 N - 1\)). It is remarkable that, up to a constant difference, the correlation entropy measure [154], \(S_C\), is identical to the relative entropy of correlation \(C_{RE}\). As it can be seen from the Slater canonical form, the natural orbitals and natural occupation numbers are the eigenvectors and eigenvalues (times the total particle number 2) of the reduced one-particle density matrix, respectively.

It is well-known that for pure states of a distinguishable bipartite system, all entanglement measures (e.g., entanglement of formation) reduce to one unique measure: the relative entropy entanglement [155]. This is a consequence of the weak additivity (i.e. \(E(\rho \otimes \rho) = 2E(\rho)\)) and continuity of any valid entanglement measures [156]. It is interesting to examine if different correlation measures for identical particles, such as \(C_{RE}\) and \(C_F\), also yield the same result for any two-particle pure state. The answer in general would be negative, since the multi-particle Hilbert space is not the tensor product of single-particle Hilbert space and thus the weak additivity is not satisfied. However, we can show that the answer is affirmative for any two-mode \((M = 2)\), two-electron system with nontrivial quantum correlation, for which the Schliemann concurrence and correlation of formation are well-defined. In this case we have only two Slater coefficients, \(z_1\) and \(z_2\), with \(4(|z_1|^2 + |z_2|^2) = 1\). Let \(4|z_1|^2 = \cos^2 \theta\) and \(4|z_2|^2 = \sin^2 \theta\). The Schliemann concurrence becomes \(C_S(|w\rangle) = 8|z_1z_2| = \sin 2\theta\). We can write \(C_F\) and \(C_{RE}\)
in terms of $\theta$ explicitly:

$$C_F(|w\rangle) = -\frac{1 + \cos 2\theta}{2} \log_2 \left[ \frac{1 + \cos 2\theta}{2} \right]$$

$$C_R(|w\rangle) = -\frac{1 - \cos 2\theta}{2} \log_2 \left[ \frac{1 - \cos 2\theta}{2} \right],$$

which yields:

$$C_F(|w\rangle) = C_R(|w\rangle),$$

from which we arrive at $C_F = C_R$. Thus, we have a unique correlation measure\(^4\) for such two-electron systems.

We expect the correlation measure of relative entropy is still a good measure for higher-dimension two-particle systems and for two-electron correlation of a many-particle system, analogous to the bipartite entanglement measures for distinctly-partitioned systems. For any N-fermion state, we can trace out N-1 fermions in some basis and get the reduced one-particle density matrix. The von Neumann entropy of the 1PDM, as we call the relative entropy of correlation or correlation entropy, describes the correlation of one fermion with the other N-1 fermions and quantifies the deviation of the N-particle wave function from its Hartree-Fock approximation. What’s more, we can trace out N-2 fermions and get the reduced two-particle density matrix, which can be expressed as a convex combination of two-particle pure states: $\rho_{R2} = \sum_j P_j |\Phi_j\rangle\langle \Phi_j|$ with $|\Phi_j\rangle$ being two-particle pure state and $\sum_j P_j = 1, P_j > 0$. Analogous to the entanglement of formation for two-qubit mixed states [153], we can define the correlation of formation \(^5\) for $\rho_{R2}$ as:

$$C_F(\rho_{R2}) = \min_{\{P_j, |\Phi_j\rangle\}} \left\{ \sum_j P_j C_R(|\Phi_j\rangle) \right\}$$

where the minimum is taken over any possible pure state decomposition of $\rho_{R2}$. This kind of correlation measure describes the averaged two-particle correlation for a many-particle system. As discussed in Sec. 8.1, the 1PDM

\(^4\)In Ref. [157] Li et. al. also proposed a correlation measure for two-boson system similar to $C_{RE}$ defined in Ref. [154].

\(^5\)In Ref. [151] the Slater correlation measure is defined as $C_{SL}(\rho) = \min_{\{P_j, |\Phi_j\rangle\}} \left\{ \sum_j P_j C_S(|\Phi_j\rangle) \right\}$, where $C_S$ is the Schliemann concurrence measure, for any two-electron mixed state with 4 single-particle modes (including spin). By noticing the formal similarity of our definition with the entanglement of formation, and the fact that $C_F$ and $C_{RE}$ yield the same result for pure states, our correlation measure for mixed states seems more plausible.
and 2PDM are enough to characterize a many-electron system, since there are at most two-body interactions in nature. Therefore, unlike entanglement between distinctly-partitioned subsystems, the relative entropy of correlation resulting from the 1PDM and the correlation of formation resulting from the 2PDM, are probably the only significant kinds of quantum correlation for many-particle systems.

8.4 Entanglement and correlation in two-site Hubbard model

The usefulness of various kinds of entanglement measures [144] between physically distinguishable subsystems has been illustrated in their applications to QIP-related issues [143]. Since indistinguishable particles cannot be applied to quantum information processing in a similar way, one needs to identify the physical significance of quantum correlation measures for indistinguishable particles other than that they are mathematically consistent.

To clarify the physical significance of entanglement and correlation measures, we consider the dynamics of the two-site two-electron system in an extended Hubbard model which includes the inter-site Coulomb interaction:

\[
H = t_H \sum_\sigma [c_{A\sigma}^\dagger c_{B\sigma} + c_{A\sigma}^\dagger c_{B\sigma}^\dagger] + U_1 \sum_{i=A,B} c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} + U_2 \sum_{\sigma_1\sigma_2} (c_{A\sigma_1}^\dagger c_{A\sigma_1})(c_{B\sigma_2}^\dagger c_{B\sigma_2}).
\] (8.17)

where \(t_H\) is the coupling constant characterizing single-electron hopping between two sites, \(U_1\) and \(U_2\) the on-site and inter-site Coulomb interaction, respectively. The sum of the first two terms in \(H\) is the regular Hubbard model.

We choose the six orthonormal states given in Eq. (8.6) as the basis. Note that the three triplet states \(T^+, T^-1, T^0\) are degenerate eigenstates with energy \(U_2\). By diagonalizing the Hamiltonian, we can solve analytically
the other three normalized eigenstates and their correspondingly eigenvalues:

\[
|S_g\rangle = \frac{1}{\sqrt{\alpha + 1}}[\alpha|S_0\rangle + |D^+\rangle], \quad E_g = U_2 + \frac{1}{2}(U - \Delta);
\]

\[
|D^-\rangle = \frac{1}{\sqrt{2}}(|D_A\rangle - |D_B\rangle), \quad E_{D^-} = U_1 = U_2 + U;
\]

\[
|S_h\rangle = \frac{1}{\sqrt{\alpha + 1}}[-|S_0\rangle + \alpha|D^+\rangle], \quad E_h = U_2 + \frac{1}{2}(U + \Delta).
\]

(8.18)

where \(\alpha = \alpha(U/4t_H) = U/4t_H + \sqrt{1 + (U/4t_H)^2}\), \(\Delta = \sqrt{U^2 + 16t_H^2}\), and \(U = U_1 - U_2\). Note that we can subtract \(U_2\) from each eigenenergy so that only the effective Coulomb interaction \(U\) enters their expressions. All of the six eigenvectors, if not parameter-independent, only depend on the ratio of the ”effective” Coulomb interaction \(U\) and the hopping strength \(t_H\).

We denote the entanglement between sites (modes) A and B by \(E_M\) and the quantum correlation between two electrons by \(C_F\) (\(\cong C_{RE}\) for pure states). For the three triplet states, we have \(E_M(|T^{\pm1}\rangle) = C_F(|T^{\pm1}\rangle) = 0; \quad E_M(|T^0\rangle) = C_F(|T^0\rangle) = 1\).

It should be mentioned that the single-site doubly occupied states, \(D_A\) or \(D_B\), which have no entanglement between sites, also have zero quantum electron correlation since they are single Slater determinants. We have only one spatial level per site, which makes Hartree-Fock states the only possible doubly-occupied states.

To study the dependence of \(E_M\) and \(C_F\) on dynamic parameters, we concentrate our analysis on the ground state \(|S_g\rangle\). Let \(\cos \theta = \frac{\alpha}{\sqrt{\alpha^2 + 1}}\) and \(\sin \theta = \frac{1}{\sqrt{\alpha^2 + 1}}(\pi/4 \leq \theta \leq \pi/2)\), we have

\[
E_M(|S_g\rangle) = 1 - \cos^2 \theta \log_2 \cos^2 \theta - \sin^2 \theta \log_2 \sin^2 \theta
\]

\[
C_S(|S_g\rangle) = |\cos^2 \theta - \sin^2 \theta| = |\cos 2\theta|
\]

\[
C_F(|S_g\rangle) = 1 - \frac{1}{2}[\log_2(1 + \sin 2\theta) + \log_2(1 - \sin 2\theta)].
\]

(8.19)

It is not hard to see that \(E_M\) reaches its maximum 2 at \(\theta = \frac{\pi}{4}\) while \(C_F\) (\(C_S\)) reaches its maximum 1 at \(\theta = \frac{\pi}{2}\).

