Quantum Computing Simulation of the Hydrogen Molecule System with Rigorous Quantum Circuit Derivations

Yili Zhang
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ABSTRACT

Quantum Computing Simulation of the Hydrogen Molecule System with Rigorous Quantum Circuit Derivations

by

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Utah State University, 2022

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Quantum computing has been an emerging technology in the past few decades. It utilizes the power of programmable quantum devices to perform computation, which can solve complex problems in a feasible time that is impossible with classical computers. Simulating quantum chemical systems using quantum computers is one of the most active research fields in quantum computing. However, due to the novelty of the technology and concept, most materials in the literature are not accessible for newbies in the field and sometimes can cause ambiguity for practitioners due to missing details.

This report provides a rigorous derivation of simulating quantum chemistry systems using quantum computers. The Hydrogen molecule is used as an example throughout the process to make it readable to a broader audience. Specifically, the ground state energies and the first-excited energies of the Hydrogen molecule, as well as the ground state energies of the Lithium Hydride molecule at different bond lengths under the governing of their corresponding Hamiltonians are explored through the Schrodinger’s equation, the Phase Estimation Algorithm (PEA), the second quantization, the Bravyi-Kitaev transformation (BKT), and the Hamiltonian establishment. Then, a quantum circuit is built from scratch based on the second-quantization and BKT Hamiltonian to demonstrate the process of quantum circuit derivation for quantum chemistry system. Lastly, Simulations on both the
ground and excited state energies of the Hydrogen molecule and the ground state energies of the Lithium Hydride molecule are carried out based on the design of the circuits with Google’s Cirq quantum simulator. Finally, some quantitative and qualitative comparisons and analysis are conducted with the results.
DEDICATION

To my mother, Junling Pang. Thanks for your unconditional love and support in both my life and career. I love you forever.
# CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
</tr>
<tr>
<td>DEDICATION</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
</tr>
<tr>
<td>1 Introduction</td>
</tr>
<tr>
<td>1.1 Quantum computing</td>
</tr>
<tr>
<td>1.2 Quantum algorithms</td>
</tr>
<tr>
<td>1.3 Quantum chemistry on a quantum computer</td>
</tr>
<tr>
<td>1.4 Qubits and vector notations of quantum states</td>
</tr>
<tr>
<td>1.5 Quantum probabilities and statistics</td>
</tr>
<tr>
<td>1.6 Schrodinger’s equation</td>
</tr>
<tr>
<td>1.7 Motivation of this study</td>
</tr>
<tr>
<td>2 Quantization and Bravyi-Kitaev Transformation for the Quantum Hamiltonian</td>
</tr>
<tr>
<td>2.1 First and second quantization</td>
</tr>
<tr>
<td>2.2 Bravyi-Kitaev transformation</td>
</tr>
<tr>
<td>2.2.1 Mathematical background</td>
</tr>
<tr>
<td>2.2.2 Occupation number basis transformation</td>
</tr>
<tr>
<td>2.2.3 Parity basis transformation</td>
</tr>
<tr>
<td>2.2.4 Bravyi-Kitaev basis transformation</td>
</tr>
<tr>
<td>2.2.4.1 Basis encoding</td>
</tr>
<tr>
<td>2.2.4.2 Parity set</td>
</tr>
<tr>
<td>2.2.4.3 Update set</td>
</tr>
<tr>
<td>2.2.4.4 Flip set</td>
</tr>
<tr>
<td>2.2.5 Representing creator and annihilator operation on qubits</td>
</tr>
<tr>
<td>2.2.5.1 Even index case</td>
</tr>
<tr>
<td>2.2.5.2 Odd index case</td>
</tr>
<tr>
<td>2.3 Bravyi-Kitaev transformation for the Hydrogen molecule Hamiltonian</td>
</tr>
<tr>
<td>2.3.1 Number operator</td>
</tr>
<tr>
<td>2.3.2 Coulomb and exchange operator</td>
</tr>
<tr>
<td>2.3.3 Double excitation operator</td>
</tr>
<tr>
<td>2.3.4 Complete BK transformation for the Hydrogen molecule Hamiltonian</td>
</tr>
<tr>
<td>3 Quantum Circuits for the Hydrogen Molecule Hamiltonian</td>
</tr>
<tr>
<td>3.1 Background on exponentiation of tensor products between Pauli matrices</td>
</tr>
<tr>
<td>3.2 Exponentiation of tensor products between Pauli-Z matrices</td>
</tr>
<tr>
<td>3.2.1 One-qubit case</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Features of the first- and second-quantization.</td>
<td>10</td>
</tr>
<tr>
<td>2.2 The sets table.</td>
<td>31</td>
</tr>
<tr>
<td>2.3 Summary of Pauli matrices products.</td>
<td>40</td>
</tr>
<tr>
<td>2.4 The operator table.</td>
<td>45</td>
</tr>
<tr>
<td>4.1 Comparisons between minimum ground state energies and corresponding bond lengths in two studies.</td>
<td>71</td>
</tr>
<tr>
<td>4.2 Average absolute and relative differences of ground state energies between this and the Kolos et al. studies.</td>
<td>71</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Bloch sphere [1].</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Encode the Hydrogen molecule system on the Bravyi-Kitaev basis.</td>
<td>25</td>
</tr>
<tr>
<td>3.1 Circuit of exponentiation of the Pauli-Z matrix for one qubit.</td>
<td>50</td>
</tr>
<tr>
<td>3.2 Circuit of exponentiation of the tensor products between Pauli-Z matrix for two qubits.</td>
<td>51</td>
</tr>
<tr>
<td>3.3 Circuits of exponentiation of the products between Pauli-Z matrix for more than two qubits.</td>
<td>53</td>
</tr>
<tr>
<td>3.4 Circuit of exponentiation of the Pauli-X matrix for one qubit.</td>
<td>54</td>
</tr>
<tr>
<td>3.5 Circuit of exponentiation of the Pauli-Y matrix for one qubit.</td>
<td>56</td>
</tr>
<tr>
<td>3.6 Circuit of exponentiation of the tensor products between Pauli-X matrices and between Pauli-Y matrices for two qubits.</td>
<td>57</td>
</tr>
<tr>
<td>3.7 Circuit of exponentiation of the Pauli-I matrix for one qubit.</td>
<td>58</td>
</tr>
<tr>
<td>3.8 Circuit of exponentiation of the tensor products between Pauli-I matrices for two qubits.</td>
<td>59</td>
</tr>
<tr>
<td>3.9 Circuits of exponentiation of the products between Pauli-I matrix for more than two qubits.</td>
<td>60</td>
</tr>
<tr>
<td>3.10 Circuit of exponentiation of the tensor products between Pauli-Y and Pauli-X matrices for two qubits.</td>
<td>61</td>
</tr>
<tr>
<td>3.11 Circuits for Sub-Hamiltonians (a).</td>
<td>62</td>
</tr>
<tr>
<td>3.12 Circuits for Sub-Hamiltonians (b).</td>
<td>63</td>
</tr>
<tr>
<td>3.13 Circuit of the Hamiltonian.</td>
<td>64</td>
</tr>
<tr>
<td>3.14 Core circuit for one-qubit Phase Estimation Algorithm (PEA).</td>
<td>66</td>
</tr>
<tr>
<td>4.1 Ground state energy curves from this study and the Kolos et al. study in [2].</td>
<td>70</td>
</tr>
<tr>
<td>4.2 Ground state energy and excited state energy curves for the hydrogen molecule.</td>
<td>72</td>
</tr>
<tr>
<td>4.3 Ground state energy and excited state energy curves for the $LiH$.</td>
<td>73</td>
</tr>
</tbody>
</table>
CHAPTER 1

Introduction

1.1 Quantum computing

The idea of quantum computing originated in the 1980s, when Manin and Feynman independently described a vision for using a quantum mechanical system to perform computation [3, 4]. Quantum computers are quantum systems that can be initialized, sufficiently controlled, and measured in order to perform a computational task [5].

In the year of 2021, the biggest quantum computer is IBM’s 127-qubit processor [6]. However, due to the fact that most types of the quantum processors require a strict working environment, such as absolute zero temperature and near-zero noise level, the quantum hardware devices are used along with the classical computers in most of the current applications, such as the cloud access to the quantum computer. Essentially, any computational problems that can be solved by a classical computer can also, in principle, be solved by a quantum computer. However, there are certain problems that can be solved by the quantum computers with significantly lower time or space complexity, including but not limited to: (a) simulating the property of quantum systems [7]; (b) cryptography with the quantum key distribution (QKD); and (c) simulate the structure or dynamics of some chemistry molecules. And this is the informal definition of quantum supremacy. According to Aaronson et al. [8], Quantum supremacy is a clear quantum speedup for some tasks, motivated by the goal of overturning the Extended Church-Turing Thesis as confidently as possible, which is the goal of the majority of quantum computing developers nowadays.

In summary, quantum computers can easily outperform classical computers in tasks that have small input and output datasets but large amounts of computation to get from input to output [7].
1.2 Quantum algorithms

Quantum algorithms are the algorithms that run on a quantum computer and achieve a speedup, or other efficiency improvements, over any possible classical algorithm [9]. Most quantum algorithms are related to three quantum phenomena: superposition, interference, and entanglement. The superposition is the fact that a quantum particle is in the state of 0 and 1 at the same time. In addition, the quantum interference effects normally refer to the wave-like interference pattern experimentally generated by individually shooting the quantum particles through the two-slit board, and it was proved that the pattern could appear in the experiment with different types of quantum particles such as the photons or electrons. Lastly, the entanglement is a phenomenon in quantum that the global states of a composite system cannot be written as a product of the states of individual subsystems [10].

Serving for different purposes, there are different types of quantum algorithms. For example, the Grover’s algorithm can reduce the computational complexity from $O(N)$ to $O(\sqrt{N})$ in searching unstructured data. The intuition of the algorithm is simply to leverage the superposition property of quantum computing and repeatedly reflect the register about the state being searched for. Another popular quantum algorithm, the Shor’s algorithm, can reduce the computational complexity from exponential to polynomial for integer factorization tasks. Some important cryptographic algorithms, such as the RSA (Rivest–Shamir–Adleman), critically depend on the fact that prime factorization of large numbers takes a long time with the classically computational power, but the Shor’s algorithm can potentially endanger the functionality of such cryptography by leveraging the superposition, interference property of the quantum computing along with the Quantum Fourier Transform (QFT) algorithm [11].

Most of the quantum algorithms, including the ones just mentioned, are not very applicable with the limited scale of the current quantum processor. However, quantum annealing can be a very promising applicable algorithm within sight. Quantum annealing is a computing paradigm that has the ambitious goal of efficiently solving large-scale combinatorial optimization problems of practical importance [12]. The working principle of the quantum
annealer is based on the phenomenon that, as classical systems are slowly cooled, the configuration space density tends to condense in regions where the potential energy is small. If the cooling process is slow enough, then the system ultimately finds the physical arrangement that minimizes its potential energy. Hence, by assigning the function to be minimized to be the analog of the potential energy and some control parameter as the analog of temperature, the global minimum of a function can be found by simulating the annealing process as the "temperature" is taken to zero [13].

In summary, the quantum algorithm is currently an active research area, and its importance will thrive as the quantum hardware matures rapidly.

1.3 Quantum chemistry on a quantum computer

As the quantum computer continues to mature, it can solve many chemistry-related problems that are hard for the classical computer to solve because the quantum computers can aid those quantum chemistry computations that require an explicit representation of the wave function, either because of a high accuracy requirement of simulated properties or because of a high degree of entanglement in the system. In these cases, the exponential growth of the dimension of the wave function makes manipulation and storage very inefficient on a classical computer [14].

When it comes to quantum chemistry, the common issues to be solved are about simulating the chemistry system, in which the initial state of the chemistry system, the Hamiltonian and the period to be simulated are normally given, and the final state of the simulated system can be found by Schrodinger’s equation. In particular, when simulate the ground state of the chemistry system, the Phase Estimation Algorithm (PEA) may be needed besides the initial states and the Schrodinger’s equation, because PEA can be simulated in quantum computers to measure the phase evolution frequency of the chemistry system, which is directly related to the ground state energies of the chemistry system.

As of today, quantum computing has already demonstrated some successful examples on solving the chemistry molecule structure problems, but it is still in its early age of research, and more relevant algorithms are expected to be developed in the quantum chemistry
1.4 Qubits and vector notations of quantum states

Unlike classical computer where information is stored in bits (with 0 or 1 in each bit), quantum computers use qubits to encode the information. A qubit is a quantum analogy to bit but can store enormous information. A qubit is a state in a linear combinations of $|0\rangle$ and $|1\rangle$, i.e.,

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle, \quad \alpha, \beta \in \mathbb{C}, \quad |\alpha|^2 + |\beta|^2 = 1.$$  

(1.1)

We say the state $|\psi\rangle$ is a superposition of the two basis states $|0\rangle$ and $|1\rangle$. Here $\alpha$ and $\beta$ are known as the probability amplitudes. When this qubit is measured, $|\psi\rangle$ will collapse into the basis state $|0\rangle$ with a probability $|\alpha|^2$ and into the basis state $|1\rangle$ with a probability $|\beta|^2$.

We denote the two basis qubit states with vectors

$$|0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |1\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

so that the general qubit state in (1.1) can be denoted as

$$|\psi\rangle := \alpha |0\rangle + \beta |1\rangle = \begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$ 

Furthermore, the state of the single qubit can be represented in a three-dimensional sphere called the Bloch sphere, as shown in Fig. 1.1, where the state $|0\rangle$ and the state $|1\rangle$ are represented at the positive and the negative tips of the Z-axis in the Bloch sphere, respectively. The positive tip of the X-axis represents the state $|+\rangle$ and the negative tip of the X-axis represents the state $|−\rangle$, where

$$|+\rangle = \frac{|0\rangle + |1\rangle}{\sqrt{2}}$$

$$|−\rangle = \frac{|0\rangle - |1\rangle}{\sqrt{2}}$$
Moreover, the positive and the negative tips of the Y-axis represent the following states, respectively:

\[
\frac{|0\rangle + i|1\rangle}{\sqrt{2}} \\
\frac{|0\rangle - i|1\rangle}{\sqrt{2}}
\]

In general, $|\psi\rangle$ in the Bloch sphere represents a random state of the qubit, and it can be expressed in the following equation:

\[
|\psi\rangle = e^{i\gamma} \left( \cos \frac{\theta}{2} |0\rangle + e^{i\phi} \sin \frac{\theta}{2} |1\rangle \right)
\]

(1.2)

where the parameter $\theta$ determines the probabilities of the state $|\psi\rangle$ in $|0\rangle$ or $|1\rangle$ basis, while the parameter $|\phi\rangle$ is called the relative phase and can represent the phase status of the qubit. The $\gamma$ parameter is called the global phase, which has no physical significance and is normally ignored in applications. The Bloch sphere implies that the information a qubit can represent is essentially infinite, which makes the key difference between the bit and the qubit.