To see the parameter dependence, we plot in Fig. 8.1 to demonstrate\(^6\)

\(^6\)Zanardi [148] obtained similar result for the entanglement between two sites with the
Figure 8.1: Comparison of the entanglement between sites $E_M$ (solid), and the quantum correlation between electrons $C_F$ (dotted) of the ground state $|S_g\rangle$ in two-electron two-site extended Hubbard model. Both of them are illustrated as functions of the dynamic ratio $U/4t$. 
$E_M$ and $C_F$ of the ground state $|S_g\rangle$ as functions of single dynamic parameter $U/4t_H$. At $U = 0$ or $t_H \to \infty$, the ground state is an equal superposition of $|S^0\rangle$ and $|D^+\rangle$, which has maximal inter-site entanglement 2 but no quantum correlation between electrons. This is reasonable since without Coulomb interaction, electrons move as independent particles, while at infinity hopping strength, electrons can effectively avoid Coulomb interaction by always staying in between sites. As we increase the ratio $U/4t_H$ (increasing the effective Coulomb interaction or suppressing electron hopping by raising the energy barrier between sites), $E_M$ decreases monotonically while $C_F$ increases monotonically. It can be understood by the following argument. Either increasing Coulomb interaction or raising the inter-site energy barrier will suppress electron hopping between sites, which is the only means to build inter-site correlation. So $E_M$ decreases monotonically as we increase $(U/t_H)$. On the other hand, $t_H$ is the strength of single-electron hopping (like interaction between sites), which does not help the correlation between electrons, while $U$ is the genuine interaction between electrons. As $U/t_H \to \infty$, electrons can maximally build their correlations by their effectively interaction, with the maximum of electronic quantum correlation saturated by the available configuration dimensions. Note that $U = U_1 - U_2$; thus, if we increase the inter-site Coulomb interaction ($U_2$) while keeping all other parameters fixed, the electronic quantum correlation will be suppressed and the entanglement between sites will be enhanced.

Since Hartree-Fock wave function is our reference state defining electronic quantum correlation, it may be of interest to figure out the deviation of the true ground state wave function $|S_g\rangle$ from its HF approximation. In the HF approximation we first solve the natural orbitals as the eigenvectors of the reduced 1PDM of the ground state, which are the single-particle binding (+) and antibinding (−) molecular orbitals, respectively,

$$|\pm \sigma\rangle = \frac{1}{\sqrt{2}} (c_{A\sigma}^\dagger \pm c_{B\sigma}^\dagger) |0\rangle \equiv c_{\pm \sigma}^\dagger |0\rangle \quad (8.20)$$

Thus the two-electron Hartree-Fock state closest to $|S_g\rangle$ is $|G_{HF}\rangle = c_{+\uparrow}^\dagger c_{+\downarrow}^\dagger |0\rangle$ with $E_{HF} = U/2 - 2t_H$ the corresponding energy. The absolute correlation energy for the ground state $|S_g\rangle$ is $E_{\text{corr}} = \sqrt{U^2/4 + 4t_H^2} - 2t_H$. We linear entropy measure.
can define the deviation of $|S_g\rangle$ from $|G_{HF}\rangle$ by the overlap (fidelity) function:

$$D(S_g|HF) = 1 - |\langle S_g | G_{HF} \rangle|^2$$

$$= \frac{1}{2}[1 - \sin 2\theta] = \frac{1}{2}[1 - \sqrt{1 - C_S^2}].$$

(8.21)

Like $C_F$ or $C_{RE}$, $D$ is a monotonous function of the Schliemann concurrence $C_S$. Therefore $D$ is also a measure of electronic quantum correlation, which is analogous to the entanglement measures determined by the distance from the closest separable state to the entangled state considered. Actually, the relative entropy of entanglement [158] for distinctly-partitioned systems (or the relative entropy of correlation $C_{RE}$ for fermions) can also be regard as measuring the distance from the considered state to the closet separable states (HF states) where the distance measure is given by $D(\rho, \sigma) = -\text{Tr}[\rho \log \rho - \rho \log \sigma]$ for any density matrix pair $\rho$ and $\sigma$.

Since the correlation energy $E_{corr}$ is also a popular correlation measure in quantum chemistry, we may compare it to $C_{RE}$ ($C_F$). Unlike $C_{RE}$, $E_{corr}$ depends on the absolute value of $U$ and $t_H$. To compare, we fix the hopping strength $t_H$ and write $E_{corr}/2t_H = \sqrt{(U/(4t_H)^2 + 1} - 1$, which, like the $C_{RE}$ (or correlation entropy $S_C$), increases monotonically as we increase the effective Coulomb interaction. However, as an energetic measure for electron correlation, $E_{corr}$ yields the same correlation for energetically degenerate states, while $C_{RE}$ ($C_F$), as a kinetic measure, gives finer ordering of states according to the degree of electron correlation.

Therefore, we can argue that $E_M$ is the entanglement between sites which can be enhanced by sending electrons from one site to the other site (via single-electron hopping). This is similar to the regular case where Alice can prepare a two-qubit singlet state locally and send one qubit to Bob. By such a one-way quantum information transmission Alice and Bob (initially unentangled) can share one ebit of entanglement. On the other hand, by quantifying identical-particle quantum correlation in a dynamic system, $C_F$ or $C_{RE}$ characterizes the deviation of the wave function from its closest Hartree-Fock states, which is determined by the effective two-particle interaction. The maximal value of $C_{RE}$ is limited by the available two-particle configurations (degrees of freedom). Thus, the dependence of genuine quantum correlation on dynamic parameters would reflect the effective interaction between particles.
Recently Gittings and Fisher [159] criticized the Schliemann measure by arguing that its value can be changed under one-site two-particle unitary transformation and remain invariant under two-site one-particle unitary transformation. It is worth pointing out that their criticism is not justified. In using the Schliemann measure to quantify quantum correlations between two identical particles, single-particle operations (either two-site or one-site) are analogous to local operations on individual subsystems in distinctly-partitioned system, while two-particle operations (either two-site or one-site) are analogous to nonlocal operations. Locality and nonlocality are relative terms, which have no absolute meanings but depend on how we partition the composite system.

It would be of great interest to apply this concept to strongly correlated systems such as superconductors and quantum Hall systems. In fact, there is a recent attempt [160] to study the electron quantum correlation for some fractional quantum Hall liquids, where the von Neumann entropy of the reduced single-particle density matrix for the Laughlin wave function is calculated. It would be of interest, though much harder, to evaluate the correlation of formation for the reduced two-particle density matrix.

8.5 Subspace-restricted entanglement

In this section we introduce another entanglement concept. Let’s consider a composite system \( Q \) partitioned into two distinct subsystems \( Q_A \) and \( Q_B \) with its Hilbert space decomposed as \( H_Q = H_{Q_A} \otimes H_{Q_B} \). Correspondingly, the environment can also be partitioned into two subsystems, \( H_E = H_{E_A} \otimes H_{E_B} \). The total Hilbert space including environment can be written as \( H_{QE} = H_Q \otimes H_E \). For any state \( |\Psi\rangle \in H_{QE} \), if we have no access to the environment, then \( |\Psi\rangle \) is reduced to a density matrix supported by \( H_Q \), \( \rho_Q = Tr_E(|\Psi\rangle\langle\Psi|) \). The amount of entanglement for the system state \( \rho_Q \), will depend on the amount of classical information we have about the system-environment coupling [161].

Now we consider the most general case where system \( Q \) and environment \( E \) can exchange identical particles. We are interested in systems in which the total number of particles, \( N \), is conserved. By superselection rules, we can reduce \( H_{QE} \) to \( H_{QE}^* = \bigoplus_k H_{Q_k} \otimes H_{E_{N-k}} \), where \( H_{Q_k} \) is the
k-particle subspace of \( H_Q \), and similarly for \( H_{E,N-k} \). If by space-time boundary conditions or superselection rules, the only possible decomposition is 
\[ H_{QE}^* = H_{QN}^* \bigotimes \{ |\text{vac}\rangle_E \} \bigoplus \{ |\text{vac}\rangle_Q \} \bigotimes H_{EN}^* \],
then by isomorphism we can map \( H_{QE}^* \) to \( H_{QN}^* \bigoplus H_{EN}^* \). Since \( H_{QN}^* \subseteq H_Q \) and \( H_{EN}^* \subseteq H_E \), we can partition the system according to A and B, so that \( H_{QN}^* = H_{Q_A}^{(N)} \bigotimes H_{Q_B}^{(N)} \).

Without causing any confusion, we can drop the index N and simply write the total Hilbert space of physically allowed states as:
\[ H_{QE}^* = [ H_{Q_A}^* \bigotimes H_{Q_B}^* ] \bigoplus H_{E}^* \]  \( (8.22) \)

Thus, for any physically allowed state of the coupled system-environment QE, we can decompose it as
\[ |\Psi\rangle = c_Q |\Psi_Q\rangle + c_E |\Psi_E\rangle, \] with \( |\Psi_Q\rangle \in H_Q^* \) and \( |\Psi_E\rangle \in H_E^* \). The normalization condition reads: \( |c_Q|^2 + |c_E|^2 = 1 \). Clearly, with such a kind of system-environment structure, for any state \( |\Psi\rangle \in H_{QE}^* \), if we have no access to the environment, then the only accessible entanglement between A and B is due to the system part, and we can define the subspace-restricted entanglement as
\[ E_Q^*(|\Psi\rangle) = |c_Q|^2 E(|\Psi_Q\rangle), \]  \( (8.23) \)

where \( |c_Q|^2 \) is the probability of finding the residual state in \( H_Q^* \) after performing a projection measurement \( P_Q \) \( (P_Q + P_E = I_{QE}) \) on the state \( |\Psi\rangle \).