Fig. 1.1: Bloch sphere [1].
For quantum states in multiple qubits, the Kronecker product will be used. For example

\[ |00\rangle := |0\rangle \otimes |0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \]

In a similar manner, we can derive

\[ |01\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \quad |10\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \quad |11\rangle = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \]

So a general two-qubit state can be represented as

\[ |\psi\rangle = a |00\rangle + b |10\rangle + c |01\rangle + d |11\rangle, \quad a, b, c, d \in \mathbb{C}, \]

with further constraint \(|a|^2 + |b|^2 + |c|^2 + |d|^2 = 1\). Or, in the vector form, it is given as

\[ |\psi\rangle = \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix}, \quad a, b, c, d \in \mathbb{C}, \quad |a|^2 + |b|^2 + |c|^2 + |d|^2 = 1. \]

### 1.5 Quantum probabilities and statistics

In most of the quantum applications, the measurement on a quantum state \(|\psi\rangle\) is needed. In quantum computing, the measurement is normally noted as \(\langle M\rangle\), where \(M\) is the chosen measurement basis. For instance, \(\langle 0\rangle\) means measuring on the \(|0\rangle\) basis, and the results will be the probability of the quantum state being measured collapsing to the state \(|0\rangle\). In general, the probability of observing the state "M" as the measurement results for
a random quantum state $|\psi\rangle$ can be expressed as:

$$\Pr(M|\psi\rangle) = |\langle M|\psi\rangle|^2$$

(1.3)

For instance, assume the quantum state $|\psi\rangle$ is $|+\rangle$ and the measurement is $|0\rangle$ basis, then the probability of observing the state $|0\rangle$ as the measurement results for $|+\rangle$ can be calculated as below:

$$\Pr(0|+) = |\langle 0|+\rangle|^2 = \left| \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} \\frac{1}{\sqrt{2}} \end{bmatrix} \right|^2 = \left| 1 \cdot \frac{1}{\sqrt{2}} + 0 \cdot \frac{1}{\sqrt{2}} \right|^2 = \frac{1}{2} = \frac{1}{2}.\quad (1.4)$$

It is worth noting that the composite quantum state will collapse from a random state to a certain state after the measurement is carried out on the quantum state. Therefore, the state of a quantum system cannot be determined with a single measurement. Instead, in quantum computing, the state of a quantum system is inferred by the measurement on large number of systems which are identically prepared on the same state [15].

### 1.6 Schrodinger’s equation

The Schrodinger’s equation describes how the state of a quantum system state changes over time (i.e.: the derivative term on the left of the equation) under the governing of the corresponding Hamiltonian:

$$\frac{\partial}{\partial t} |\psi\rangle = -i\hat{H} |\psi\rangle.\quad (1.5)$$

In the hydrogen molecule system specifically, the state of the system $|\psi\rangle$ can be interpreted as the combination of the four orbitals in the system, $|\chi\rangle$, where:

$$|\chi_0\rangle = |\varphi_g\rangle |\alpha\rangle, \quad (1.6a)$$

$$|\chi_1\rangle = |\varphi_g\rangle |\beta\rangle, \quad (1.6b)$$

$$|\chi_2\rangle = |\varphi_u\rangle |\alpha\rangle, \quad (1.6c)$$

$$|\chi_3\rangle = |\varphi_u\rangle |\beta\rangle. \quad (1.6d)$$
and $|\varphi_g\rangle$ is the symmetric (low-energy) molecular spatial orbital, while $|\varphi_u\rangle$ is the anti-symmetric (high-energy) molecular spatial orbital. In addition, $|\alpha\rangle$ is the spin-down spin function, while $|\beta\rangle$ is the spin-up spin function. As a result, the combination of the two spatial functions and the two spin functions of the two electrons in the hydrogen molecule system can result in four distinguished orbitals in the system.

The Schrödinger’s equation in Eq. (1.5) is essentially a linear partial derivative equation (PDE). By solving the PDE, the state of the system $|\psi(x, t)\rangle$ can obtained after the evolution period $\Delta t$:

$$|\psi(x, t)\rangle = e^{-iH\Delta t}|\psi(x, 0)\rangle,$$

and most of the quantum chemistry simulation is heavily related to the results in Eq. (1.7).

### 1.7 Motivation of this study

In this study, the focus is on simulating the chemistry system with the quantum computing, because many chemistry systems are within the scale of quantum and exhibits quantum behaviors. The quantum computers can aid those quantum chemistry computations that requires an explicit representation of the wave function.

Specifically, to simulate the chemistry system with the quantum computing, the Schrödinger’s equation, Eq. 1.7, is mainly used, where the states of the chemistry system at different time can be represented by $|\psi\rangle$. They key to successfully simulate the quantum state of the chemistry system with the Schrodinger’s equation is to represent the Hamiltonian of the corresponding chemistry system in a quantum computational form, and that is where the quantization and the Bravyi-Kitaev transformation (BKT) approaches become useful. The quantization approaches, especially the second-quantization approach, can mathematically represent the physical Hamiltonian of the chemistry system, which is described in detail in Sec. 2.1. Then, with the Bravyi-Kitaev transformation (BKT), the creation ($a^\dagger$) and annihilation ($a^-$) operators from the second-quantization formula can be correctly and efficiently represented in the quantum computing framework, and the derivation process is thoroughly discussed in Sec. 2.2. With the second-quantization formula and the creation
(\text{a}^\dagger) \text{ and annihilation } (\text{a}^-) \text{ operators derived from the Bravyi-Kitaev transformation, the Hamiltonian as well as the state of the chemistry system can be explicitly represented in quantum computational form, and the details are summarized in Sec. 2.3. It is worth noting that, throughout the study, the Hydrogen molecule (H}_2\text{) is used as an example, for it is the simplest molecule and can help the audiences who are not familiar with the topics before understand the concepts and derivation processes better.}

With the quantum computational Hamiltonian and state of the chemistry system available, the simulation still cannot be carried out without the corresponding quantum circuits. Therefore, in Ch. 3, the method on deriving a ready-to-run quantum circuit for a Hamiltonian is demonstrated step by step.

After the quantum circuits for the corresponding chemistry system is ready, the simulation for the chemistry system can be carried out. In Ch. 4, the ground-state energies and the first-excited energies of the Hydrogen molecule (H}_2\text{) at different bond lengths are simulated, and the simulated results are qualitatively and quantitatively compared with the past published results to demonstrate the validity of the derived quantum Hamiltonian and circuits, as well as the correctness of the derivation procedures. In addition, the ground-state energies of the Lithium Hydride molecule (LiH) at different bond lengths are also simulated and the results are qualitatively evaluated to show that the proposed derivation procedures can also be extended to the simulation of other chemistry system besides the Hydrogen molecule (H}_2\text{).
CHAPTER 2
Quantization and Bravyi-Kitaev Transformation for the Quantum Hamiltonian

In this chapter, the process of deriving the energy Hamiltonian of the Hydrogen molecule system based on the second-quantization and the Bravyi-Kitaev transformation (BKT) is demonstrated in detail.

2.1 First and second quantization

Quantization in quantum computing is an approach to interpret the molecular Hamiltonians. There are generally two approaches with the development of quantum computing: first- and second- quantization, as summarized in Tab. 2.1.

<table>
<thead>
<tr>
<th></th>
<th>First-quantization</th>
<th>Second-quantization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavefunction encoded</td>
<td>continuous</td>
<td>quantized</td>
</tr>
<tr>
<td>Qubits needed</td>
<td>$3n$</td>
<td>$n$</td>
</tr>
<tr>
<td>Molecular Hamiltonian ($\hat{H}$)</td>
<td>$\sum_i \frac{p_i^2}{2m_i} + \sum_{i&lt;j} \frac{q_i q_j}{r_{ij}}$</td>
<td>$\sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$</td>
</tr>
</tbody>
</table>

According to Zalka et al. [16–18], in the first-quantization, particles are simulated under the governance of the Schrodinger’s equation on a grid in real space, where the particles are treated as wave functions. In the second quantization, the Born-Oppenheimer approximation (BOA) [19] is used to separate the electronic and nuclear motion in the purely electronic molecular problem [20]. In terms of the computational convenience, the major differences between the first- and the second quantization are as follows:

1. For simulating the same number of particles, the first quantized formation would require more qubits than the second one.
2. In simulating quantum particles, the wavefunction used in the second quantized formulation is quantized, while the wavefunction used in the first quantized formulation is continuous.

Due to the limited hardware capacity of the current quantum computers and the quantized nature of the chemistry systems, the second-quantization approach is more preferred in the field of quantum chemistry simulation. For those reasons, the second quantization is chosen in this study.

There is an essential assumption in the second-quantization called the Born-Oppenheimer approximation (BOA). It assumes the two nuclei in the Hydrogen molecule are fixed, and only the electron-relevant dynamics are considered in the simulation. Therefore, the electronic Hamiltonian of the Hydrogen molecule system in the second quantization form is as follows:

\[
H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_r^\dagger a_s a_s,
\]

(2.1)

where the first term simply counts how many electrons there are in the system, and then, for each electron, it adds the eigenvalue of the operator corresponding to the single electron state (the kinetic energy of each electron and the potential energies between each electron and each proton) the the electron occupies, and the corresponding parameter, \( h_{pq} \), is called the one-electron overlap integral. The second term calculates the transitions where the system starts with two electrons in orbitals \( r \) and \( s \), then ends up with two electrons in orbitals \( p \) and \( q \), and the corresponding parameter, \( h_{pqrs} \), is called the two-electron overlap integral. In addition, \( a_p^\dagger \) in the equation is called the creator, meaning there is an electron being created in the corresponding orbital, while \( a_p^- \) is called the annihilator, meaning there is an electron being destroyed in the corresponding orbital.

The Hamiltonian can be numerically represented with second-quantization and the Bravyi-Kitaev transformation (BKT) for the Hydrogen molecule.
2.2 Bravyi-Kitaev transformation

Bravyi-Kitaev transformation (BKT) is a method of representing the creation ($a^\dagger$) and annihilation ($a^-$) operations in a quantum computer correctly and efficiently. To do that, there are in general three steps. Firstly, the fermionic states in a quantum chemistry system is encoded with qubits in a Bravyi-Kitaev basis, and this process is called the Bravyi-Kitaev transformation. Secondly, by following the creation and annihilation operation rules in the transformed basis, the qubits operations are carried out to represent the corresponding fermionic operations. Lastly, the encoding can be inverted to obtain the actual fermionic operations.

In this section, some basic mathematical operation rules for the fermionic system are explained first. Then, by leveraging the Hydrogen molecule system as an example, two transformation basis, the occupation number and the parity basis, are illustrated in detail. Lastly, the Bravyi-Kitaev basis, which combines the two transformation basis, is demonstrated.

2.2.1 Mathematical background

Due to the Born-Oppenheimer approximation (BOA), only the electron-related operations are considered in simulating the Hydrogen molecule system. Specifically, a system of four qubits is used to represent the four orbitals in the Hydrogen molecule, and the tensor product of the four qubits can represent the state of the system, as indicated in Eq. (2.2).

$$|H_2\rangle = |q_0\rangle \otimes |q_1\rangle \otimes |q_2\rangle \otimes |q_3\rangle .$$

In the study of the chemistry system, a subspace of the full Fock space which is spanned by $2^n$ electronic basis state is considered. The electronic basis state can be represented as $|f_{n-1}f_{n-2}\cdots f_1f_0\rangle$, where $f_i \in \{0, 1\}$ is the occupation number of the orbital $i$. In addition, any interaction of a fermionic system can be expressed in terms of its product of the creation and annihilation operators $a_j^\dagger$ and $a_j^-$, for $j \in \{0, \cdots, n-1\}$. In the Hydrogen molecule specifically, since there are four orbitals in the system, its corresponding electronic basis
state would thus be $|f_3 f_2 f_1 f_0\rangle$ with $n = 4$.

Furthermore, there are two operation rules for the fermionic system. First of all, the rule for fermionic creation and annihilation operators is

$$a^\dagger |0\rangle = |1\rangle,$$  \hspace{1cm} (2.3a)  

$$a^\dagger |1\rangle = 0,$$ \hspace{1cm} (2.3b)  

$$a^- |0\rangle = 0,$$ \hspace{1cm} (2.3c)  

$$a^- |1\rangle = |0\rangle,$$ \hspace{1cm} (2.3d)  

where Eq. (2.3a) means if the original electronic orbital is empty, then by applying the creation operator $a^\dagger$ on the orbital, the orbital now contains one electron. Eq. (2.3b) means if the original electronic orbital is filled with one electron, then by applying the creation operator $a^\dagger$ on the orbital, the orbital turns the whole system into invalid and the algebraic 0 is used to represent this situation. This happens because of the Pauli exclusion principle [21], which claims that no quantum state can be occupied by more than one electron. Eq. (2.3c) means if the original electronic orbital is empty, then by applying the annihilation operator $a^-$ on the orbital, the orbital turns the whole system into invalid and the algebraic 0 is used to represent this situation, because no electron can be destroyed any more if the orbital has already been empty. Sometimes $a$ and $a^-$ are used interchangeably. Eq. (2.3d) means if the original electronic orbital is filled with one electron, then by applying the annihilation operator $a^-$ on the orbital, the electron is destroyed and the orbital becomes empty.

Secondly, the rule for Anti-commutator of operators A and B is

$$[A, B]_\dagger \equiv AB + BA = 0 \rightarrow AB = -BA,$$ \hspace{1cm} (2.4)  

which means if two particle states, A and B, are switched, then there is a -1 phase added on the system. This is derived from the anti-symmetric nature of the fermions [22].
2.2.2 Occupation number basis transformation

The occupation number basis transformation, or Jordan-Wigner transformation [23], encodes the fermionic states as the occupation number basis qubits:

\[ |f_{n-1} \cdots f_0 \rangle \rightarrow |q_{n-1} \rangle \otimes \cdots \otimes |q_0 \rangle . \] (2.5)

In the equation, each qubit \(|q_i\rangle\) stores the state of the corresponding orbital \(f_i\), where if the qubit equals to \(|0\rangle\), the orbital it represents is empty; otherwise, if the qubit equals to \(|1\rangle\), the orbital it represents is filled with one electron.