As a comparison, for the regular tensor product system-environment structure, the accessible entanglement is the mixed-state entanglement of the reduced density matrix, \( E = E(Tr_E(|\Psi\rangle\langle\Psi|)) \). It is well-known that the entanglement of a mixed state depends on what measure we use. In our case, the residual state obtained by performing a system-environment projection measurement is always pure (Note that QE is a closed system and the total state is pure). Therefore, for our specific system-environment structure, the accessible entanglement or the entanglement contributed by system is measure-independent since all valid measures must yield the same amount of entanglement for pure states.

Quite recently S. D. Barlett and H. M. Wiseman [162] discussed the entanglement in the presence of general superselection rules (SSRs) by noticing their restrictions on the allowed operations on a system. The allowed operations determine the Hilbert space structure. For a specific decomposition of
the Hilbert space, coherent superposition of different subspaces (e. g., fixed-particle-number subspaces for fermions) is prohibited. It is worth pointing out that, the authors refer to SSRs not only the restrictions imposed by fundamental theory but also practical restrictions (e. g., the collective nature of NMR operations). The space-time boundary conditions we consider here, of course, also determine the Hilbert space structure by selecting out relevant subspaces. If we only have partial access to the Hilbert space and/or to the operations, the available entanglement could be greatly reduced. For an operational definition of entanglement of indistinguishable particles due to particle-number superselection rules, see a recent study by Wiseman and Vaccaro [163].

Our discussion can be generalized to any system (either open or closed) shared by A and B, if, by superselection rules or by some appropriate space-time boundary conditions, the physically allowed Hilbert space \( H^* \) can be decomposed as \( H^* = \bigoplus_k (H_{Ak} \otimes H_{Bk}) \). We can define the contribution of subspace \( H_{Ak} \otimes H_{Bk} \) to the entanglement for any state \( \rho \) supported by \( H^* \) (the system states can be mixed, so we use density matrix representation) as

\[
E_{AkBk}(\rho) = |c_k|^2 E(P_{AkBk} \rho P_{AkBk}), \tag{8.24}
\]

where \( |c_k|^2 \) is the probability of finding the residual state (which in general is a mixed state) supported by \( H_{Ak} \otimes H_{Bk} \) by performing a projection measurement \( \{P_{AkBk}, \sum_k P_{AkBk} = I_{H^*}\} \) on the state \( \rho \).

This definition is useful, since, we may not have access to the full space of \( H_A \) and \( H_B \), but only to \( H_{Ak} \) and \( H_{Bk} \). Thus the only accessible entanglement which can be used to perform useful tasks is the restricted entanglement \( E_{AkBk}(|\Psi\rangle) \) defined in Eq. (8.24). Note that we can calculate the entanglement restricted on subspace \( \bigoplus_{i} (H_{Ai} \otimes H_{Bi}) \) (where \( \{k_i\} \subset \{k\} \)) in a similar way.

In the same spirit, for a system containing indistinguishable particles, we can define \( H_k \)-restricted quantum particle correlation if the physically allowed multi-particle Hilbert space can be decomposed as \( H = \bigoplus_k H_k \). In the followed section we will illustrate the usefulness of such concepts in quantum computing.
8.6 Entanglement of qubits in quantum computing

The power of quantum computing comes from entanglement. More precisely, the classically tough problem such as the factoring of any large integer [5], can be solved in a fascinatingly efficient way by a quantum computer (QC) via collective processing of entangled multi-qubits. Thus it is important to analyze the evolution of entanglement during a multi-qubit operation. However, as logical qubits (elementary quantum information units) are represented by physical elements differently in different quantum computer architectures, the entanglement analysis may involve complicated Hilbert space structures. Especially, in the most promising scalable solid state QC architectures such as quantum-dot or silicon-based QC, multi-qubit operation is realized by the dynamic evolution of a composite system containing indistinguishable particles such as electrons. Thus, as indistinguishable particles often lead to confusions on the partitions of a composite system, we should proceed entanglement analysis carefully.

We concentrate on the two-qubit unitary process, which, combined with single-qubit operations, can realize any multi-qubit operation. We consider QC architectures where qubits are encoded by localized electron spins, and the effective dynamics of such systems can be described by a two-site two-electron Hubbard model. The promising quantum-dot spin-based QC [25] and Si:P spin-based QC [28, 32] belong to this case. Other solid-state QC models, such as the silicon-based nuclear spin QC proposed by Kane [26], can be mapped to extended two-site Hubbard model or can be analyzed in the same spirit. Note that the Heisenberg spin exchange model is just a special approximation to the Hubbard model when the on-site Coulomb interaction is large compared to other dynamic parameters.

Before we discuss entanglement of qubits in a quantum computer, let us first analyze the properties of qubits. Generally speaking, a qubit is a logical abstraction of a two-level system. The standard notion of a qubit is the following [8]:

1. A qubit is a vector in a two-dimensional Hilbert space \( H_i = \text{span}\{|0_i\rangle, |1_i\rangle\} \) (like a fermion), and
An N-qubit Hilbert space has a tensor product structure: \( H = \bigotimes_{i=1}^{N} H_i \) (like bosons).

Qubits have peculiar particle properties: they are neither fermions nor bosons. As pointed out by Wu and Lidar [164], qubits can be regarded as parafermions and can be represented by parafermionic operators in the Fock space. Like fermions, doubly-occupied state cannot be realized; like bosons, the number of qubits can change or qubits can be destroyed by coupling with the environment. The most important thing for qubits we need to point out is that, unlike fermions or bosons, qubits are distinguishable if treated like particles, and we can label qubits since they have distinct Hilbert spaces. Qubits are more like modes (such as spins) than particles. So, we should treat entanglement between qubits in the same way as entanglement between modes.

Let us label the two qubits involved in a two-qubit process by A and B, where A and B can be the locations of quantum dots or donor nucleus, which are usually separated by a distance and can be addressed separately. The configurations of qubits, which carries quantum information, have a one-to-one correspondence to the spin states of localized electrons. The Hilbert space for qubit A is \( H_{QA} = \{ |\uparrow_A\rangle, |\downarrow_A\rangle \} \) and similarly \( H_{QB} = \{ |\uparrow_B\rangle, |\downarrow_B\rangle \} \).

Let the initial state of the two qubit to be \( \rho_i \) supported by \( H_{QAB} = H_{QA} \bigotimes H_{QB} \), which can be entangled and mixed for the most general case. However, during any nontrivial two-qubit operation, qubits can disappear (i.e., the two-electron state completely lies outside of \( H_{QA} \bigotimes H_{QB} \)) due to leakage and their labels can be lost due to the inherent indistinguishability of electrons. The point is that only the final state is of significance no matter what happens in the intermediate process. If some qubit is lost at the end of an operation, then we say the operation completely fails. Otherwise, the final two-qubit state \( |\Psi_f\rangle \) must be supported by \( H_{QA} \bigotimes H_{QB} \). The successfulness of a unitary operation (or gate) \( \mathcal{U} \) on a specific initial state \( \rho_i \) can be characterized by [165]:

\[
\mathcal{F}(\mathcal{U}, \rho_i) = \left\{ \text{Tr} \left[ (\sqrt{\rho_i} \hat{U}^\dagger \rho_f \hat{U} \sqrt{\rho_i})^{1/2} \right] \right\}^2, \quad (8.25)
\]

where \( \rho_i \) and \( \rho_f \) denote the density matrix for the initial and final states. Note that in Ref. [166] the gate fidelity is defined as the average value of
\( \mathcal{F}(U, \rho_i) \) over all pure initial states.

Now we consider the Hilbert space structure in the Hubbard model. The single-electron hopping term \( t_H \) couples the two-qubit space \( H_{Q_{AB}} \) to the environment \( H_E = \{ |0_{AB}\rangle, |\uparrow_A; \downarrow_A\rangle, |\uparrow_B; \downarrow_B\rangle \} \). From here we can see that the system-environment coupling, which would cause double-occupancy errors, is intrinsic to our two-qubit operation. That is, the environment is not only the spoiler which reduces the gate fidelity, but at the same time the only helper, without which we cannot realize any nontrivial two-qubit operation. The Heisenberg spin exchange model corresponds to the ideal case when the double-occupancy errors introduced by system-environment coupling can be ignored.

Since the number of electrons is fixed to 2, the total Hilbert space has the structure discussed in the previous section: \( H^\ast_{AB} = (H_{Q_A} \otimes H_{Q_B}) \oplus H_E \). Thus, the relevant entanglement in quantum computing is the \( H_{Q_{AB}} \)-restricted entanglement \( E_Q \), which is the only useful entanglement resource for performing tasks by collectively processing entangled multi-qubits. A two-qubit operation is realized by the evolution of the initial state under the Hubbard model Hamiltonian which can be controlled adiabatically by varying the hopping strength in time [69].

First let us consider the case when the initial two-qubit state is a pure product state, i.e., \( |\Psi_i\rangle = (\alpha_{A\uparrow}|\uparrow_A\rangle + \alpha_{A\downarrow}|\downarrow_A\rangle)(\beta_{B\uparrow}|\uparrow_B\rangle + \beta_{B\downarrow}|\downarrow_B\rangle) \) with \( |\alpha_{A\uparrow}|^2 + |\alpha_{A\downarrow}|^2 = 1 \) and \( |\beta_{B\uparrow}|^2 + |\beta_{B\downarrow}|^2 = 1 \). Initially, the two qubits are decoupled from each other, and if \( t_H(0) = 0 \), they are also decoupled from the environment. The two electrons can be regarded as distinguishable since they are labelled by distinct sites and have no wave function overlap. If we increase \( t_H \) to a tiny amount \( \epsilon \) in a time \( \tau \) with \( \epsilon \tau \) approaching zero, the electrons becomes indistinguishable. However, since \( \epsilon \tau \) is infinitesimal, the state at \( \tau \) should be almost the same as the initial state by the continuity of wave function on time. Similar argument holds for any initial state lying in \( H_E \). So we can build a one-to-one correspondence from our qubits-environment Hilbert space to the two-site two-electron basis expressed by the creation and
annihilation operators.

\[
|\sigma_A;\sigma'_B\rangle \rightarrow C_{A\sigma}^\dagger C_{B\sigma}'^\dagger |0\rangle;
|\uparrow_A\downarrow_A\rangle \rightarrow C_{A\uparrow}^\dagger C_{A\downarrow}^\dagger |0\rangle;
|\uparrow_B\downarrow_B\rangle \rightarrow C_{B\uparrow}^\dagger C_{B\downarrow}^\dagger |0\rangle. \tag{8.26}
\]

By this correspondence we can express within our basis the six eigenfunctions (and corresponding eigenvalues), with three singlet states given by Eq. (8.18) and the triplet given in Eq. (8.6). Thus we can compute the contribution of two-qubit space to the entanglement of the ground state \(|S_g\rangle\):

\[
E_Q(|S_g\rangle) = \frac{\alpha^2}{1 + \alpha^2} E_M(|S_0\rangle) = \frac{\alpha^2}{1 + \alpha^2}. \tag{8.27}
\]

If the initial state is \(|S_0\rangle\), then by adiabatically controlling the coupling strength \(t_H = t_H(t)\), the system will always stay in its instant ground state. In this special case \(E_Q(|S_g(t)\rangle)\) only depends on \(|\langle S_0|S_g\rangle|\). The initial state has a maximal entanglement 1. As we increase the system-environment coupling, \(E_Q\) decreases due to the mixing with doubly-occupied configurations.

Now we consider the pure product initial state. Without losing generality, let \(|\Psi(0)\rangle = |\uparrow_A;\downarrow_B\rangle = \frac{1}{\sqrt{2}}[|T^0\rangle + |S^0\rangle]\), since we can perform a rotation in the spin space. In such an adiabatic process, the \(T^{-1}, T^+\) and \(D^-\) states are decoupled from our instant state. At time t, the state evolves to \((\hbar \equiv 1)\)

\[
|\Psi(t)\rangle = \frac{1}{\sqrt{2}}[|T^0\rangle + \exp(i \int_0^t J(\tau)d\tau)|S_g(t)\rangle] \tag{8.28}
\]

where \(J(\tau)\) is the instantaneous exchange splitting at time \(\tau\):

\[
J(\tau) = \varepsilon(|T^0(\tau)\rangle) - \varepsilon(|S_g(\tau)\rangle) = \frac{1}{2}[\sqrt{U^2 + 16t_H^2(\tau)} - U]. \tag{8.29}
\]

Note that the time-dependence of \(J(t)\) and \(|\Psi(t)\rangle\) is completely determined by \(t_H(t)\). For the adiabatic approximation to be valid, the change of \(t_H(t)\) should be slow enough so that the two electrons has a very small probability to leak out of \(H_Q \otimes H_E\) during the whole process. To study the dynamic evolution of entanglement, an explicit pulse shape of \(t_H(t)\) is needed. As described in a recent study on coupled donors in Si:P spin-based
quantum computer [35], the J-gate can be modelled as a single-parameter-controlled parabolic potential, and it was found that the exchange splitting has exponential dependence on the parameter: $J = J_0 \exp(\beta \mu)$ with $\beta$ being a constant and $\mu$ the depth of the parabolic potential well\(^7\), which can be controlled by electrodes put in the neighborhood of the coupled donors. $J_0$ is the bare exchange splitting when J-gate is off, which is pretty small for a well-separated donor pair.

If we vary the controlling parameter parabolically in time, $\mu(t) = \eta[(T/2)^2 - (t - T/2)^2]$, we will get a symmetric Gaussian pulse shape for $J(t)$:

$$J(t) = J_0 \exp\{-\gamma[(t - T/2)^2 - (T/2)^2]\}$$

(8.30)

where $\gamma = \beta \eta$ and $T$ is the total switching time of J-gate depending on what operation we want to perform. $J(0) = J(T)$ is the bare exchange coupling in the absence of J-gate, while the peak value of the $J(t)$ pulse shape is achieved in the middle point of switching time: $J_{\text{max}} = J(T/2) = J_0 \exp[\gamma(T/2)^2]$. Correspondingly, the pulse shape for $t_H(t)$ is

$$t_H(t) = \frac{1}{2}\left\{ J_0^2 e^{-2\gamma[(t-T/2)^2-(T/2)^2]} + J_0 U e^{\gamma[(t-T/2)^2-(T/2)^2]} \right\}^{1/2}$$

(8.31)

With such a pulse shape we write $|\Psi(t)\rangle$ explicitly:

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}[(|T^0\rangle + \exp(i \int_0^t J(\tau)d\tau) \times (\cos(\theta(t))|S^0\rangle + \sin(\theta(t))|D^+\rangle)].$$

(8.32)

where $\sin \theta(t) = 1/\sqrt{\alpha^2[U/4t_H(t)] + 1}$ and $\cos \theta(t) = \sqrt{1 - \sin^2 \theta(t)}$. At the end of a two-qubit operation, $t = T$, the leakage probability is $P_{lk} = \sin^2 \theta(T)$, while the operation fidelity is $F = \cos^2 \theta(T) = 1 - P_{lk}$ since the only mechanism imperiling our gate fidelity is due to double-occupancy errors in this simple model. Note that they only depend on the residual electron hopping (exchange coupling) $t_H(T) = t_H(0)$. $P_{lk} \sim 0$ and $F \sim 1$ if and only if $t_H(T)/U = t_H(0)/U \sim 0$. Thus we can decrease the double-occupancy error (or increase gate fidelity) by suppressing $t_H(0)$ (for example, by raising the

\(^7\)A realistic J-gate potential is given in Appendix I. Approximately, the exchange coupling depends gate voltages exponentially, as our calculation in Chapter 7 shows [34].

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energy barrier between two neighboring donors (quantum dots)).

It is important to note that such a two-qubit adiabatic unitary operation is solely determined by the phase factor, \( \phi = \int_0^T J(\tau) d\tau \). Thus we can write \( U = U_\phi \). Specially, \( U_x \) is the swap operation, \( U^2_x \) is the "square root of swap" operation. For gate \( U_\phi \), we have

\[
\phi = \int_0^T J(\tau) d\tau = J_{\text{max}} \int_0^T \exp\left[-\gamma(t-T/2)^2\right]
= \sqrt{\frac{\pi}{\gamma}} J_{\text{max}} \text{erf}(\sqrt{\gamma}T/2)
\]

with \( J_{\text{max}} = J(0) \exp(\gamma(T/2)^2) \) and \( \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \) the error function. The off-state exchange coupling \( J(0) \) is usually optimized, so, for the desired gate \( U_\phi \), the total switching time is uniquely determined by the controlling parameter \( \gamma \). Since error function is an increasing function, from Eq. (8.33) we see that, the faster we tune the J-gate, the shorter time we need to complete a desired two-qubit operation. This is coincident with our intuition. However, we cannot tune the J-gate arbitrarily fast, due to the adiabatic requirement.

Now we want to track the evolution of entanglement between qubits during the operation \( U_\phi \). By projecting the total state \( |\Psi(t)\rangle \) to the two-qubit space and using the regular Bell magic basis, we obtain the two-qubit concurrence

\[
C_Q(|\Psi(t)\rangle) = \frac{1}{2} |1 - \cos^2 \theta(t) \exp 2i\tilde{\phi}(t)|,
\]

where \( \tilde{\phi}(T) = \phi \) for a \( U_\phi \) gate operation. Note that \( C_Q \) depends on both the leakage parameter \( \theta(t) \) and the dynamic phase factor \( \tilde{\phi}(t) \).