When it comes to creating or annihilating an electron in an orbital of the fermionic system, the two operation rules from Sec. 2.2.1 need to be incorporated, and the effects of applying the operations on an arbitrary \(j^{th}\) orbital in a general fermionic system are as follows [24]:

\[
\hat{a}^+_j |f_{n-1} \cdots f_{j+1}0f_{j-1} \cdots f_0 \rangle = (-1)^{\sum_{s=0}^{j-1} f_s} |f_{n-1} \cdots f_{j+1}1f_{j-1} \cdots f_0 \rangle , \] (2.6a)

\[
\hat{a}^+_j |f_{n-1} \cdots f_{j+1}f_{j-1} \cdots f_0 \rangle = 0 , \] (2.6b)

\[
\hat{a}^-_j |f_{n-1} \cdots f_{j+1}f_{j-1} \cdots f_0 \rangle = (-1)^{\sum_{s=0}^{j-1} f_s} |f_{n-1} \cdots f_{j+1}0f_{j-1} \cdots f_0 \rangle , \] (2.6c)

\[
\hat{a}^-_j |f_{n-1} \cdots f_{j+1}0f_{j-1} \cdots f_0 \rangle = 0 , \] (2.6d)

where Eq. (2.6a) means that, when the \(j^{th}\) orbital in the electronic system with \(n\) qubits were empty, by applying the creation operator on the \(j^{th}\) orbital, an electron is created in the orbital, and therefore the status of the \(j^{th}\) orbital is turned from \(|0\rangle\) to \(|1\rangle\). In Eq. (2.6b), the \(j^{th}\) orbital were initially at the state of \(|1\rangle\), and by applying the creation operator on the orbital, the whole system turns into algebraic 0. It happens because of the Pauli exclusion principal, which discovered that only one electron is allowed in an orbital for an electronic system. In the scenario of Eq. (2.6b), since there were already an electron in the \(j^{th}\) orbital, by applying the operation of creating an extra electron in the orbital, it violates the Pauli exclusion principal and therefore the whole system becomes physically meaningless, which is mathematically represented by the algebraic 0. Furthermore, the Eq. (2.6c) means that,
when the $j^{th}$ orbital in the electronic system with $n$ qubits were filled with an electron, by applying the annihilation operator on the $j^{th}$ orbital, the electron is destroyed in the orbital, and therefore the state of the $j^{th}$ orbital is turned from $|1\rangle$ to $|0\rangle$. In Eq. (2.6d), the $j^{th}$ orbital were initially at the state of $|0\rangle$, and by applying the annihilation operator on the orbital, the whole system turns into algebraic 0. It happens because the orbital initially contains zero electron, and there is no more electron to be destroyed. By applying the annihilation operator on the orbital, there is no correspondingly physical phenomenon to follow, and therefore the whole system becomes physically meaningless, which is again mathematically represented by the algebraic 0.

For the occupation number basis transformation, it is desired to mathematically represent the corresponding creator and annihilator on an electronic system with the occupation number basis, so that any creation and annihilation operations being applied on the physical system can be mathematically calculated to reflect the correspondingly physical reactions in an accurate way.

There are in general four steps to accomplish this goal. Firstly, encode the fermionic states of the system into the occupation number basis qubits, as demonstrated in Eq. (2.5). For the second step, only consider the effects on the $j^{th}$ qubit of applying the creator or annihilator on the arbitrary $j^{th}$ orbital, and assume the corresponding creator and annihilator to be $\hat{Q}^+$ and $\hat{Q}^-$, respectively [24]. With the occupation number basis, the creation and annihilation effects on an arbitrary $j^{th}$ qubit in an electronic system should be as follows:

$$Q^+ |0\rangle = |1\rangle,$$  
$$Q^+ |1\rangle = 0,$$  
$$Q^- |0\rangle = 0,$$  
$$Q^- |1\rangle = |0\rangle,$$

which exactly follows the rules of fermionic creation and annihilation operators as exhibited in Eq. (2.3). Next, deriving from the Eq. (2.7), the $\hat{Q}^+$ and $\hat{Q}^-$ operators in an electronic
system with occupation number basis is as follows:

\[ \hat{Q}^+ = |1 \rangle \langle 0|, \quad (2.8a) \]
\[ \hat{Q}^- = |0 \rangle \langle 1|. \quad (2.8b) \]

The Eq. (2.8) can be verified by substituting them into Eq. (2.7):

\[ \hat{Q}^+ |0 \rangle = (|1 \rangle \langle 0|) |0 \rangle = |1 \rangle (\langle 0|0 \rangle) = |1 \rangle \cdot 1 = |1 \rangle, \quad (2.9a) \]
\[ \hat{Q}^+ |1 \rangle = (|1 \rangle \langle 0|) |1 \rangle = |1 \rangle (\langle 0|1 \rangle) = |1 \rangle \cdot 0 = 0, \quad (2.9b) \]
\[ \hat{Q}^- |0 \rangle = (|0 \rangle \langle 1|) |0 \rangle = |0 \rangle (\langle 1|0 \rangle) = |0 \rangle \cdot 0 = 0, \quad (2.9c) \]
\[ \hat{Q}^- |1 \rangle = (|0 \rangle \langle 1|) |1 \rangle = |0 \rangle (\langle 1|1 \rangle) = |0 \rangle \cdot 1 = |0 \rangle. \quad (2.9d) \]

In quantum computation, it is always desired to mathematically represent the operators in Pauli matrices, which are composed of the following four basic matrices:

Pauli-X: \[ \sigma^x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad (2.10a) \]

Pauli-Y: \[ \sigma^y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad (2.10b) \]

Pauli-Z: \[ \sigma^z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad (2.10c) \]

Pauli-I: \[ \sigma^I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (2.10d) \]
Therefore, the $\hat{Q}^+$ and $\hat{Q}^-$ operators in an electronic system with occupation number basis can be re-written in the combination of Pauli matrices form:

$$\hat{Q}^+ = |1\rangle \langle 0| = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & 0 \\ 2 & 0 \end{bmatrix}$$

$$= \frac{1}{2} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \right) = \frac{1}{2} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \right)$$  \hspace{1cm} (2.11a)

$$= \frac{1}{2} (\sigma^x - i\sigma^y),$$

$$\hat{Q}^- = |0\rangle \langle 1| = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & 2 \\ 0 & 0 \end{bmatrix}$$

$$= \frac{1}{2} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \right) = \frac{1}{2} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \right)$$  \hspace{1cm} (2.11b)

$$= \frac{1}{2} (\sigma^x + i\sigma^y).$$

For the third step on mathematically representing the corresponding creator and annihilator on an electronic system with the occupation number basis, consider the effects on qubits with an index less than $j$ in the electronic system by applying the creator or annihilator on the arbitrary $j^{th}$ orbital. Since it is on the occupation number basis, each qubit in the encoded system is directly correlated with the corresponding orbital in the electronic system. Therefore, for all the qubits with an index less than the arbitrary index $j$, the anti-communication rule discussed in Sec. 2.2.1 is followed. It works in the following steps. Firstly, put the state of the $j^{th}$ qubit at the $0^{th}$ index system of qubits:

$$|f_{n-1} \cdots f_{j+1} f_{j-1} \cdots f_0 f_j \rangle \rightarrow |q_{n-1}\rangle \otimes \cdots \otimes |q_{j+1}\rangle \otimes |q_{j-1}\rangle \cdots |q_0\rangle \otimes |q_j\rangle. \hspace{1cm} (2.12)$$

Then applying the creator or annihilator on the $j^{th}$ qubit, and there are in general two scenarios. One scenario is when the operation turns the entire system into physically mean-
ingless, such as the ones indicated in Eq. (2.7b) and Eq. (2.7c), and in those cases, the system is turned into algebraic 0, and therefore nothing else needs to be done. The other scenario is when the state of the \( j^{th} \) qubit is flipped, as indicated in Eq. (2.7a) and Eq. (2.7d). In the latter scenario, the position of the \( j^{th} \) qubit is switched with each of the qubits with an index less than \( j \), all the way from \( 0^{th} \) qubit to the \( (j - 1)^{th} \) qubit, and those are where the anti-communication rule is applied.

For every qubit being switched with the arbitrary \( j^{th} \) qubit, if the state of the qubit is \( |0\rangle \), no phase is added into the system, otherwise a \(-1\) phase is added into the system according to the anti-communication rule. Thus, the operations to be incorporated into the creator and annihilator of the electronic system on occupation number basis should reflect those effects, and the Pauli-Z matrix in Eq. (2.10c) can do the work:

\[
\sigma^z |0\rangle = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = |0\rangle ,
\]

(2.13a)

\[
\sigma^z |1\rangle = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ -1 \end{bmatrix} = - \begin{bmatrix} 0 \\ 1 \end{bmatrix} = -|1\rangle ,
\]

(2.13b)

where the Eq. (2.13a) indicates that, by applying the Pauli-Z matrix on an qubit with an initial state of \( |0\rangle \), its state does not change; while the Eq. (2.13b) indicates that, by applying the Pauli-Z matrix on an qubit with an initial state of \( |1\rangle \), a \(-1\) phase is generated. Thus, by applying the Pauli-Z gate on every qubit with index less than \( j \), the effects on orbitals with index less than \( j \) is incorporated into the creator or annihilator. According to Seeley et al. [24], these operations can be mathematically summarized by \( \sigma^z \otimes |j\rangle \), meaning applying the Pauli-Z matrix on every qubit with index less than \( j \).

For the fourth step on mathematically representing the corresponding creator and annihilator on an electronic system with the occupation number basis, consider the effects on qubits with an index greater than \( j \) in the electronic system by applying the creator or annihilator on the arbitrary \( j^{th} \) orbital. Since it is the occupation number basis, the qubits with an index greater than \( j \) should not be impacted by the state change of the arbitrary
$j^{th}$ orbital, and thus, the operation on the qubits with an index greater than $j$ should have no effects. The Pauli-I matrix shows such effects:

$$\sigma^I |0\rangle = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |0\rangle,$$  \hspace{1cm} (2.14a)

$$\sigma^I |1\rangle = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |1\rangle.$$  \hspace{1cm} (2.14b)

Where the Eq. (2.14a) indicates that, by applying the Pauli-I matrix on a qubit with an initial state of $|0\rangle$, its state does not change; and same for Eq. (2.14b) on $|1\rangle$. Thus, by applying the Pauli-I matrix on every qubit with index greater than $j$, the effects on orbitals with index greater than $j$ is incorporated into the creator or annihilator. Again, according to Seeley et al. [24], these operations can be mathematically summarized by $1^{n-j-1}$, meaning applying the Pauli-I matrix on every qubit with index greater than $j$, and here $1 \equiv \sigma^I$.

In summary, by combining the derivations from step one to four, the creator and annihilator in an electronic system on the occupation number basis can be represented as:

$$\hat{a}_j^\dagger = 1^{n-j-1} \otimes \hat{Q}^+ \otimes [\sigma^z \otimes j],$$  \hspace{1cm} (2.15a)

$$\hat{a}_j^- = 1^{n-j-1} \otimes \hat{Q}^- \otimes [\sigma^z \otimes j],$$  \hspace{1cm} (2.15b)

which is consistent with the Eq. (11) in Seeley et al. [24] study, in which the Eq. (2.15) are further simplified into Eq. (12) and Eq. (13).

### 2.2.3 Parity basis transformation

The parity basis transformation is a different approach to encode the fermionic states into qubits. Different from occupation number basis, every qubit in the electronic system is correlated to the corresponding orbital in the fermionic system indirectly by the parity

...
of the orbitals.

\[ |f_{n-1} \cdots f_0\rangle \rightarrow |q_{n-1}\rangle \otimes \cdots \otimes |q_0\rangle \rightarrow |p_{n-1}\rangle \otimes \cdots \otimes |p_0\rangle. \quad (2.16) \]

To understand the parity basis, assume the state of the arbitrary \( j^{th} \) qubit in an electronic system with \( n \) qubits is \( |p_j\rangle \) on the parity basis, where \( j \) corresponds to the \( j^{th} \) orbital in the fermionic system. As shown in Eq. (2.16), the orbitals in fermionic system can be firstly encoded into qubits in occupation basis and then can be further encoded into qubits in a parity basis by following the Eq. (2.17):

\[ |p_j\rangle = \left( \sum_{i=0}^{j} q_i \right) \mod 2, \quad (2.17) \]

which means the state of an arbitrary \( j^{th} \) qubit on the parity basis is obtained by adding up the all the state values of the qubits with index less than or equal to \( j \) on the occupation basis then taking the modulo of 2. In this way the system phase information correlated with the state of each orbital is encoded into the corresponding qubit.

Similar to that with the occupation number basis, to mathematically represent the creator and annihilator on an electronic system with a parity basis, there are in general four steps. Firstly, encode the fermionic states of the system into the parity basis by following the Eq. (2.16) and Eq. (2.17). For the second step, only consider the effects on the \( j^{th} \) qubit of applying the creator or annihilator on the arbitrary \( j^{th} \) orbital, and also assume the corresponding creator and annihilator to be \( \hat{Q}^+ \) and \( \hat{Q}^- \), respectively. With the parity basis, the creation and annihilation effects on an arbitrary \( j^{th} \) qubit in an electronic system depend not only on the state of \( j^{th} \) orbital, but also on the parity value of the \((j-1)^{th}\) qubit, because:

\[ |p_j\rangle = |(q_j + p_{j-1}) \mod 2\rangle, \quad (2.18) \]

where \( |q_j\rangle = |f_j\rangle \).