In typical conditions, to satisfy the requirement of quantum error correction, the switching time \( T \) should be at least one in \( 10^4 \) of the spin decoherence time. Here we assume the interactions which lead to the spin decoherence have the same order of magnitude as the bare exchange, \( J_0 \).
So $T = 10^{-4}/J_0$. Combining Eq. (8.33) with this assumption, we obtain $T = 6.62745/\sqrt{\gamma}$ for the "square root of swap operation", $\mathcal{U}_{\pi/2}$. Thus $1/\sqrt{\gamma}$ is the characteristic time scale. We further assume $U/J_0 = 100$ for well separated donors (quantum dots).

With these assumptions the time-dependence of $\theta(t)$ and $\tilde{\phi}(t)$ are completely determined:

\[
\frac{U}{4\hbar} = 50 \times \frac{e^{2\gamma[(t-T/2)^2-(T/2)^2]} + 100e^{3[(t-T/2)^2-(T/2)^2]}}{\sqrt{\gamma}T/2} + \frac{\phi}{2} \times \frac{\text{erf}[\sqrt{\gamma}T/2] + \text{erf}[\sqrt{\gamma}(t - T/2)]}{\text{erf}[\sqrt{\gamma}T/2]}.
\]

(8.36)

Note that $\theta(t)$ and $\tilde{\phi}(t)$, and hence $C_Q(t)$, up to a phase scaling factor, have the same time dependence for any two-qubit unitary operation $\mathcal{U}_d$.

We plot in Fig. 8.2 the evolution of $C_Q(|\Psi(t)\rangle)$ for the $\mathcal{U}_{\pi/2}$ operation. Initially, we have $C_Q = 0$ since we start from a product state. As time increases [i.e., the J-gate or $t_H(t)$ is switched on] $C_Q$ increases due to the effective spin coupling. At $t = T/2$, the electron hopping is the strongest and the "fidelity" factor $\cos^2 \theta(T/2)$ is the smallest with $\tilde{\phi}(T/2) = \pi/4$. The rate of increase in entanglement is extremely large at this point. At the end of the $\mathcal{U}_{\pi/2}$ operation, the state is maximally entangled. Thus we gain 1 ebit of entanglement between the qubits by applying a "square root of swap" gate on an initially unentangled state.

In Ref. [69] Schliemann et. al. analyzed the evolution of quantum electron correlation during a gate operation with the concurrence measure $C_S$ as reviewed in Sec. 8.2. For $|\Psi(t)\rangle$ (which should be expressed by electron creation operators), the electron correlation reads:

\[
C_S(|\Psi(t)\rangle) = \frac{1}{2} |1 - \cos 2\theta(t) \exp(2i\tilde{\phi}(t))|.
\]

(8.37)

From Fig. 8.2 we can see that initially $C_S$ coincides with $C_Q$ since the two qubits are almost decoupled from the environment. The electron correlation also increases monotonically with time during the whole operation. However, $C_S$ does not describe entanglement between qubits correctly because it also contains the contribution from the doubly-occupied environment. $C_S$ is larger than $C_Q$ before they cross each other near the midpoint of the gate time.
Figure 8.2: Entanglement of qubits measured by concurrence, $C_Q$ (solid), during a "square root of swap" process described by adiabatic evolution of two-site Hubbard model with the Gaussian pulse shape of exchange coupling $J(t)$ (dot-dashed). As a comparison, we also plot the electron correlation measured by Schliemann concurrence $C_S$ (dotted). The total gate switching time is $T = 6.62745\gamma^{-1/2}$. 
After that point, $C_Q$ turns larger until they coincide again at the end of gate operation where the two qubits are again decoupled with the environment and the double occupancy is almost completely suppressed. As a function of time, $C_S$ increases very quickly at the beginning and end of the switching process when the effective Coulomb interaction ($\sim U/t_H(t)$) is considerably large. Moreover, $C_S$ exhibits a wide plateau near $C_S = 0.5$ in the middle of switching since the effective Coulomb interaction is small. This verifies our argument in Sec. 8.4 that the electron correlation reflects the magnitude of effective Coulomb interaction.

In comparison, $C_Q$ increases very fast in the beginning, in the middle and in the end of the switching process, thus exhibits two plateaus. This is due to the fact that, $C_Q$, as a part of the entanglement between sites ($E_{AB}$), not only depends on the effective electron hopping ($\sim t_H(t)/U$) like $E_{AB}$, but also depends on the fidelity of the two-qubit space (or singly-occupied two-electron space). The two plateaus of $C_Q$ appear due to the interplay of these two aspects. As pointed out in Section 8.4, $C_Q$ (part of entanglement between sites) and $C_S$ are totally different quantities describing different kinds of quantum correlation, since they partition the Hilbert space into subspaces in different ways.

However, if we project the $|\Psi(t)\rangle$ into the singly-occupied space and calculate $C_S$ of the projected state, we will get the same result as $C_Q$ since the singly-occupied two-electron Hilbert space can be mapped exactly to the two-qubit space as the Hubbard model reduces to the Heisenberg exchange model when $U/t_H \gg 1$ (the doubly-occupied configurations are suppressed).

### 8.7 Concluding remarks

In conclusion, we have analyzed the existing entanglement measures for composite system containing indistinguishable particles. By going from distinguishable wave function representation to second-quantized representation, we have illuminated the importance of physically allowed Hilbert space. As a consequence the entanglement of modes (or sites) for an identical-particle system is shown to be consistent with the regular entanglement for a distinctly-partitioned system. Then we compare two different identical-particle correlation measures and find they coincide with each other for a two-electron
system with two spatial single-particle modes. Quantum correlation measure for two-particle pure states is generalized to the reduced two-particle mixed states for a many-particle system. The relative entropy of correlation is identical to the concept of correlation entropy developed by quantum chemists several years ago, which is defined by the deviation from Hartree-Fock approximations.

With the extended Hubbard model, we are able to study the dependence of entanglement between sites and electronic quantum correlation on dynamic parameters, via which we have clarified the physical meaning of entanglement between modes (sites) and quantum correlation between identical particles. The former is determined by the inter-site coupling via exchange of particles, while the latter is determined by the effective two-particle interaction. This identical-particle correlation measure may be used to study strongly correlated system.

Moreover, we have introduced the "subspace-restricted entanglement" and "subspace-restricted quantum correlation" between particles for a composite system whose physical Hilbert space reduces to a specific structure due to superselection rules and/or space-time boundary conditions. With such a measure we have studied the evolution of entanglement between qubits (encoded by localized electron spins) during an adiabatic two-qubit operation. The results and methods presented in this paper should prove useful for understanding entanglement-related issues for composite systems containing identical particles, especially in scalable solid-state quantum computer architectures.
Calculation of Gate Potential Profile

In this appendix we present calculation of gate potential profile for the quantum computer design shown in Fig. 2.1.

We start from the profile with a single gate electrode in each period. We want to solve the partial differential equation (PDE)

$$[-\nabla^2 + V(x, z)]\phi(x, z) = 0 \quad (A.1)$$

with the following boundary conditions (BC’s):

$$\phi(x, L) = \phi_0 \quad \text{for all } x.$$  

$$V(x, z) = \begin{cases} 
U_0 \gg 1 & \text{for } |x| < d/2 \text{ and } 0 < z < t, \\
0 & \text{otherwise}. 
\end{cases} \quad (A.2)$$

$$\phi(x, -b) = \phi_1 \quad \text{for all } x.$$  

The system has reflection symmetry about $x = 0$ and is periodic in the $x$ direction with period $p$. We divide the system into three regions:

(i) $t < z < L$ (the region above gate electrodes), we have

$$\phi_I(x, z) = \sum_n \cos(n) D_n [e^{-k_n(z-t)} - e^{k_n(z+t-2L)}] + \phi_0 + D_0(z - L) \quad (A.3)$$

with $k_n = 2\pi n/p; n = 0, 1, 2 \cdots$.