There are in general two scenarios. If the parity value of the \((j-1)^{th}\) qubit is 0, then
the Eq. (2.18) can be simplified as \( |p_j \rangle \equiv |q_j \rangle \). Thus, the creator and annihilator working on the occupation basis, as summarized in Eq. (2.8), can also work on the parity basis as well given the \((j - 1)\text{th}\) qubit value is 0 on the parity basis. On the other hand, if the parity value of the \((j - 1)\text{th}\) qubit is 1, then the Eq. (2.18) can be simplified as:

\[
|p_j \rangle = |(q_j + 1) \mod 2 \rangle,
\]

(2.19)

where \( |p_j \rangle \equiv |0 \rangle \) if \( |q_j \rangle = |1 \rangle \), and \( |p_j \rangle \equiv |1 \rangle \) if \( |q_j \rangle = |0 \rangle \). Therefore, it can be concluded that the state of the arbitrary \(j\text{th}\) qubit on the parity basis is the flip state of that on the occupation number basis given the \((j - 1)\text{th}\) qubit value is 1 on the parity basis. Thus, the operation of creating an electron in an arbitrary \(j\text{th}\) orbital of an fermionic system is equivalent to turning the state of the arbitrary \(j\text{th}\) qubit on the parity basis from \(|1 \rangle\) to \(|0 \rangle\) or from \(|0 \rangle\) to \(|0 \rangle\), which is the operation with \(Q^-\); and the operation of annihilating an electron in an arbitrary \(j\text{th}\) orbital of an fermionic system is equivalent to turning the state of the arbitrary \(j\text{th}\) qubit on the parity basis from \(|0 \rangle\) to \(|1 \rangle\) or from \(|1 \rangle\) to \(|0 \rangle\), which is the operation with \(Q^+\). In addition, due to the anti-commutator rule indicated in Eq. (2.4) and the \((j - 1)\text{th}\) qubit value on the parity basis being 1, which means the sum of all the state value of orbitals with index less than \(j\) taking modulo of 2 is non-zero, the \(-1\) phase should be added into the system after applying the creator or annihilator on the \(j\text{th}\) orbital. Lastly, by summarizing the two scenarios, the creation and annihilation operators for an arbitrary \(j\text{th}\) orbital only in the electronic system on the parity basis can be represented with two qubits:

\[
\hat{P}^\pm_j = \hat{Q}^\pm_j \otimes |0\rangle \langle 0|_{j - 1} - \hat{Q}^\mp_j \otimes |1\rangle \langle 1|_{j - 1},
\]

(2.20)

where \(\hat{P}^+_j\) and \(\hat{P}^-_j\) are the creation and annihilation operators on an arbitrary \(j\text{th}\) orbital in an electronic system on the parity basis, which is also the conclusion from Seeley et al. [24] study.
The Eq. (2.20) can be verified by substituting the equation into the two scenarios mentioned above:

\[
\hat{P}_j^\pm |0\rangle_{j-1} = \left( \hat{Q}_j^\pm \otimes |0\rangle_{j-1} - \hat{Q}_j^\mp \otimes |1\rangle_{j-1} \right) |0\rangle_{j-1}
\]

\[
= \hat{Q}_j^\pm |0\rangle_{j-1} \langle 0|_{j-1} \langle 0|_{j-1} - \hat{Q}_j^\mp |1\rangle_{j-1} \langle 1|_{j-1} \langle 0|_{j-1}
\]

\[
= \hat{Q}_j^\pm |0\rangle_{j-1} \langle 0|_{j-1} - \hat{Q}_j^\mp |1\rangle_{j-1} \langle 1|_{j-1} - \hat{Q}_j^\mp |1\rangle_{j-1} \langle 1|_{j-1} = \hat{Q}_j^\pm |0\rangle_{j-1}
\]

\[
\hat{P}_j^\pm |1\rangle_{j-1} = \left( \hat{Q}_j^\pm \otimes |0\rangle_{j-1} - \hat{Q}_j^\mp \otimes |1\rangle_{j-1} \right) |1\rangle_{j-1}
\]

\[
= \hat{Q}_j^\pm |0\rangle_{j-1} \langle 0|_{j-1} \langle 0|_{j-1} - \hat{Q}_j^\mp |1\rangle_{j-1} \langle 1|_{j-1} \langle 0|_{j-1}
\]

\[
= \hat{Q}_j^\pm |0\rangle_{j-1} \langle 0|_{j-1} - \hat{Q}_j^\mp |1\rangle_{j-1} \langle 1|_{j-1} = \hat{Q}_j^\pm |1\rangle_{j-1}
\]

where Eq. (2.21a) verifies that \( \hat{P}_j^\pm \equiv \hat{Q}_j^\pm \) when the \((j-1)th\) qubit on parity basis is of the state \(|0\rangle\), while Eq. (2.21b) verifies that \( \hat{P}_j^\pm \equiv -\hat{Q}_j^\mp \) when the \((j-1)th\) qubit on parity basis is of the state \(|1\rangle\).

Furthermore, by substituting Eq. (2.11) to Eq. (2.20) along with some derivation, the creator and annihilator, \( \hat{P}_j^+ \) and \( \hat{P}_j^- \), can be represented in the combination of Pauli matrices
form:

\[ \hat{P}_j^\pm = \hat{Q}_j^\mp |0\rangle \langle 0|_{j-1} - \hat{Q}_j^\pm |1\rangle \langle 1|_{j-1} \]

\[ = \frac{1}{2} (\sigma^x_j \mp i\sigma^y_j) \otimes \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}_{j-1} - \frac{1}{2} (\sigma^x_j \pm i\sigma^y_j) \otimes \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}_{j-1} \]

\[ = \frac{1}{2} \sigma^x_j \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}_{j-1} - \frac{1}{2} i\sigma^y_j \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}_{j-1} \]

\[ = \frac{1}{2} \sigma^x_j \otimes \sigma^z_{j-1} - \frac{1}{2} i\sigma^y_j \otimes \sigma^I_{j-1} \]

\[ = \frac{1}{2} \left( \sigma^x_j \otimes \sigma^z_{j-1} \mp i\sigma^y_j \right). \]  

(2.22)

For the third step on mathematically representing the corresponding creator and annihilator on an electronic system with the parity basis, consider the effects on qubits with an index less than \( j \) in the electronic system by applying the creator or annihilator on the arbitrary \( j^{th} \) orbital. Since it is on the parity basis, the accumulated system phase caused by the anti-communication rule of switching the position of the arbitrary \( j^{th} \) orbital with all the orbitals with an index less than \( j \) is already incorporated into the \( \hat{P}_j^\pm \) operator as illustrated in the derivation process above. Thus, on the parity basis, the operations on the qubits with an index smaller than arbitrary \( j \) should have no effects, and applying the Pauli-I matrix on every qubit with an index less than \( j \) can meet such effects according to Eq. (2.14). Similar to the fourth step on the occupation number basis, these operations can be mathematically summarized by \( 1^j \), where \( 1 \equiv \sigma^I \).

For the fourth step on mathematically representing the corresponding creator and annihilator on an electronic system with the parity basis, consider the effects on qubits with an index greater than \( j \) in the electronic system by applying the creator or annihilator on the arbitrary \( j^{th} \) orbital. Since it is on the parity basis, all the qubits with an index greater than the arbitrary index \( j \) are impacted by the state change of the \( j^{th} \) qubit, because:
\[ |p_{j+1} \rangle = |(q_{j+1} + p_j) \mod 2 \rangle, \]  
(2.23)

where \(|q_{j+1} \rangle = |f_{j+1} \rangle\). Thus, by applying the creation or annihilation operation on an arbitrary \(j^{th}\) orbital on parity basis, the state of \(j^{th}\) qubit flips as long as it does not turn to algebraic 0, and therefore the states of all the qubits with index greater than \(j\) in the electronic system would flip as well. Applying the Pauli-X matrix on each of the qubits with index greater than \(j\) can cause such effects:

\[ \sigma^x |0\rangle = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} = |1\rangle, \]  
(2.24a)

\[ \sigma^x |1\rangle = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = |0\rangle. \]  
(2.24b)

Here the Eq. (2.24a) indicates that, by applying the Pauli-X matrix on an qubit with an initial state of \(|0\rangle\), its state flips to \(|1\rangle\); while the Eq. (2.24b) indicates that, by applying the Pauli-X matrix on an qubit with an initial state of \(|1\rangle\), its state flips to \(|0\rangle\). These operations can be mathematically summarized by \(\sigma^x \otimes (n-j-1)\), meaning applying the Pauli-X matrix on every qubit with index greater than \(j\).

In summary, by combining the derivations from step one to four, the creator and annihilator in an electronic system on the parity basis can be represented as:

\[ \hat{a}_j^+ = \left[ \sigma^x \otimes (n-j-1) \right] \otimes \hat{P}^+ \otimes \mathbf{1}_j, \]  
(2.25a)

\[ \hat{a}_j^- = \left[ \sigma^x \otimes (n-j-1) \right] \otimes \hat{P}^- \otimes \mathbf{1}_j, \]  
(2.25b)

which is consistent with the further simplified equations, Eq. (20) and Eq. (21), in Seeley et al. [24] study.

### 2.2.4 Bravyi-Kitaev basis transformation

With the occupation number basis transformation, the orbital occupation information
is stored locally in each qubit, but the orbital parity information is stored non-locally; while with the parity basis transformation, the orbital parity information is stored locally, but the orbital occupation information is stored non-locally. However, both basis encoding algorithms are of $O(n)$ computational complexity, where $n$ is the total number of orbitals in an fermionic system. To reduce the computational complexity of the basis encoding algorithm, the Bravyi-Kitaev transformation (BKT) that combines the occupation number basis and parity basis encoding algorithms are introduced by Seeley et al. [24]. As the result, the BKT algorithm reduces the computational complexity of basis encoding to $O(\log n)$, with the sacrifice of the algorithm design simplicity.

2.2.4.1 Basis encoding

The BKT algorithm divides the qubits into two categories, the qubits with even index and the qubits with odd index. Assume the qubit on the Bravyi-Kitaev basis with an arbitrary index $j$ are represented by $|b_j\rangle$, then, for the qubits with even index, the qubits stores the occupation information of the corresponding orbital in the fermionic system, and for the qubits with odd index, the qubits stores the partial parity information of the corresponding orbital in the fermionic system.

Fig. 2.1: Encode the Hydrogen molecule system on the Bravyi-Kitaev basis.

Take the Hydrogen molecule as an example. As shown in Fig. 2.1, assume the states of the four orbitals are represented as $|n_0\rangle$, $|n_1\rangle$, $|n_2\rangle$ and $|n_3\rangle$, respectively, and the corresponding qubit states on Bravyi-Kitaev basis are $|x_0\rangle$, $|x_1\rangle$, $|x_2\rangle$ and $|x_3\rangle$, respectively, then
the following relations are established:

\[ |x_0\rangle = |n_0 \mod 2\rangle, \quad (2.26a) \]
\[ |x_1\rangle = |(n_0 + n_1) \mod 2\rangle, \quad (2.26b) \]
\[ |x_2\rangle = |n_2 \mod 2\rangle, \quad (2.26c) \]
\[ |x_3\rangle = |(n_0 + n_1 + n_2 + n_3) \mod 2\rangle. \quad (2.26d) \]

By extending the pattern to a fermionic system with \( n \) orbitals, where \( n \) is even, the qubits states on Bravyi-Kitaev basis are formed by firstly splitting the orbitals in the correspondingly fermionic system into two groups from the middle, and then the states of orbitals with even indexes are equivalent to the states of corresponding qubits on the Bravyi-Kitaev basis. In addition, the states of qubits with odd indexes on the left group (the group starting from the 0\(^{th}\) qubit to the \((\frac{n}{2} - 1)\(^{th}\) qubit) are calculated from the sum of all the state value of orbitals with an index smaller than or equal to the index of the current qubit then taking the modulo of 2. The states of qubits with odd indexes on the right group except for the last qubit (the group starting from the \((\frac{n}{2})\(^{th}\) qubit to the \((n - 2)\(^{th}\) qubit) are calculated from the sum of all the state value of orbitals with index both greater than \((\frac{n}{2} - 1)\) and smaller than or equal to the index of the current qubit then taking the modulo of 2. The state of the last qubit (i.e., \((n - 1)\(^{th}\) qubit) is calculated from the sum of all the state values of orbitals in the fermionic system then taking the modulo of 2.

Furthermore, if all the operations in the Bravyi-Kitaev basis are assumed to automatically take the modulo of 2, and by removing the ket notations from the Eq. (2.26), the Eq. (2.26) can be rewritten as:

\[ x_0 = n_0, \quad (2.27a) \]
\[ x_1 = n_0 + n_1, \quad (2.27b) \]
\[ x_2 = n_2, \quad (2.27c) \]
\[ x_3 = n_0 + n_1 + n_2 + n_3. \quad (2.27d) \]
By sorting the system of equations into matrix form, the following linear equation can be obtained:

\[
\begin{bmatrix}
1 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
n_3 \\
n_2 \\
n_1 \\
n_0 \\
\end{bmatrix}
= 
\begin{bmatrix}
x_3 \\
x_2 \\
x_1 \\
x_0 \\
\end{bmatrix},
\]

(2.28)

and the matrix in the equation is called the Bravyi-Kitaev basis encoding matrix \( \beta_4 \):

\[
\beta_4 = 
\begin{bmatrix}
1 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1 \\
\end{bmatrix},
\]

(2.29)

where the subscript 4 implies there are in total 4 orbitals in the corresponding fermionic system.

According to the Fig. 2 of Seeley et al. study [24], the recursive method can be leveraged to extend the matrix pattern to \( \beta_n \), where \( n \) is a positive even natural number. Firstly, the matrix can be divided into four parts. Secondly, in the upper right quarter of the matrix, fill the entries of the top row with 1s, and the rest with 0s; and fill all entries in the lower left quarter of the matrix with 0s. Thirdly, in both the upper left and the lower right quarter of the matrix, apply the matrix \( \beta_{n-1} \), with the base case \( \beta_1 = [1] \).

### 2.2.4.2 Parity set

After applying the creator or annihilator on an arbitrary \( j^{th} \) orbital encoded with the Bravyi-Kitaev basis, it is important to know which set of qubits of index less than \( j \) can impact the phase change of the system, and this set of qubits is called the "parity set", or \( P(j) \).
In the Hydrogen molecule system, the parity set for each qubit can be easily found from its Bravyi-Kitaev encoding algorithm. According to Fig. 2.1, it can be concluded that:

\[
P(0) = \emptyset, \tag{2.30a}
\]
\[
P(1) = \{0\}, \tag{2.30b}
\]
\[
P(2) = \{1\}, \tag{2.30c}
\]
\[
P(3) = \{2, 1\}, \tag{2.30d}
\]

where Eq. (2.30a) means no qubit of index smaller than 0 can impact the system phase when applying the creation or annihilation operator on the 0\(^{th}\) orbital; Eq. (2.30b) means the state of the 0\(^{th}\) qubit can impact the system phase when applying the creation or annihilation operator on the 1\(^{st}\) orbital; Eq. (2.30c) means the state of the 1\(^{st}\) qubit can impact the system phase when applying the creation or annihilation operator on the 2\(^{nd}\) orbital; and Eq. (2.30d) means the state of the 1\(^{st}\) and 2\(^{nd}\) qubits can impact the system phase when applying the creation or annihilation operator on the 3\(^{rd}\) orbital.