(ii) $0 < z < t$ (the region with gate electrodes inside), we have

$$\phi_{II}(x, z) = \sum_m \beta_m(x) [B_m e^{-q_m z} + C_m e^{q_m(z-t)}] \quad (A.4)$$
where the basis functions \( \beta_m(x) \) must satisfy the 1D Schrödinger equation,

\[
[-\partial_x^2 + V(x)]\beta_m(x) = q_m^2 \beta_m(x). \tag{A.5}
\]

Writing \( \beta_m(x) \) in the form

\[
\beta_m(x) = \sum_n F_{nm} S_n \cos(k_n x); \quad S_n = \frac{1}{\sqrt{p}} \left[ \sqrt{2}(1 - \delta_{n0}) + \delta_{n0} \right]. \tag{A.6}
\]

then \( F_{nm} \) can be obtained numerically by solving the eigenvalue problem

\[
\sum_n' [k_n^2 \delta_{nn'} + V_{nn'}] F_{n'm} = q_m^2 F_{nm}. \tag{A.7}
\]

where

\[
V_{nn'} = U_0 S_n S_{n'} \int_{-d/2}^{d/2} \cos(k_n x) \cos(k_{n'} x) dx = U_0 S_n S_{n'} \left[ \frac{\sin((k_n + k_{n'})d/2)}{(k_n + k_{n'})} + \frac{\sin((k_{n'} - k_n)d/2)}{(k_{n'} - k_n)} \right]. \tag{A.8}
\]

(iii) \(-b < z < 0\) (the region below gate electrodes), we have

\[
\phi_{III}(x, z) = \sum_n \cos(k_n x) A_n [e^{k_n z} - e^{-k_n(z+2b)}] + A_0(z + b) + \phi_1. \tag{A.9}
\]

The coefficients are determined by the following BC’s:

(i) At \( z = t \), we have

\[
S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \phi_{II}(x, t) dx
= S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \phi_{I}(x, t) dx
\Rightarrow S_n \sum_m F_{nm} [B_m e^{-q_m t} + C_m] = D_n (1 - e^{-2k_n(L-t)})
+ \delta_{n0} [\phi_0 + D_0(t - L)]. \tag{A.10}
\]

Use \( \epsilon_I E_I \cdot \hat{z} = \epsilon_{II} E_{II} \cdot \hat{z} \), we have

\[
\epsilon_{II} S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \partial_z \phi_{II}(x, t) dx
\]
\[
\epsilon S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \partial_z \phi_I(x, t) \, dx
\]

\[
\Rightarrow \eta S_n \sum_m F_{nm} q_m [-B_m e^{-q_n t} + C_m]
\]

\[
= -D_n (1 + e^{-2k_n (L-t)}) k_n + D_0 \delta_{n0}.
\]

(A.11)

where \( \eta \equiv \epsilon_{II}/\epsilon_I \). Eliminating \( D_n \) (including \( D_0 \)) by combining the above two equations yields

\[
S_n \sum_m F_{nm} \left\{ \left[ 1 + e^{-2k_n (L-t)} \right] \left[ B_m e^{-q_n t} + C_m \right] + q_m \left[ (1 - e^{-2k_n (L-t)}) \eta/k_n \right] \left[ -B_m e^{-q_n t} + C_m \right] \right\}
\]

\[
= 2 \phi_0 \delta_{n,0}.
\]

(A.12)

where it is understood that \( \left[ (1 - e^{-2k_n (L-t)}) \eta/k_n \right] \) is replaced by \( 2 \eta (L-t) \) for \( n = 0 \).

(ii) At \( z = 0 \), we have

\[
\epsilon_{II} S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \phi_{II}(x, 0) \, dx
\]

\[
= \epsilon_{II} S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \phi_{III}(x, 0) \, dx
\]

\[
\Rightarrow S_n \sum_m F_{nm} [B_m + C_m e^{-q_n t}]
\]

\[
= A_n (1 - e^{-2k_n b}) + \delta_{n0} [A_0 b + \phi_1].
\]

(A.13)

\[
\epsilon_{II} S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \partial_z \phi_{II}(x, 0) \, dx
\]

\[
= \epsilon_{III} S_n^2 \int_{-p/2}^{p/2} \cos(k_n x) \partial_z \phi_{III}(x, 0) \, dx
\]

\[
\Rightarrow \zeta_S \sum_m F_{nm} q_m [-B_m + C_m e^{-q_n t}]
\]

\[
= A_n (1 + e^{-2k_n b}) k_n + A_0 \delta_{n0}.
\]

(A.14)
where $\zeta \equiv \epsilon_{II}/\epsilon_{III}$. Eliminating $A_n$ (including $A_0$) by combining the above two equations yields

$$S_n \sum_m F_{nm} \{ (1 + e^{-2k_n b}) [B_m + C_m e^{-q_m t}] - q_m [(1 - e^{-2k_n b}) \zeta/k_n] [-B_m + C_m e^{-q_m t}] \} = 2\phi_1 \delta_{n,0}. $$

(A.15)

where it is understood that $[(1 - e^{-2k_n b}) \zeta/k_n]$ is replaced by $2\zeta b$ for $n = 0$.

Eqs. (A.12) and (A.15) constitute a set of coupled linear equations for the coefficients $B_m$ and $C_m$, which can be solved numerically.

Now we double the period of the system ($-2p < x < 2p$) and raise the voltage on the strip with $|x| < d/2$ (within the first period) by $V_c$ and the strip with $2p - d/2 < |x| < 2p$ by $V_g$, and similarly for all other periods. The solution to $\phi(x, z)$ in regions I and III are written in the same form as the case with $V_g = 0$, except that $k'_n$s are replaced by $k'_n, \pi n/2p; n = 0, 1, 2 \cdots$ and the unknown coefficients are denoted $A'_n$ and $D'_n$. In region II, we need a set of basis functions

$$\beta'_n(x) = \sum_n F'_{nm} S'_n \cos(k'_n x); \quad S'_n = \frac{1}{2\sqrt{p}} \left[ \sqrt{2}(1 - \delta_{n0}) + \delta_{n0} \right].$$

(A.16)

where $F'_{nm}$ are solved similarly as in the $V_g = 0$ case with

$$V_{nn'} = U_0 S_n S'_n 2 \int_0^{d/2} \cos(k'_n x) \cos(k'_n' x) dx$$

$$+ \int_{p-d/2}^{p+d/2} \cos(k'_n x) \cos(k'_n' x) dx$$

$$+ \int_{2p-d/2}^{2p} \cos(k'_n x) \cos(k'_n' x) dx$$

$$= U_0 \delta_{n,n'} + U_0 S_n S'_n \left\{ \frac{\sin(k'_n + k'_n') d/2}{(k'_n + k'_n')} + \frac{\sin(k'_n - k'_n') d/2}{(k'_n - k'_n')} \right.$$ 

$$- \frac{\sin((k'_n + k'_n') (p-d/2))}{(k'_n + k'_n')} - \frac{\sin((k'_n - k'_n') (p-d/2))}{(k'_n - k'_n')}$$

$$+ \frac{\sin((k'_n + k'_n') (p+d/2))}{(k'_n + k'_n')} + \frac{\sin((k'_n - k'_n') (p+d/2))}{(k'_n - k'_n')}$$

$$- \frac{\sin((k'_n + k'_n') (2p-d/2))}{(k'_n + k'_n')} - \frac{\sin((k'_n - k'_n') (2p-d/2))}{(k'_n - k'_n')} \right\}.$$

(A.17)
Furthermore, we add a particular solution defined as

\[ \phi_p(x) = \begin{cases} V_c & \text{for } |x| < d/2 \\ \frac{V_c}{p-d} |x| - \frac{d}{2} & \text{for } d/2 < |x| < p - d/2 \\ 0 & \text{for } p - d/2 < |x| < p + d/2 \\ \frac{V_g |x| - p - d/2}{p-d} & \text{for } p + d/2 < |x| < 2p - d/2 \\ V_g & \text{for } 2p - d/2 < |x| < 2p. \end{cases} \]

Note that \( \phi_p(x) \) satisfies the homogeneous PDE and it leads to correct potential difference between the adjacent metallic strips in region II. Thus, the potential function in region II takes the form

\[ \phi_{II}(x, z) = \phi_p(x) + \sum_m \beta_m(x) \left[ B_m e^{-m\pi z/2p} + C_m e^{m\pi (z-t)/2p} \right]. \tag{A.18} \]

After matching the boundary conditions, we obtain two sets of coupled equations similar to Eqs. (A12) and (A15), except that we subtract a term \([1 + e^{-2k_n(L-t)}] F_{pm} \) and \([1 + e^{-2k_n} b] F_{pm} \) from the right hand sides of these equations.

\[ F_{pm} \equiv S_n^2 \int_{-2p}^{2p} \cos(k_n x) \phi_p(x) dx \]

\[ = 2V_c S_n^2 \left\{ \sin\left[ k_n'(p - d/2) \right] \right\} \]

\[ + \frac{d}{2(p-d)} \left[ \sin\left[ k_n'(p - d/2) \right] - \sin\left( k_n'd/2 \right) \right] \]

\[ - \frac{1}{p-d} \left[ x \sin k_n' x + \cos k_n' x \right]_{d/2}^{p-d/2} / k_n' \]

\[ + V_g \delta_{n0} - 2V_g S_n^2 \left\{ \sin\left[ k_n'(p + d/2) \right] \right\} \]

\[ + \frac{2p - d/2}{(p-d)} \left[ \sin\left[ k_n'(2p - d/2) \right] - \sin(k_n'(p + d/2)) \right] \]

\[ - \frac{1}{p-d} \left[ x \sin k_n' x + \cos k_n' x \right]_{p+d/2}^{2p-d/2} / k_n'. \tag{A.19} \]

The region \(-a < z < 0\) is now filled with a dielectric \((\text{Si}_3\text{N}_4)\) with dielectric constant \(\epsilon_a\) (the dielectric screening constants for the silicon layer and SiGe layer are close to each other, so we ignore their differences and use
\( \epsilon \simeq 12 \). In this region, the potential function is replaced by

\[
\phi_a(x, z) = \sum_n \cos(k'_n x) [\bar{A}_n e^{k'_n z} - R_n e^{-k'_n(z+2a)}] + \bar{A}_0(z + a) + \phi_a. \tag{A.20}
\]

Matching \( \phi_a(x, z) \) with \( \phi_{III}(x, z) \) at boundary \( z = -a \) gives

\[
\bar{A}_n = [\xi(1 + \gamma) + (1 - \gamma)] A'_n / 2 \equiv \chi^+ A'_n, \]
\[
R_n = [\xi(1 + \gamma) - (1 - \gamma)] A'_n / 2 \equiv \chi^- A'_n, \tag{A.21}
\]

and

\[
\phi_a = A'_0(b - a) + \phi_1, \quad \bar{A}_0 = \xi A'_0. \tag{A.22}
\]

where \( \gamma = e^{-2k'_n(b - a)} \) and \( \xi = \epsilon_{III}/\epsilon_a \).