In the meantime, the parity sets of the Hydrogen molecule system can also be found from the the matrix \(\pi_4 \beta_4^{-1}\), where:

\[
\pi_4 = \begin{bmatrix}
0 & 1 & 1 & 1 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0
\end{bmatrix}, \quad \beta_4^{-1} = \begin{bmatrix}
1 & 1 & 1 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1
\end{bmatrix}. \tag{2.31}
\]

\[
\pi_4 \beta_4^{-1} = \begin{bmatrix}
0 & 1 & 1 & 1 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0
\end{bmatrix} \begin{bmatrix}
1 & 1 & 1 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1
\end{bmatrix} = \begin{bmatrix}
0 & 1 & 1 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0
\end{bmatrix}. \tag{2.32}
\]

In the matrix \(\pi_4 \beta_4^{-1}\), assume the rightmost column is the 0\(^{th}\) column, and the lowest row is the 0\(^{th}\) row, then the parity set of the \(i\(^{th}\) qubit are the column index of the nonzero
entries to the right of the main diagonal in the $i^{th}$ row.

The pattern can be extended to a system of $n$ qubits, with the matrix $\pi_n$ equal to the Eq. (17) in [24].

### 2.2.4.3 Update set

Similar to that of the parity set, after applying the creator or annihilator on an arbitrary $j^{th}$ orbital encoded with the Bravyi-Kitaev basis, it is important to know which set of qubits of index greater than $j$ are impacted by state, and this set of qubits is called the "update set", or $U(j)$.

In the Hydrogen molecule system, again, the update set for each qubit can be easily found from its Bravyi-Kitaev encoding algorithm. According to Fig. 2.1, it can be concluded that:

$$U(0) = \{1, 3\}, \quad (2.33a)$$
$$U(1) = \{3\}, \quad (2.33b)$$
$$U(2) = \{3\}, \quad (2.33c)$$
$$U(3) = \emptyset, \quad (2.33d)$$

where Eq. (2.33a) means the state of the 0$^{th}$ and the 3$^{rd}$ qubits can be impacted when applying the creation or annihilation operator on the 0$^{th}$ orbital; Eq. (2.33b) means the state of the 3$^{rd}$ qubit can be impacted when applying the creation or annihilation operator on the 1$^{st}$ orbital; Eq. (2.33c) means the state of the 3$^{rd}$ qubit can be impacted when applying the creation or annihilation operator on the 2$^{nd}$ orbital; and Eq. (2.33d) means no qubit of index greater than 3 can be impacted when applying the creation or annihilation operator on the 3$^{rd}$ orbital.

In the meantime, the update sets of the Hydrogen molecule system can also be found from the matrix $\beta_4$, as shown in Eq. (2.29). Specifically, again, assume the rightmost column is the 0$^{th}$ column, and the lowest row is the 0$^{th}$ row, then update set of the $i^{th}$ qubit are the row index of the nonzero entries to the upper of the main diagonal in the $i^{th}$ column.
The pattern can be extended to a system of \( n \) qubits with the matrix \( \beta_n \).

### 2.2.4.4 Flip set

Similar to that of the parity and update sets, after applying the creator or annihilator on an arbitrary \( j^{th} \) orbital encoded with the Bravyi-Kitaev basis, it is important to know which set of qubits of index smaller than \( j \) can determine if the state of the \( j^{th} \) qubit is consistent or flipped with the state of the \( j^{th} \) orbital, and this set of qubits is called the "flip set", or \( F(j) \).

In the Hydrogen molecule system, again, the flip set for each qubit can be easily found from its Bravyi-Kitaev encoding algorithm. According to Fig. 2.1, it can be concluded that:

\[
F(0) = \emptyset, \quad (2.34a) \\
F(1) = \{0\}, \quad (2.34b) \\
F(2) = \emptyset, \quad (2.34c) \\
F(3) = \{2, 1\}, \quad (2.34d)
\]

where Eq. (2.34a) means no qubit determines if the state of the 0\( ^{th} \) qubit is consistent or flipped with the state of the 0\( ^{th} \) orbital when applying the creation or annihilation operator on the 0\( ^{th} \) orbital; Eq. (2.34b) means the 0\( ^{th} \) qubit can determine if the state of the 1\( ^{st} \) qubit is consistent or flipped with the state of the 1\( ^{st} \) orbital when applying the creation or annihilation operator on the 1\( ^{st} \) orbital; Eq. (2.34c) means no qubit determines if the state of the 2\( ^{nd} \) qubit is consistent or flipped with the state of the 2\( ^{nd} \) orbital when applying the creation or annihilation operator on the 2\( ^{nd} \) orbital; and Eq. (2.34d) means the 1\( ^{st} \) and the 2\( ^{nd} \) qubits can determine if the state of the 3\( ^{rd} \) qubit is consistent or flipped with the state of the 3\( ^{rd} \) orbital when applying the creation or annihilation operator on the 3\( ^{rd} \) orbital.

In the meantime, the flip sets of the Hydrogen molecule system can also be found from the matrix \( \beta_4^{-1} \), as shown in Eq. (2.31). Specifically, again, assume the rightmost column is the 0\( ^{th} \) column, and the lowest row is the 0\( ^{th} \) row, then the flip set of the \( i^{th} \) qubit are
the column index of the nonzero entries to the right of the main diagonal in the $i^{th}$ row.

The pattern can be extended to a system of $n$ qubits with the matrix $\beta_n^{-1}$.

### 2.2.5 Representing creator and annihilator operation on qubits

To represent the creator and annihilator operation on qubits with the Bravyi-Kitaev basis, all the relevant sets derived above are critical. For convenience, they are systematically summarized in Tab. 2.2.

**Table 2.2: The sets table.**

<table>
<thead>
<tr>
<th>Parity set</th>
<th>Update set</th>
<th>Flip set</th>
<th>Reminder set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>$P(i)$</td>
<td>$U(i)$</td>
<td>$F(i)$</td>
</tr>
<tr>
<td><strong>Definition</strong></td>
<td>The set of qubits of index less than $j$ that can impact the phase change of the system</td>
<td>The set of qubits of index greater than $j$ that can be impacted by the state change of the $j^{th}$ qubit</td>
<td>The set of qubits of index smaller than $j$ that can determine if the state of the $j^{th}$ qubit is consistent with that of the $j^{th}$ orbital</td>
</tr>
<tr>
<td><strong>Equation</strong></td>
<td>$\pi_4\beta_4^{-1}$</td>
<td>$\beta_4$</td>
<td>$\beta_4^{-1}$</td>
</tr>
</tbody>
</table>
| **Matrix** | \[
\begin{pmatrix}
0 & 1 & 1 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0
\end{pmatrix}
\] | \[
\begin{pmatrix}
1 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1
\end{pmatrix}
\] | \[
\begin{pmatrix}
1 & 1 & 1 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 1
\end{pmatrix}
\] | - |
| **Method** | The parity set of the $i^{th}$ qubit are the column index of the nonzero entries to the right of the main diagonal in the $i^{th}$ row | The update set of the $i^{th}$ qubit are the row index of the nonzero entries to the upper of the main diagonal in the $i^{th}$ column | The flip set of the $i^{th}$ qubit are the column index of the nonzero entries to the right of the main diagonal in the $i^{th}$ row | $R(i) = P(i) \setminus F(i)$ |
| **Set** | $\{P(3) = \{2,1\}, P(2) = \{1\}, P(1) = \{0\}, P(0) = \emptyset\}$ | $\{U(3) = \emptyset, U(2) = \{3\}, U(1) = \{3\}, U(0) = \{1,3\}\}$ | $\{F(3) = \{2,1\}, F(2) = \emptyset, F(1) = \{0\}, F(0) = \emptyset\}$ | $\{R(3) = \emptyset, R(2) = \{1\}, R(1) = \emptyset, R(0) = \emptyset\}$ |

### 2.2.5.1 Even index case

As mentioned in Sec. 2.2.4.1, with the Bravyi-Kitaev basis, the qubits with an even index are directly correlated with the occupation state of the corresponding orbitals. Thus, the creator and annihilator operation on an arbitrary $j^{th}$ orbital with $j$ even is straight-
forward. Firstly, when creating an electron in the $j^{th}$ orbital, apply the $\hat{Q}_j^+$ on the $j^{th}$ qubit with Bravyi-Kitaev basis, while applying the $\hat{Q}_j^-$ on the $j^{th}$ qubit when destroying an electron in the $j^{th}$ orbital. Secondly, in both cases, apply the Pauli-Z gate on all the qubits in the parity set of the $j^{th}$ qubit, $P(j)$, to take into account the accumulated phase change for the system. Lastly, in both cases, apply the Pauli-X gate on all qubits in the update set of the $j^{th}$ qubit, $U(j)$, to update the state of all qubits that are impacted by the state change of the $j^{th}$ qubit.

The formulas for representing creator and annihilator operation on qubits with even indexes are summarized in the Eq. (32) and Eq. (33) in [24].

### 2.2.5.2 Odd index case

Different from applying creator or annihilator on qubits with even index on the Bravyi-Kitaev basis, the qubits with odd index store the partial parity information of the corresponding orbital in the fermionic system, which makes it involve more factors when applying the creator or annihilator operation on those qubits.

Firstly, to create or destroy an electron in the $j^{th}$ orbital with $j$ odd, the corresponding creation and annihilation operators on the $j^{th}$ qubit encoded with the Bravyi-Kitaev basis maybe $\hat{Q}_j^\pm$ or $\hat{Q}_j^{\mp}$, depending on if the state of the qubit is consistent with or flipped from the state of the corresponding orbital. To determine which case it is, the parity of the sum of the state value of qubits in the flip set of the $j^{th}$ qubit needs to be calculated. If the parity value is 0, then it means the state of the $j^{th}$ qubit is consistent with the state of the corresponding orbital, so that the creator operation should be $\hat{Q}_j^+$, and the annihilator operation should be $\hat{Q}_j^-$. Otherwise, if the parity value is 1, then it means the state of the $j^{th}$ qubit is flipped from the state of the corresponding orbital so that the creator operation should be $\hat{Q}_j^-$, and the annihilator operation should be $\hat{Q}_j^+$ instead. To merge the two cases into one mathematical expression, the following equation is proposed according to [24]:

$$\hat{\Pi}_j^+ = \hat{Q}_j^+ \otimes (|0\rangle \langle 0|)_{F(j)} - \hat{Q}_j^- \otimes (|1\rangle \langle 1|)_{F(j)},$$

(2.35)
where $\hat{\Pi}_j^+$ represents creator operation on the $j^{th}$ qubit with the index $j$ being odd, and $\hat{\Pi}_j^-$ annihilator operation. The Eq. (2.35) can be verified by substituting examples of the two cases into the equation:

$$\hat{\Pi}_j^\pm |0\rangle_{F(j)} = \left( \hat{Q}_j^\pm \otimes (|0\rangle \langle 0|)_{F(j)} - \hat{Q}_j^\mp \otimes (|1\rangle \langle 1|)_{F(j)} \right) |0\rangle_{F(j)}$$

$$= \hat{Q}_j^\pm (|0\rangle \langle 0|)_{F(j)} - \hat{Q}_j^\mp (|1\rangle \langle 1|)_{F(j)}$$

$$= \hat{Q}_j^\pm (|0\rangle \cdot 1)_{F(j)} - \hat{Q}_j^\mp (|1\rangle \cdot 0)_{F(j)} \implies \hat{\Pi}_j^\pm \equiv \hat{Q}_j^\pm, \quad (2.36a)$$

$$\hat{\Pi}_j^\pm |1\rangle_{F(j)} = \left( \hat{Q}_j^\pm \otimes (|0\rangle \langle 0|)_{F(j)} - \hat{Q}_j^\mp \otimes (|1\rangle \langle 1|)_{F(j)} \right) |1\rangle_{F(j)}$$

$$= \hat{Q}_j^\pm (|0\rangle \cdot 1)_{F(j)} - \hat{Q}_j^\mp (|1\rangle \cdot 1)_{F(j)}$$

$$= 0 - \hat{Q}_j^\mp |1\rangle_{F(j)} \implies \hat{\Pi}_j^\pm \equiv -\hat{Q}_j^\mp, \quad (2.36b)$$

where Eq. (2.36a) shows that the creator and annihilator operations on the $j^{th}$ qubit are equivalent to $\hat{Q}_j^+$ and $\hat{Q}_j^-$, respectively, when the parity value of the corresponding flip set is 0, while Eq. (2.36b) shows that the creator and annihilator operations on the $j^{th}$ qubit are flipped when the parity value of the corresponding flip set is 1, and a $-1$ phase is added into the system due to the non-zero parity value.
Furthermore, the Eq. (2.35) can be represented by Pauli matrices by substituting the Eq. (2.11) into the equation along with some conversions:

\[
\hat{\Pi}_j^\pm = \hat{Q}_j^\pm \otimes \langle 0 \rangle \langle 0 \rangle_{F(j)} - \hat{Q}_j^\pm \otimes \langle 1 \rangle \langle 1 \rangle_{F(j)} \\
= \frac{1}{2} (\sigma_x \mp i \sigma_y)_j \otimes \left( \begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array} \right)_{F(j)} - \frac{1}{2} (\sigma_x \pm i \sigma_y)_j \otimes \left( \begin{array}{cc} 0 & 0 \\ 0 & 1 \end{array} \right)_{F(j)} \\
= \frac{1}{2} (\sigma_x \mp i \sigma_y)_j \otimes \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right)_{F(j)} + \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right)_{F(j)} \\
- \frac{1}{2} (\sigma_x \pm i \sigma_y)_j \otimes \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right)_{F(j)} - \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right)_{F(j)} \\
= \frac{1}{2} (\sigma_x \mp i \sigma_y)_j \otimes \frac{1}{2} (\sigma^I + \sigma^z)_{F(j)} - \frac{1}{2} (\sigma_x \pm i \sigma_y)_j \otimes \frac{1}{2} (\sigma^I - \sigma^z)_{F(j)} \\
= \frac{1}{4} \left( \sigma_j^x \sigma_{F(j)}^I + \sigma_j^y \sigma_{F(j)}^z \mp i \sigma_j^y \sigma_{F(j)}^I \mp i \sigma_j^y \sigma_{F(j)}^z \right) \\
- \frac{1}{4} \left( \sigma_j^z \sigma_{F(j)}^I - \sigma_j^z \sigma_{F(j)}^z \mp i \sigma_j^y \sigma_{F(j)}^I \mp i \sigma_j^y \sigma_{F(j)}^z \right) \\
= \frac{1}{4} \left( 2 \cdot \sigma_j^x \sigma_{F(j)}^z \mp 2 \cdot i \sigma_j^y \sigma_{F(j)}^I \right) \\
= \frac{1}{2} \left( \sigma_j^x \sigma_{F(j)}^z \mp i \sigma_j^y \right).
\]

For the second step on representing creator and annihilator operation on an arbitrary \(j^{th}\) qubit with the index being odd, it is similar to that with the index being even, but with a slight difference. To take into account the accumulated phase change for the system, the Pauli-Z gate needs to be applied on all the qubits in the parity set of the \(j^{th}\) qubit. However, since part of the qubits in the parity set has already been taken into account of system phase change when being used in the flip set, only the rest of the qubits on the parity set need to be applied with the Pauli-Z gate, and the set of these remainder qubits are called the "remainder set" according to [24]:

\[
R(j) = P(j) \setminus F(j).
\]
Lastly, apply the Pauli-X gate on all qubits in the update set of the $j^{th}$ qubit to update the state of all qubits that are impacted by the state change of the $j^{th}$ qubit.

The formulas for representing creator and annihilator operation on qubits with odd index are summarized in the Eq. (36) and Eq. (37) in [24], and the one with both even and odd indexes are summarized in the Eq. (39) and Eq. (40).

### 2.3 Bravyi-Kitaev transformation for the Hydrogen molecule Hamiltonian

In this section, the energy Hamiltonian of the Hydrogen molecule is mathematically represented with the combination of Pauli matrices by leveraging the second-quantization and Bravyi-Kitaev transformation (BKT).

#### 2.3.1 Number operator

The number operator is of the form $h_{ii} \hat{a}_i^\dagger \hat{a}_i$, where $\hat{a}_i^\dagger \hat{a}_i$ is the number operator, and $h_{ii}$ is the corresponding overlap integral parameter. The eigenvalues of the number operator correspond to the occupation number of the arbitrary $i^{th}$ orbital, and the mathematical representation of the number operator can be calculated and simplified from the following derivation:

$$
\hat{a}_i^\dagger \hat{a}_i = \frac{1}{2} \left( \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) - i \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) + \frac{1}{2} \left( \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) + i \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \right) \right)
$$

$$
= \frac{1}{4} \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) + \frac{1}{4} \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) + \frac{1}{4} \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1) \otimes \sigma_\uparrow(1)
$$

$$
= \frac{1}{4} \sigma^x \otimes \sigma^y + \frac{1}{4} i \sigma^x \otimes \sigma^y + \frac{1}{4} \sigma^x \otimes \sigma^y - \frac{1}{4} \sigma^x \otimes \sigma^y \otimes \sigma^x \otimes \sigma^y
$$

$$
= \frac{1}{4} \left[ \sigma^x + i (\sigma^y \otimes \sigma^y) + \sigma^z \otimes \sigma^z \right] - \frac{1}{4} \left( \sigma^x \otimes \sigma^y \otimes \sigma^z \otimes \sigma^z \right) + \frac{1}{4} \sigma^x \otimes \sigma^y \otimes \sigma^z \otimes \sigma^z
$$

$$
= \frac{1}{4} \left[ 2 \sigma^x - \sigma^x \otimes \sigma^y \otimes \sigma^z \otimes \sigma^z \right] - \frac{1}{4} \left( \sigma^x \otimes \sigma^y \otimes \sigma^z \otimes \sigma^z \right)
$$

$$
= \frac{1}{2} \left[ \sigma^x \otimes \sigma^y \otimes \sigma^z \otimes \sigma^z \right],
$$

(2.39)
and

\[
i(\sigma_i^x \otimes \sigma_i^y) = i \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}_i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}_i = \begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}_i \begin{bmatrix} 0 & -i \\ 1 & 0 \end{bmatrix}_i = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}_i = -\sigma_i^z, \tag{2.41a}\]

\[
i(\sigma_i^y \otimes \sigma_i^x) = i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}_i \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}_i = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}_i \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}_i = \sigma_i^z. \tag{2.41b}\]

In addition, in the process of simplification, there is:

\[
\sigma_{P(i)}^z \otimes \sigma_{\rho(i)}^z \equiv \sigma_{\rho(i)}^z \otimes \sigma_{P(i)}^z \equiv \sigma_{P(i) \setminus \rho(i)}, \tag{2.42}\]

because the terms \(\sigma_{P(i)}^z \otimes \sigma_{\rho(i)}^z\) and \(\sigma_{\rho(i)}^z \otimes \sigma_{P(i)}^z\) both mean applying the Pauli-Z gate on quibits set \(P(i)\) and \(\rho(i)\). However, there can be overlapped quibits from the two sets. According to Eq. (2.40), by applying the Pauli-Z gate on the same qubit for twice, the effects is equivalent to applying the Pauli-I gate on the qubit once. Moreover, according to Eq. (2.38) and the following definition of \(\rho(i)\) from [24]:

\[
\rho(i) = \begin{cases} 
P(i) & i \text{ even}, \\
R(i) & i \text{ odd}. 
\end{cases} \tag{2.43}\]

it can be concluded that \(\rho(i) \subseteq P(i)\). Thus, the set \(P(i) \setminus \rho(i)\) means only the quibits in the parity set, \(P(i)\), but not in the \(\rho(i)\) set need to be applied with the Pauli-Z gate.

Furthermore, according to Eq. (2.38) and Eq. (2.43), when the qubit index \(i\) is even, \(\rho(i)\) turns to be equivalent to \(P(i)\), and therefore the term \(P(i) \setminus \rho(i)\) becomes to an empty set, which is equivalent to the flip set \(F(i)\) for \(i\) even. On the other other, when the qubit index \(i\) is odd, \(\rho(i)\) turns to be equivalent to \(R(i) \equiv P(i) \setminus F(i)\), and therefore the term
\[ P(i) \setminus \rho(i) \text{ becomes } P(i) \setminus (P(i) \setminus F(i)) \equiv F(i). \] Therefore, it can be concluded that:

\[
P(i) \setminus \rho(i) \equiv F(i), \tag{2.44}
\]

for both \( i \) even and odd.

Also, in the last step of derivation in Eq. (2.39), the term \( \sigma_i^z \otimes \sigma_{P(i) \setminus \rho(i)}^z \) means applying the Pauli-Z gate on the qubits with index \( i \) and with \( F(i) \). In [24], this term is further simplified by introducing a new concept:

\[
F(i) = \{ i \} \cup \{ F(i) \}. \tag{2.45}
\]

Thus, the number operator in Eq. (2.39) can be finally simplified into:

\[
\hat{a}_i^\dagger \hat{a}_i = \frac{1}{2} \left[ \sigma^I - \sigma_{F(i)}^z \right]. \tag{2.46}
\]

According to the Eq. (2.1), there exists number operator in the Hydrogen molecule Hamiltonian. Then, by leveraging the flip set summarized in Eq. (2.34) and the conclusion from Eq. (2.45), it can be obtained that:

\[
F(0) = \{ 0 \}, \tag{2.47a}
\]
\[
F(1) = \{ 1, 0 \}, \tag{2.47b}
\]
\[
F(2) = \{ 2 \}, \tag{2.47c}
\]
\[
F(3) = \{ 3, 2, 1 \}. \tag{2.47d}
\]

By substituting the Eq. (2.47) into Eq. (2.46), the number operator of four orbitals, \( h_{00} \hat{a}_0^\dagger \hat{a}_0 \), \( h_{11} \hat{a}_1^\dagger \hat{a}_1 \), \( h_{22} \hat{a}_2^\dagger \hat{a}_2 \), \( h_{33} \hat{a}_3^\dagger \hat{a}_3 \), can be obtained. The corresponding mathematical expressions are summarized from Eq. (63) to Eq. (66) in [24].

### 2.3.2 Coulomb and exchange operator

The Coulomb and exchange operators is of the form \( h_{ijji} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i \), and the \( h_{ijji} \) is the
corresponding overlap integral parameter. In the Hydrogen molecule system, the Coulomb and exchange operators account for the dynamics caused by the electronic potential energies between electrons and between electrons and nuclei.

As the name implies, there are the Coulomb operator and the exchange operator in the Coulomb and exchange operator, where the Coulomb operator is of the form $\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i$, and the exchange operator is of the form $\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_j$. However, by leveraging the anti-commutator rule in Eq. (2.4), the exchange operator can be converted to the form of the Coulomb operator:

$$\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_j = -\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i. \quad (2.48)$$

And it is important to note that the exchange operation can only happen between orbital 0 and orbital 2, or between orbital 1 and orbital 3.

To mathematically represent the Coulomb operator, the number operator can be leveraged along with the anti-commutator rule:

$$\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_j = -\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i = \left(\hat{a}_i^\dagger \hat{a}_i\right) \left(\hat{a}_j^\dagger \hat{a}_j\right). \quad (2.49)$$

in which the Coulomb operator is transformed into the product between two number operators.

The specific follow-up derivations are summarized from Eq. (46) to Eq. (49) in [24]. For the Coulomb and exchange operator in the Hydrogen molecule system, the key is to find the $F_{ij}$ set defined in Eq. (48) in [24]:

\begin{align*}
F_{01} &= \{1\}, \quad (2.50a) \\
F_{02} &= \{2, 0\}, \quad (2.50b) \\
F_{03} &= \{3, 2, 1, 0\}, \quad (2.50c) \\
F_{12} &= \{2, 1, 0\}, \quad (2.50d) \\
F_{13} &= \{3, 2, 0\}, \quad (2.50e) \\
F_{23} &= \{3, 1\}. \quad (2.50f)
\end{align*}
By substituting the Eq. (2.50) into Eq. (49), the six Coulomb and exchange operator terms of the Hydrogen molecule Hamiltonian can be obtained, including
\[h_{0110} \hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_1 \hat{a}_0, (h_{0220} - h_{0202}) \hat{a}_0^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_0, h_{0330} \hat{a}_0^\dagger \hat{a}_3^\dagger \hat{a}_3 \hat{a}_0, h_{1221} \hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_1, (h_{1331} - h_{1313}) \hat{a}_1^\dagger \hat{a}_3^\dagger \hat{a}_3 \hat{a}_1, h_{2332} \hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_3 \hat{a}_2.\]
The corresponding mathematical expressions are summarized from Eq. (68) to Eq. (73) in [24].

2.3.3 Double excitation operator

The double excitation operator is of the form
\[h_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l + \hat{a}_l^\dagger \hat{a}_k^\dagger \hat{a}_j \hat{a}_i,\]
and accounts for the excitation of both electrons in all four orbital exchanges. Therefore, there are two scenarios of double excitation operators in the Hydrogen molecule system:

\[h_{0312}(\hat{a}_0^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_3 \hat{a}_0) = h_{0312} \left[(\hat{a}_0^\dagger \hat{a}_2)(\hat{a}_3^\dagger \hat{a}_1) + (\hat{a}_2^\dagger \hat{a}_0)(\hat{a}_3^\dagger \hat{a}_1)\right], \quad (2.51a)\]
\[h_{0132}(\hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_0) = h_{0132} \left[(\hat{a}_0^\dagger \hat{a}_2)(\hat{a}_1^\dagger \hat{a}_3) + (\hat{a}_2^\dagger \hat{a}_0)(\hat{a}_3^\dagger \hat{a}_1)\right], \quad (2.51b)\]

where both Eq. (2.51a) and Eq. (2.51b) are rearranged to be of the combination of the products of the form \(\hat{a}_i^\dagger \hat{a}_j\) with the anti-commutator rule. Different from the number operator, the creator \(\hat{a}^\dagger\) and the annihilator \(\hat{a}\) in the term \(\hat{a}_i^\dagger \hat{a}_j\) are applied on the different qubits instead the same ones, which makes the whole derivation much more complex. However, Seeley et al. [24] summarized all the scenarios into different categories, and the corresponding mathematical expression for \(\hat{a}_i^\dagger \hat{a}_j\) can be easily found from the Tab. II in the paper by answering the following conditional questions:

1. The oddness of \(i, j\)

2. If \(i \in P(j)\) and if \(j \in U(i)\)

In this study, the mathematical expression of the Eq. (2.51b) is derived in detail as an example, and by following the same procedure, the mathematical expression of the Eq. (2.51a) can be derived as well. Before the derivation, a few relevant mathematical concepts are introduced. Firstly, it can be observed in Eq. (2.51b) that the second term is
the Hermitian adjoint of the first term:

\[
\hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_0 = (\hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2)^\dagger.
\] (2.52)

Therefore, the mathematical expression of the term \(\hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_0\) can be easily obtained by keeping all the non-imaginary terms in \(\hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2\) as what they are and flipping the sign of all the imaginary terms. Secondly, all the results between two Pauli matrices product are summarized in Tab. 2.3 to be used in the process of derivation.