Matching \( \phi_a(x, z) \) with \( \phi_{II}(x, z) \) at boundary \( z = 0 \) gives

\[
S_n \sum_m F'_{nm} \{ (\chi^+ + \chi^- e^{-2k'_n a})[B'_m + C'_m e^{-\eta'_m t}] - q'_m (\chi^+ - \chi^- e^{-2k'_n a}) \zeta/k'_n] [B'_m + C'_m e^{-\eta'_m t}] \}
= 2\phi_a \delta_{n,0} - [\chi^+ + \chi^- e^{-2k'_n a}] F_{pn}. \tag{A.23}
\]

where \( \zeta = \epsilon_{II}/\epsilon_a \). It is understood that \( (\chi^+ - \chi^- e^{-2k'_n a}) \zeta/k'_n \) will be replaced by \( 2\zeta[b + (\xi - 1)a] \) for \( n = 0 \).
In this appendix we present calculations of integrals involved in Chap. 6, where single-valley hydrogenic effective mass equation is employed.

We denote the basis function as

\[ |\alpha_m \rangle = \exp[-\alpha(y^2 + z^2)] \times \sqrt{2} \frac{m^* \pi}{L} \sin \left[ \frac{m \pi}{L} (x + L/2) \right] \]  

(B.1)

where the artificial confining box expands \([-L/2, L/2]\]. \(m=1, 2, ..., n_x\), where \(n_x\) the number of basis functions along x axis.

The overlap is simply given by

\[ \langle \alpha_m | \alpha'_{m'} \rangle = \langle \alpha | \alpha' \rangle \frac{\pi}{\alpha + \alpha'} \delta_{mm'} \]  

(B.2)

The kinetic energy term can also be calculated analytically:

\[ \langle \alpha_m | T | \alpha'_{m'} \rangle = \frac{\hbar^2}{2m^*} \left[ -\frac{4\alpha \alpha'}{\alpha + \alpha'} \langle \alpha | \alpha' \rangle + \frac{m^2 \pi^2}{L^2} \right] \delta_{mm'} \]  

(B.3)

The matrix element for a uniform electric field \((-eFx\) along x-axis is also straightforward:

\[ \langle \alpha_m | -eFx | \alpha'_{m'} \rangle = -eF \langle \alpha | \alpha' \rangle \times 2 \int_0^1 dx \sin(m\pi x) \sin(m'\pi x)(x - 1/2) \]

\[ = \begin{cases} 0 & \text{if } m+m' \text{ even} \\ -eFL \langle \alpha | \alpha' \rangle \times \frac{2}{\pi^2} \frac{4mm'}{(m^2-m'^2)^2} & \text{if } m+m' \text{ odd.} \end{cases} \]  

(B.4)

The potential energy term for a donor ion at \((x_0, 0, 0)\) can be simplified via the help of the integral

\[ \frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^{+\infty} dq \exp(-q^2r^2) \]  

(B.5)

Explicitly, for the Coulomb potential \(V(x_0) = -1/\sqrt{(x-x_0)^2 + y^2 + z^2}\),
we have

\[
\langle \alpha m | V(x_0) | \alpha' m' \rangle = -2 \int_0^1 dx \sin(m\pi x) \sin(m'\pi x) \times \frac{2}{\sqrt{\pi}} \int_0^{+\infty} dq \frac{\pi}{q^2 + \alpha + \alpha'} \exp[-q^2(x - x_0)^2]. \tag{B.6}
\]

The integration over q turns out an error function

\[
\int_0^{+\infty} \exp(-q^2(x - x_0)^2) dq = \frac{\pi}{\bar{\alpha}} \left[ 1 - erf(\sqrt{\bar{\alpha}}|x - x_0|) \right] \exp(\bar{\alpha}|x - x_0|^2). \tag{B.7}
\]

where \( \bar{\alpha} = \alpha + \alpha' \) and the error function is defined as \( erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \).

Using the relation of trigonometric functions, we only need to evaluate the following simple type of one-dimensional integral

\[
\int_0^1 f(|x - x_0|) \cos(\bar{m}\pi x) dx \tag{B.8}
\]

which can process collectively via the Fast Fourier Transform for \( \bar{m} = 0, ..., 2n_x \).

The matrix elements for mutual Coulomb interaction \( V_{ee}(|\mathbf{r}_1 - \mathbf{r}_2|) = 1/|\mathbf{r}_1 - \mathbf{r}_2| \) involve more complicated calculations. We can also simplify the 6-dimensional integral via the integral expression Eq. (B.5) into one-dimensional after lengthy derivations. We first integrate the Gaussian-type integrals involving coordinates \( y_1, y_2, z_1 \) and \( z_2 \), after which the matrix element is reduced to 3-dimensional on \( x_1, x_2 \) and \( q \). Explicitly, we have (we omit for simplicity the coefficients that can be pulled outside the integrand)

\[
\langle \alpha_1 m_1, \alpha_2 m_2 | V_{ee} | \alpha_1' m_1', \alpha_2' m_2' \rangle \sim \int_0^1 \int_0^1 dx_1 dx_2 \sin(m_1\pi x_1) \sin(m_1'\pi x_1) \times \sin(m_2\pi x_2) \sin(m_2'\pi x_2) \times \int_0^{+\infty} dq \frac{1}{q^2 + \bar{\alpha}} \exp(-q^2(x_1 - x_2)^2) \tag{B.9}
\]

where \( \bar{\alpha} = (\alpha_1 + \alpha'_1)(\alpha_2 + \alpha'_2)/(\alpha_1 + \alpha'_1 + \alpha_2 + \alpha'_2) \).

Again, the integral over \( q \) can be expressed via Eq. (B.5). We are left with a two-dimensional integral

\[
I(\bar{\alpha}, \bar{m}_1, \bar{m}_2) \sim \int_0^1 dz_1 \int_0^1 dz_2 f(\sqrt{\bar{\alpha}}|z_1 - z_2|) \cos(\bar{m}_1\pi z_1) \cos(\bar{m}_2\pi z_2). \tag{B.10}
\]

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The above integral can be reduced to linear combinations of one-dimensional integrals [via changing of variables $u = (x_1 + x_2)/2$ and $v = (x_1 - x_2)/2$] in the following forms
\[
\int_0^1 g_1(t) \sin(n\pi t) dt \quad \text{or} \quad \int_0^1 g_2(t) \cos(n\pi t) dt;
\]
with $n$ varying from 0 to $2n_x$.

Both of the above integrals can be collectively processed with Fast Fourier Transforms.
In this chapter we calculate the involved integrals in evaluating the matrix elements of Sec. IV of Chap.6 (effect of perpendicular electric field).

We write the basis function as

$$|\alpha m\rangle_\mu = \exp[-\alpha(y^2 + (x - \mu x_0)^2)] \times \sqrt{\frac{2}{L}} \sin[\frac{m^*\pi}{L}(z + L/2)]$$ (C.1)

where $\mu = +$ or $-$ labels the basis centered at the right or left donor along x axis, respectively. The confining box along z axis expands $[-L/2, L/2]$.

The overlap and kinetic energy term for the basis functions with the same center ($\mu \langle\alpha m|\alpha' m'\rangle_\mu$ and $\mu \langle\alpha m|T|\alpha' m'\rangle_\mu$) have the same expressions as those in Appendix B. The overlap between differently-centered basis functions is given by

$$+\langle\alpha m|\alpha' m'\rangle_- = +\langle\alpha|\alpha'\rangle_-\delta_{mm'} = \frac{\pi}{\alpha + \alpha'} \exp(-\tilde{\alpha} x_0^2)\delta_{mm'}$$ (C.2)

where $\tilde{\alpha} = 4\alpha\alpha'/(\alpha + \alpha')$.

The kinetic energy term between differently-centered basis functions can be reduced to

$$+\langle\alpha m|T|\alpha' m'\rangle_- = \frac{\hbar^2}{2m*}\{\tilde{\alpha}[1 + (\tilde{\alpha} - 2\tilde{\alpha})x_0^2] + \langle\alpha|\alpha'\rangle_- + \frac{m^2\pi^2}{L^2}\} \delta_{mm'}$$ (C.3)

where $\tilde{\alpha} = \alpha + \alpha'$.