**Table 2.3: Summary of Pauli matrices products.**

<table>
<thead>
<tr>
<th>Pauli matrices product</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma_i^x \otimes \sigma_i^x)</td>
<td>(\sigma^I_i)</td>
</tr>
<tr>
<td>(\sigma_i^y \otimes \sigma_i^y)</td>
<td>(\sigma^I_i)</td>
</tr>
<tr>
<td>(\sigma_i^z \otimes \sigma_i^z)</td>
<td>(\sigma^I_i)</td>
</tr>
<tr>
<td>(\sigma_i^x \otimes \sigma_i^y)</td>
<td>(i\sigma_i^z)</td>
</tr>
<tr>
<td>(\sigma_i^y \otimes \sigma_i^x)</td>
<td>(i\sigma_i^x)</td>
</tr>
<tr>
<td>(\sigma_i^z \otimes \sigma_i^x)</td>
<td>(i\sigma_i^y)</td>
</tr>
<tr>
<td>(\sigma_i^y \otimes \sigma_i^z)</td>
<td>(-i\sigma_i^z)</td>
</tr>
<tr>
<td>(\sigma_i^z \otimes \sigma_i^y)</td>
<td>(-i\sigma_i^y)</td>
</tr>
<tr>
<td>(\sigma_i^x \otimes \sigma_i^z)</td>
<td>(-i\sigma_i^x)</td>
</tr>
</tbody>
</table>

So far, the mathematical derivation of the Eq. (2.51b) has been simplified to the derivation of two terms, \(\hat{a}_0^\dagger \hat{a}_2\) and \(\hat{a}_1^\dagger \hat{a}_3\), and to finding the product of the two terms. Firstly, the term \(\hat{a}_0^\dagger \hat{a}_2\) is derived. According to the Eq. (2.30c) and Eq. (2.33a), \(P(2) = \{1\}\) and \(U(0) = \{1, 3\}\), so the two conditional questions can be answered as follows:

1. \(i = 0\) is even and \(j = 2\) is even
2. \(0 \notin P(2)\) and if \(2 \notin U(0)\)
Thus, by referring to the Tab. \textit{II}, the corresponding mathematical expression for the term $\hat{a}^\dagger_0 \hat{a}_2$ is:

$$\hat{a}^\dagger_0 \hat{a}_2 = \frac{1}{4} \sigma^x_{U_{02}} \sigma^y_{02} \sigma^z_{P_{02}} \left[ \sigma^y_2 \sigma^x_0 - \sigma^y_0 \sigma^x_0 + i (\sigma^x_2 \sigma^y_0 + \sigma^y_2 \sigma^x_0) \right]. \quad (2.53)$$

According to Eq. (51) and Eq. (54) from the paper, the qubits set in Eq. \textit{(2.53)} can be found as follows:

$$U_{02} = (U(0) \triangle U(2)) \setminus (U(0) \cap U(2)) = \{1\}, \quad (2.54a)$$

$$\alpha_{02} = U(0) \cap P(2) = \{1\}, \quad (2.54b)$$

$$P^0_{02} = (P(0) \triangle P(2)) \setminus (P(0) \cap P(2)) = \{1\}. \quad (2.54c)$$

By substituting the set in Eq. \textit{(2.54)} into the Eq. \textit{(2.53)}, the mathematical expression of the term $\hat{a}^\dagger_0 \hat{a}_2$ can be obtained as shown in Eq. \textit{(2.55)}:

$$\hat{a}^\dagger_0 \hat{a}_2 = \frac{1}{4} \sigma^y_1 \left[ \sigma^y_2 \sigma^x_0 - \sigma^y_0 \sigma^x_0 - i \sigma^x_2 \sigma^y_0 + \sigma^y_2 \sigma^x_0 \right]$$

$$= \frac{1}{4} \left( \sigma^y_2 \sigma^y_1 \sigma^x_0 - \sigma^y_0 \sigma^y_1 \sigma^x_0 - i \sigma^y_2 \sigma^x_1 \sigma^y_0 - i \sigma^y_0 \sigma^x_1 \sigma^y_0 \right), \quad (2.55)$$

where the notation $\otimes$ is hidden in the last-step expression.

Secondly, the term $\hat{a}^\dagger_1 \hat{a}_3$ is derived. According to the Eq. \textit{(2.30d)} and Eq. \textit{(2.33b)}, $P(3) = \{2, 1\}$ and $U(1) = \{3\}$, so the two conditional questions can be answered as follows:

1. $i = 1$ is odd and $j = 3$ is odd

2. $1 \in P(3)$ and if $3 \in U(1)$

Thus, by referring to the Tab. \textit{II}, the corresponding mathematical expression for the term $\hat{a}^\dagger_1 \hat{a}_3$ is:

$$\hat{a}^\dagger_1 \hat{a}_3 = \frac{1}{4} \sigma^x_{U_{13}} \sigma^y_{P_{13}} \left[ \sigma^z_1 \sigma^y_{P_{13}} + \sigma^x_{P_{13}} \sigma^y_{P_{13}} \right]$$

$$+ \sigma^z_3 \left[ -\sigma^x_1 \sigma^y_{P_{13}} + i \sigma^y_1 \sigma^z_{P_{13}} \right]. \quad (2.56)$$
where:

\[ U_{13} = U(1) \triangle U(3) = (U(1) \cup U(3)) \setminus (U(1) \cap U(3)) = \{3\}, \]  
(2.57a)

\[ P_{13}^0 = P(1) \triangle P(3) = (P(1) \cup P(3)) \setminus (P(1) \cap P(3)) = \{0, 1, 2\}, \]  
(2.57b)

\[ P_{13}^1 = P(1) \triangle R(3) = (P(1) \cup R(3)) \setminus (P(1) \cap R(3)) = \{0\}, \]  
(2.57c)

\[ P_{13}^2 = R(1) \triangle P(3) = (R(1) \cup P(3)) \setminus (R(1) \cap P(3)) = \{1, 2\}, \]  
(2.57d)

\[ P_{13}^3 = R(1) \triangle R(3) = (R(1) \cup R(3)) \setminus (R(1) \cap R(3)) = \emptyset, \]  
(2.57e)

and \( \sigma_1^{-1} \) means undoing one operation of applying the Pauli-Z gate on the 1st qubit.

By substituting the set in Eq. (2.57) into the Eq. (2.56), the mathematical expression of the term \( \hat{a}_1^\dagger \hat{a}_3 \) can be obtained as shown in Eq. (2.58):

\[
\hat{a}_1^\dagger \hat{a}_3 = \frac{1}{4} \left[ \sigma_1^{-1} \otimes (-i\sigma_y^0 \otimes \sigma_0^z \otimes \sigma_1^z \otimes \sigma_2^z + \sigma_1^x \otimes \sigma_1^z \otimes \sigma_2^z) + \sigma_3 \otimes (-\sigma_1^x \otimes \sigma_0^z + i\sigma_y^1) \right]
\]

\[ = \frac{1}{4} \left[ (-i\sigma_1^y \otimes \sigma_0^z \otimes \sigma_2^z + \sigma_1^x \otimes \sigma_2^z) + \sigma_3 \otimes (-\sigma_1^x \otimes \sigma_0^z + i\sigma_y^1) \right] \]

\[ = \frac{1}{4} \left( -i\sigma_0^y \sigma_1^y \sigma_2^z + \sigma_1^x \sigma_2^z - \sigma_0^x \sigma_1^x \sigma_3 \otimes (0 + i\sigma_y^1) \otimes \sigma_3 \right), \]  
(2.58)

where the notation \( \otimes \) is hidden in the last-step expression.

Thirdly, the mathematical expression of \( \hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2 \) can be found from the multiplication of the term \( \hat{a}_0^\dagger \hat{a}_2 \) in Eq. (2.55) and the term \( \hat{a}_1^\dagger \hat{a}_3 \) in Eq. (2.58) along with the simplifications
\begin{equation}
\hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2 = \left( \hat{a}_1^\dagger \hat{a}_2 \right) \left( \hat{a}_3^\dagger \hat{a}_3 \right)
= \frac{1}{16} \left( \sigma_2^y \sigma_2^y (\sigma_2^y - i) \sigma_2^y \sigma_1^y \sigma_0^y + \sigma_2^y \sigma_1^y \sigma_0^y \sigma_3^x \sigma_1^+ - \sigma_2^y \sigma_1^y \sigma_3^x \sigma_1^+ \sigma_0^y \right)
+ \sigma_2^y \sigma_2^y (i) \sigma_3^x \sigma_1^+ \sigma_0^y + \sigma_2^y \sigma_1^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y - \sigma_2^y \sigma_1^y \sigma_3^x \sigma_1^+ \sigma_0^y
+ \sigma_2^y \sigma_1^y \sigma_0^y \sigma_3^x \sigma_1^+ - \sigma_2^y \sigma_1^y \sigma_3^x \sigma_1^+ \sigma_0^y - \sigma_2^y \sigma_1^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y
- \sigma_2^y \sigma_1^y \sigma_3^x \sigma_1^+ \sigma_0^y - \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ + \sigma_2^y \sigma_3^x \sigma_1^+ \sigma_0^y + \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y
- \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y - \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y + \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y
\end{equation}

Fourthly, since the term \( \hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_0 \) is the Hermitian adjoint of the term \( \hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2 \), as shown in Eq. (2.52), its mathematical expression can be easily obtained from the Eq. (2.59):

\begin{equation}
\hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_0 = \frac{1}{16} \left( \sigma_2^y \sigma_2^y \sigma_0^y + \sigma_2^y \sigma_1^y \sigma_0^y + \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ - \sigma_2^y \sigma_1^y \sigma_3^x \sigma_1^+ \sigma_0^y \right)
+ \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y + \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y - \sigma_2^y \sigma_2^y \sigma_0^y \sigma_3^x \sigma_1^+ \sigma_0^y
+ \sigma_2^y \sigma_2^y \sigma_0^y + \sigma_2^y \sigma_2^y \sigma_0^y - \sigma_2^y \sigma_2^y \sigma_0^y + \sigma_2^y \sigma_2^y \sigma_0^y
\end{equation}

Lastly, the mathematical expression of \( \hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_3^\dagger \hat{a}_1 \hat{a}_0 \) can be obtained by adding up the Eq. (2.59) and Eq. (2.60). Due the two terms are Hermitian adjoint with each other, all the imaginary terms cancel out, while all the non-imaginary terms doubles. By
simplifying, the final expression is summarized in Eq. (78) of the paper [24], while the mathematical expression of $\hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_1^\dagger \hat{a}_3 \hat{a}_0$ is summarized in Eq. (77) by following the same procedures.

2.3.4 Complete BK transformation for the Hydrogen molecule Hamiltonian

The operators derived above are critical in deriving the complete BK transformation for the Hydrogen molecule Hamiltonian. For convenience, they are summarized in Tab. 2.4.

By substituting the number operators, Coulomb and exchange operators and the double excitation operators of the Hydrogen molecule system into the second-quantization in Eq. (2.1), the mathematical expression of the energy Hamiltonian derived with the Bravyi-Kitaev Transformation (BKT) can be obtained:

$$
\hat{H} = \frac{h_{00}}{2}(\sigma^I - \sigma^0) + \frac{h_{11}}{2}(\sigma^I - \sigma^1 \sigma^0) + \frac{h_{22}}{2}(\sigma^I - \sigma^2) + \frac{h_{33}}{2}(\sigma^I - \sigma^3 \sigma^2 \sigma^1) \\
+ \frac{h_{0101}}{4}(\sigma^I - \sigma^0 - \sigma^1 \sigma^0 + \sigma^1) + \frac{h_{0222}}{4}(\sigma^I - \sigma^2 - \sigma^2 \sigma^2 \sigma^1) \\
+ \frac{h_{1221}}{4}(\sigma^I - \sigma^1 \sigma^0 - \sigma^2 \sigma^2 \sigma^0 + \sigma^2 \sigma^1) + \frac{h_{2332}}{4}(\sigma^I - \sigma^2 - \sigma^2 \sigma^2 \sigma^1 + \sigma^2 \sigma^1) \\
+ \frac{h_{0220} - h_{0202}}{4}(\sigma^I - \sigma^0 - \sigma^2 + \sigma^0 \sigma^2) + \frac{h_{1313} - h_{1311}}{4}(\sigma^I - \sigma^1 \sigma^0 - \sigma^1 + \sigma^0 \sigma^1 + \sigma^1 + \sigma^2 \sigma^0) \\
eq \left( \frac{h_{00} + h_{11}}{2} + \frac{h_{22}}{2} + \frac{h_{0101}}{4} + \frac{h_{0222}}{4} + \frac{h_{1221}}{4} + \frac{h_{2332}}{4} + \frac{h_{0220} - h_{0202}}{4} + \frac{h_{1313} - h_{1311}}{4} \right) \sigma^I
$$

where $h_{0132} \equiv h_{0312}$.
<table>
<thead>
<tr>
<th><strong>Functionality</strong></th>
<th><strong>Number operator</strong></th>
<th><strong>Coulomb and exchange operator</strong></th>
<th><strong>Double excitation operator</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The eigenvalues of the number operator correspond to the occupation number of the arbitrary $i^{th}$ orbital</td>
<td>The Coulomb and exchange operators account for the dynamics caused by the electronic potential energies between electrons and between electron and nuclei</td>
<td>The double excitation operator accounts for the excitation of the two electrons in all orbital exchanges</td>
</tr>
<tr>
<td><strong>Representation</strong></td>
<td>$a_i^\dagger a_i$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_i^\dagger a_j a_j a_i$</td>
<td></td>
<td>$a_i^\dagger a_j a_k a_l + a_i^\dagger a_k a_j a_i$</td>
</tr>
<tr>
<td></td>
<td>$a_i^\dagger a_j^\dagger a_i$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_i^\dagger a_j a_i a_j$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Key of derivations</strong></td>
<td>Product of $a_i^\dagger$ and $a_j$ derived from BKT</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_i^\dagger a_j a_j a_i = (a_i^\dagger a_i)(a_j^\dagger a_j)$</td>
<td></td>
<td>$a_i^\dagger a_j a_k a_l + a_i^\dagger a_k a_j a_i = (a_i^\dagger a_l)(a_j^\dagger a_k) + (a_i^\dagger a_i)(a_k^\dagger a_j)$</td>
</tr>
<tr>
<td></td>
<td>$a_i^\dagger a_j^\dagger a_i a_j = -a_i^\dagger a_j a_j a_i$</td>
<td></td>
<td>$(a_i^\dagger a_k^\dagger a_j a_i)^\dagger = a_i^\dagger a_k^\dagger a_j a_i$</td>
</tr>
<tr>
<td></td>
<td>The oddness of $i,j$</td>
<td></td>
<td>The table (Tab. II [24]) for general products of the form $a_i^\dagger a_j$</td>
</tr>
<tr>
<td></td>
<td>If $i \in P(j)$ and if $j \in U(i)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Derived results</strong></td>
<td>$\frac{1}{2} \left(1 - \sigma_{F(i)}^z\right)$</td>
<td>$\frac{1}{4} \left(1 - \sigma_{F(i)}^z - \sigma_{F(j)}^z + \sigma_{F_{ij}}^z\right)$</td>
<td>Tab. II [24]</td>
</tr>
</tbody>
</table>

Table 2.4: The operator table.
By leveraging this relation and canceling out opposite terms in Eq. (2.61), the complete energy Hamiltonian of the Hydrogen molecule system derived with the Bravyi-Kitaev Transformation (BKT) is of the following form:

\[
\hat{H} = \left( \frac{h_{00}}{2} + \frac{h_{11}}{2} + \frac{h_{22}}{2} + \frac{h_{33}}{2} + \frac{h_{0110}}{4} + \frac{h_{0330}}{4} + \frac{h_{1221}}{4} + \frac{h_{2332}}{4} + \frac{h_{0220} - h_{0202}}{4} + \frac{h_{1331} - h_{1313}}{4} \right) \sigma^I
\]

where the parameters are the overlap integral parameters of the Hydrogen molecule system, which are generated based on the bond length of the molecule, and the details are out of the topic of this study.