The donor ion potential term and e-e mutual interaction term are more complicated than for the basis functions in Appendix B. However, similarly, we can reduce them to a series of Fast Fourier Transforms, inside which there only involves a one-dimensional integral that cannot be evaluated analytically. We can solved those one-dimension integral with Gaussian Quadrature numerical approach.
The fortran code presented here was used to calculate the multi-valley e-e mutual interaction term Eq. (7.2) relevant for chapter 7. The following code calculates the e-e interaction integrals involving a four-dimensional integral over $y_1$, $y_2$, $z_1$ and $z_2$. The left integration over $x_1$ and $x_2$ can be reduced to a series of one-dimensional Fast Fourier Transforms, similar to the way in Appendix B.

```fortran
  do 330 j=1,n2r
  do 330 i=1,j
    ij=(j-1)*n2r+i
    sij=gr(i)+gr(j)
  do 330 kq=1,n2r
  do 330 kp=1,kq
    kpq=(kq-1)*n2r+kp
    spq=gr(kp)+gr(kq)
    if (ij.le.kpq) then
      nn=(kpq-1)*nvr+ij
      vv(nn)=v(i)*v(j)*v(kp)*v(kq)
      smgr(nn)=(sij+spq)*vbox**2
      ttgr(nn)=vbox**2/(1.D0/sij+1.D0/spq)
    endif
  330 continue
  end do
  end do
  do j=1,n2r
  do i=1,j
    ij=(j-1)*n2r+i
    sug(ij)= (gr(i)+gr(j))*vbox**2
  end do
  end do
```

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wqx(j)=gxn(j)/(1.D0-gxn(j))
end do
Do 340 j2=1,n2r
do 340 i2=1,j2
do 340 j1=1,j2
do 340 i1=1,j1
ij2=(j2-1)*n2r+i2
ij1=(j1-1)*n2r+i1
if(ij1.gt.ij2) goto 340

k=(ij2-1)*nvr+ij1 ! nvr=n2r*n2r
va=ttgr(k)
vq1=sug(ij1)
vq2=sug(ij2)
vc=smgr(k)
CALL Cdix(nr,nve,i1,j1,ke1,kx1)
CALL Cdix(nr,nve,i2,j2,ke2,kx2)

kex=ke1+ke2
do mq=1,N
CALL CCtm(ke1,kx1,ke2,kx2,wqx(mq),fc0)

Qvr(k,mq)=fc0*2.D0*pi*dsqrt(xi)*vbox**(3+kex)
&/smgr(k)/vv(k)
end do
340 continue

!$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
subroutine CCtm(je1,jx1,je2,jx2,x,fx)
implicit real*8(a-h,o-z)
parameter(N=300)
dimension pra(0:2,0:2),prb(0:2,0:2),prc(0:2,0:2),pre(0:2,0:2)
dimension prd(0:2,0:2)
dimension wa1(0:2,0:2),wb1(0:2,0:2),wa2(0:2,0:2),wb2(0:2,0:2)

fx=0.D0

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If (mod(je1+je2,2).eq.0.AND.mod(jx1+jx2,2).eq.0) then
  CALL Ceum (x,pra,prb,prc,prd,pre)
  if(je1.eq.0.AND.je2.eq.0) fx=pra (jx1,jx2)
  if(je1.eq.2.AND.je2.eq.0) fx=prb (jx1,jx2)
  if(je1.eq.0.AND.je2.eq.2) fx=prd (jx1,jx2)
  if(je1.eq.2.AND.je2.eq.2) fx=prc (jx1,jx2)
  if(je1.eq.1.AND.je2.eq.1) fx=pre (jx1,jx2)
endif
If (mod(je1+je2,2).eq.1.AND.mod(jx1+jx2,2).eq.1) then
  CALL Coum (x,wa1,wb1)
  if(je1.eq.1.AND.je2.eq.0) fx=wa1(jx1,jx2)
  if(je1.eq.1.AND.je2.eq.2) fx=wb1(jx1,jx2)
  tup1=vq1
  tup2=vq2
  vq1=tup2
  vq2=tup1
  CALL Coum(x,wa2,wb2)
  vq1=tup1
  vq2=tup2
  if(je1.eq.0.AND.je2.eq.1) fx=wa2(jx2,jx1)
  if(je1.eq.2.AND.je2.eq.1) fx=wb2(jx2,jx1)
endif
return
end

**********************************************************************
subroutine Coum(qx,ua,ub)
  implicit real*8(a-h,o-z)
  parameter(N=300)
  common /parg/gxn(N),gw(N)
  dimension qk(4),uq(4),rea(4),ua(0:2,0:2),ub(0:2,0:2),pw1(4),pw2(4)

  do l=2,3
    qk(l)=dsqrt(vv0)
  end do
\( q_k(1)=0.0 \)
\( q_k(4)=-\sqrt{v_0} \)

do 11=0,2
do 12=0,2
ua(11,12)=0.0

c----- z1
ub(11,12)=0.0

c------ z1*z2**2
end do
end do

do i=1,N
rsq0=gxn(i)
rsq1=1.0-rsq0
ts0=gxn(i)**2
rs1=(1.0-gxn(i))**2

cwf=ts0+va*ts1/xi
tq2=0.5D0*ts1/(ts0+ts1*vq2/xi)
trp=vc/xi*cwf/(ts0+vq2/xi*ts1)

tew=gw(i)*(rsq1/rsq0)*dexp(-0.25D0*qx**2*ts1/ts0)
&/dsqrt(ts0+va*ts1)/dsqrt(cwf)

c------ factor 2.*pi**3/vc out
uq(1)=dsqrt(vv0/trp)
uq(2)=(1.0-tmd)*uq(1)
uq(3)=(2.0-tmd)*uq(1)
uq(4)=tmd*uq(1)

do j=1,4
rea(j)=dexp(-uq(j)**2-2.0D0*tq2*qk(j)**2)
pw1(j)=uq(j)/dsqrt(trp)*rea(j)
pw2(j)=((1.0-4.0D0*qk(j)**2*tq2)*tq2*pw1(j)
&+qk(j)*(1.0-tmd)*2.0D0*tq2/trp*fwe2(uq(j))
&-(1.0-tmd)**2/trp**1.5D0*fwe3(uq(j)))+rea(j)
end do
c----- imaginary part

ua(0,1)=ua(0,1)+tew*0.25D0*(pw1(2)+0.5D0*(pw1(3)-pw1(4)))
ub(0,1)=ub(0,1)+tew*0.25D0*(pw2(2)+0.5D0*(pw2(3)-pw2(4)))

!*******************************************************************
Subroutine Cdix(kwr,kwe,iw,jw,iet,ixt)
implicit real*8 (a-h,o-z)
intrinsic mod

iu=0
If (mod(iw,kwr).gt.kwe.OR.(iw.eq.kwr.OR.iw.eq.2*kwr)) iu=1
If (iw.le.kwe.OR.iw.gt.kwr+kwe) then
iv=0
else
iv=1
endif

ju=0
If (mod(jw,kwr).gt.kwe.OR.(jw.eq.kwr.OR.jw.eq.2*kwr)) ju=1
If (jw.le.kwe.OR.jw.gt.kwr+kwe) then
jv=0
else

ua(2,1)=ua(2,1)+tew*0.25D0*(pw1(2)-0.5D0*(pw1(3)-pw1(4)))
ub(2,1)=ub(2,1)+tew*0.25D0*(pw2(2)-0.5D0*(pw2(3)-pw2(4)))

c------sscs

ua(1,0)=ua(1,0)+tew*0.25D0*(pw1(1)+0.5D0*(pw1(3)+pw1(4)))
ub(1,0)=ub(1,0)+tew*0.25D0*(pw2(1)+0.5D0*(pw2(3)+pw2(4)))

c------cscc

ua(1,2)=ua(1,2)+tew*0.25D0*(pw1(1)-0.5D0*(pw1(3)+pw1(4)))
ub(1,2)=ub(1,2)+tew*0.25D0*(pw2(1)-0.5D0*(pw2(3)+pw2(4)))

end do
return
end

ua(1,0)=ua(1,0)+tew*0.25D0*(pw1(1)+0.5D0*(pw1(3)+pw1(4)))
ub(1,0)=ub(1,0)+tew*0.25D0*(pw2(1)+0.5D0*(pw2(3)+pw2(4)))

c------csss
end do
return
end
jv=1
endif
iet=iu+ju
ixt=iv+jv
return
end

!******************************************************************
References


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[129] A. Messiah, Quantum Mechanics (Dover, New York, 1999), P750.


[141] B. Koiller, private communication.


Curriculum Vitae

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Quantum Computation With Electron Spins
Of Phosphorous Donors In Silicon
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Publications

1. David M.-T. Kuo, Angbo Fang and Y. C. Chang,
   *Theoretical modelling of dark current and photo-response for quantum well and quantum dot infrared detectors*,

2. Angbo Fang, Y. C. Chang and J. R. Tucker,
   *Effects of J-gate potential and uniform electric field on a coupled donor pair in Si for quantum computing*,

3. Angbo Fang and Y. C. Chang,
   *Entanglement and correlation for identical particles in quantum computing*,

Preprint

Angbo Fang, Y. C. Chang and J. R. Tucker,
*Simulation of Si:P spin-based quantum computer architecture*,