In summary, in this chapter, the complete energy Hamiltonian of the Hydrogen molecule system is derived from the second-quantization and the Bravyi-Kitaev Transformation (BKT). The Hamiltonian in Eq. (2.62) is used to build the corresponding circuit for the simulation of the Hydrogen molecule system.
CHAPTER 3
Quantum Circuits for the Hydrogen Molecule Hamiltonian

In this chapter, the quantum circuit of the Hamiltonian operator governing the state of the Hydrogen molecule is built from scratch. The circuit can be used to simulate the state energy of the Hydrogen molecule system. In addition, the establishment process of this circuit demonstrates an example of building a quantum circuit based on a Hamiltonian, and this method can be extended to \( n \)-qubit system as needed.

3.1 Background on exponentiation of tensor products between Pauli matrices

According to Eq. (1.7), the Hamiltonian is the key operator on impacting the state evolution of a chemistry system. In addition, according to the Eq. (2.62), the Hamiltonian is composed of 15 terms for the Hydrogen molecule system:

\[
\hat{H} = \sum_{k=1}^{15} H_k,
\]

where the \( H_k \) represents the \( k^{th} \) sub-term in Eq. (2.62). By substituting the Eq. (3.1) to Eq. (1.7) and simplifying, there is:

\[
e^{-i\hat{H}t} = e^{-i(\sum_{k=1}^{15} H_k)t} \approx \prod_{k=1}^{15} e^{-iH_k t}.
\]

Therefore, the key to establishing the Hamiltonian operator of the Hydrogen molecule system is to build the circuits representing the exponentiation of each sub-term in the Hamiltonian and then to concatenate all the circuits together in lieu of the production effects between each sum-terms. Furthermore, as indicated in Eq. (2.62), each sub-term of the Hamiltonian is composed of the Pauli-X, -Y, -Z, or -I matrices. Thus, the key to successfully building the circuits for each sub-term is to be able to establish the exponentiation of tensor products between all different Pauli matrices in the circuit.
Before diving into the methods of each cases, some mathematical relations to be used in the derivations are summarized. Firstly, it is well-known that the Taylor series expansion for a number \( x \) is:

\[
e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots = \sum_n \frac{x^n}{n!}.
\] (3.3)

By following the same logic, the Taylor series expansion for a matrix \( A \) can be interpreted as:

\[
e^A = I + \frac{A^2}{2!} + \frac{A^3}{3!} + \cdots = \sum_n \frac{A^n}{n!}.
\] (3.4)

Also, it is useful to be familiar with the Maclaurin expansion of the trigonometric function:

\[
cos(\theta) = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \frac{\theta^6}{6!} + \cdots,
\] (3.5a)

\[
sin(\theta) = \theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \frac{\theta^7}{7!} + \cdots.
\] (3.5b)

### 3.2 Exponentiation of tensor products between Pauli-Z matrices

In this section, the circuits of exponentiation of tensor products between Pauli-Z matrices are derived, built, and validated.

#### 3.2.1 One-qubit case

Firstly, in the case where only one qubit is applied with the exponentiation of the Pauli-Z matrix, assume the qubit is the 0\(^{th}\) one for simplicity. The operation corresponding to this scenario should be \( e^{-i(\omega \sigma_z) \Delta t} \), where \( \omega \) is the overlap integral parameter of the sub-term of the Hamiltonian \( \hat{H} \). For example, in Eq. (2.62), the second sub-term is:

\[
H_2 = -\left( \frac{h_{00}}{2} + \frac{h_{0110}}{4} + \frac{h_{0330}}{4} + \frac{h_{0220} - h_{0202}}{4} \right) \sigma_z^0,
\] (3.6)
and the corresponding exponentiation operation is:

$$e^{-iH_2t} = e^{-i[\omega \sigma^z]t}, \quad \omega = - \left( \frac{h_{00}}{2} + \frac{h_{0110}}{4} + \frac{h_{0330}}{4} + \frac{h_{0220} - h_{0202}}{2} \right). \quad (3.7)$$

In addition, the term $e^{-i(\omega \sigma^z)\Delta t}$ can be further simplified by combining the two constant elements $\omega$ and $\Delta t$. By having $\theta = \omega \cdot \Delta t$, the term $e^{-i(\omega \sigma^z)\Delta t}$ can be re-written as:

$$e^{-i(\omega \sigma^z)\Delta t} = e^{-i\theta \sigma^z}. \quad (3.8)$$

By expanding the right side term in Eq. (3.8) leveraging the Eq. (3.4) and the Eq. (3.5), it can be obtained that:

$$e^{-i\theta \sigma^z} = \sigma^I + (-i\theta \sigma^z) + \frac{(-i\theta \sigma^z)^2}{2!} + \frac{(-i\theta \sigma^z)^3}{3!} + \frac{(-i\theta \sigma^z)^4}{4!} - \cdots$$

$$= \sigma^I - i\theta \sigma^z - \frac{\theta^2}{2!} \sigma^I + \frac{\theta^3}{3!} \sigma^z + \frac{\theta^4}{4!} \sigma^I - \cdots$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \cdots\right) \sigma^I + i \left( \theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} + \cdots \right) \sigma^z$$

$$= \cos(\theta) \sigma^I - i \sin(\theta) \sigma^z \quad (3.9)$$

As shown in Fig. 3.1, in quantum gates, the $R_z$ gate has the equivalent expression:

$$R_z(2\theta) = \begin{bmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{bmatrix} \quad (3.10)$$

Therefore, the circuit in Fig. 3.1 can be used to represent applying the exponentiation of Pauli-Z matrices on one qubit case.
3.2.2 Two-qubit case and beyond

Secondly, in the case of two qubits being applied with the exponentiation of tensor products between Pauli-Z matrices, for example, the $0^{th}$ and the $1^{st}$ qubit, the corresponding operation should be $e^{-i(\omega \sigma_1^z \otimes \sigma_0^z) \Delta t}$. By leveraging the relation between $\theta$ and $\omega$, the operation to be built is $e^{-i\theta(\sigma_1^z \otimes \sigma_0^z)}$.

By expanding the term leveraging the Eq. (3.4) and the Eq. (3.5), it can be obtained that:

$$e^{-i\theta(\sigma_1^z \otimes \sigma_0^z)} = \sigma^I \otimes \sigma^I + (-i \theta \sigma_1^z \otimes \sigma_0^z) + \frac{(-i \theta \sigma_1^z \otimes \sigma_0^z)^2}{2!} + \frac{(-i \theta \sigma_1^z \otimes \sigma_0^z)^3}{3!} + \cdots$$

$$= \sigma^I \otimes \sigma^I - i \theta \sigma_1^z \otimes \sigma_0^z - \frac{\theta^2}{2!} \sigma^I \otimes \sigma^I + \frac{i \theta^3}{3!} \sigma_1^z \otimes \sigma_0^z + \frac{\theta^4}{4!} \sigma^I \otimes \sigma^I - \cdots$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \cdots\right) \sigma^I \otimes \sigma^I + i \left(-\theta + \frac{\theta^3}{3!} - \frac{\theta^5}{5!} + \cdots\right) \sigma_1^z \otimes \sigma_0^z$$

$$= \cos(\theta) \sigma^I \otimes \sigma^I - i \sin(\theta) \sigma_1^z \otimes \sigma_0^z$$

\begin{equation}
(3.11)
\end{equation}

The resultant operation derived from Eq. (3.11) can be represented with the circuit shown in Fig. 3.2, where the moment in a quantum circuit is simply a collection of opera-
Fig. 3.2: Circuit of exponentiation of the tensor products between Pauli-Z matrix for two qubits.

The diagram shows three moments labeled Moment 1, Moment 2, and Moment 3, with CNOT gates applied to entangle the two qubits so that the effect of the relative phase evolution in moment 2 can be transmitted to both qubits in the system.

The CNOT gate can be represented in matrix form as follows:

\[
CNOT = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0
\end{bmatrix}.
\]  

(3.12)

and if the \(i^{th}\) moment is called \(M_i\), then there is

\[
M_1 = M_3 \equiv CNOT.
\]  

(3.13)

The matrix representation of the moment 2 can be derived by using the Eq. (3.10):

\[
M_2 = \sigma^I \otimes R_z(2\theta) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{bmatrix} = \begin{bmatrix} e^{-i\theta} & 0 & 0 & 0 \\ 0 & e^{i\theta} & 0 & 0 \\ 0 & 0 & e^{-i\theta} & 0 \\ 0 & 0 & 0 & e^{i\theta} \end{bmatrix}.
\]  

(3.14)
Thus, the operation represented in circuit of Fig. 3.2 in matrix form can be derived:

\[
M_3 \times (M_2 \times M_1) = CNOT \times \left( (\sigma^I \otimes R_z(2\theta)) \times CNOT \right)
\]

\[
= \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0
\end{bmatrix}
\times
\begin{bmatrix}
e^{-i\theta} & 0 & 0 & 0 \\
0 & e^{i\theta} & 0 & 0 \\
0 & 0 & e^{-i\theta} & 0 \\
0 & 0 & 0 & e^{i\theta}
\end{bmatrix}
\times
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0
\end{bmatrix}
\]

\[
(3.15)
\]

\[
= \begin{bmatrix}
e^{-i\theta} & 0 & 0 & 0 \\
0 & e^{i\theta} & 0 & 0 \\
0 & 0 & e^{i\theta} & 0 \\
0 & 0 & 0 & e^{-i\theta}
\end{bmatrix}.
\]

Since the right side of Eq. (3.15) is equivalent to that of Eq. (3.11), it can be concluded that:

\[
e^{-i\theta}(\sigma_1^z \otimes \sigma_0^z) \equiv (M_3 \times (M_2 \times M_1)).
\]

Therefore, it is valid to use the circuit in Fig. 3.2 to represent the operation of applying the exponentiation of products of Pauli-Z matrices on two qubits.

Furthermore, by following the similar derivation procedure, circuits of exponentiation of the tensor products between Pauli-Z matrix for three-qubit and four-qubit cases can be easily obtained, as summarized in Fig. 3.3. Most importantly, the pattern can be extended to the n-qubit case as needed.

### 3.3 Exponentiation of tensor products between Pauli-X and Pauli-Y matrices

According to [26], the exponentiation of tensor product between Pauli-X matrices and Pauli-Y matrices is very similar to that of the Pauli-Z matrices, except for two differences.

When applying the exponentiation of the tensor product between the Pauli-X matrix on a system of qubits, the Hadamard gate must be applied on the corresponding qubit before the first moment of the circuit and after the last moment of the circuit. The Hadamard
(a) Circuit of exponentiation of the tensor products between Pauli-Z matrices for three qubits.

\[ e^{-i\theta(\sigma_z^2 \otimes \sigma_z^1 \otimes \sigma_z^0)} \]

(b) Circuit of exponentiation of the tensor products between Pauli-Z matrices for four qubits.

\[ e^{-i\theta(\sigma_z^3 \otimes \sigma_z^2 \otimes \sigma_z^1 \otimes \sigma_z^0)} \]

Fig. 3.3: Circuits of exponentiation of the products between Pauli-Z matrix for more than two qubits.

gate in matrix form can be expressed as:

\[ H = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \] \hspace{1cm} (3.17)

where \( H \) in Eq. (3.17) means the Hadamard gate instead of the Hamiltonian.

When applying the exponentiation of the tensor product between the Pauli-Y matrix on a system of qubits, the \( R_x \) gate must be applied on the corresponding qubit before the first moment of the circuit and the \( R_x^\dagger \) after the last moment of the circuit. The \( R_x \) and \( R_x^\dagger \) gates in matrix form can be expressed as:

\[ R_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}, \quad R_x^\dagger = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \] \hspace{1cm} (3.18)
3.3.1 One-qubit case

Firstly, in case that only one qubit is applied with the exponentiation of the Pauli-X or Pauli-Y matrix, assume the qubit is the 0th one for simplicity. The operation corresponding to the scenario should be $e^{-i(\omega_0^x)t}$ or $e^{-i(\omega_0^y)t}$, and again, by simplifying with the relation between $\theta$ and $\omega$, the operations become $e^{-i\theta_0^x}$ or $e^{-i\theta_0^y}$.

By expanding the Pauli-X term leveraging the Eq. (3.4) and the Eq. (3.5), it can be obtained that:

$$e^{-i\theta_0^x} = \sigma^I + (-i\theta_0^x) + \frac{(-i\theta_0^x)^2}{2!} + \frac{(-i\theta_0^x)^3}{3!} + \frac{(-i\theta_0^x)^4}{4!} - \cdots$$

$$= \sigma^I - i\theta_0^x - \frac{\theta^2}{2!} \sigma^I + \frac{i\theta^3}{3!} \sigma^x + \frac{\theta^4}{4!} \sigma^I - \cdots$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \cdots\right) \sigma^I + i\left(\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} + \cdots\right) \sigma^x$$

$$= \cos(\theta)\sigma^I - i \cdot \sin(\theta)\sigma^x$$

(3.19)

$$= \begin{bmatrix} \cos(\theta) & 0 \\ 0 & \cos(\theta) \end{bmatrix} - \begin{bmatrix} 0 & i \cdot \sin(\theta) \\ i \cdot \sin(\theta) & 0 \end{bmatrix}$$

$$= \begin{bmatrix} \cos(\theta) & -i \cdot \sin(\theta) \\ -i \cdot \sin(\theta) & \cos(\theta) \end{bmatrix}.$$ 

The resultant operation derived from Eq. (3.19) can be represented with the circuit shown in Fig. 3.4, where the moment 1 and moment 3 are simply the Hadamard gates.

![Fig. 3.4: Circuit of exponentiation of the Pauli-X matrix for one qubit.](image)
Thus the operation represented in circuit of Fig. 3.4 in matrix form can be derived:

\[ M_3 \times (M_2 \times M_1) = H \times (R_z(2\theta) \times H) \]

\[
= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \times \left( \begin{bmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{bmatrix} \times \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \right)
\]

\[
= \frac{1}{2} \begin{bmatrix} e^{-i\theta} + e^{i\theta} & e^{-i\theta} - e^{i\theta} \\ e^{-i\theta} - e^{i\theta} & e^{-i\theta} + e^{i\theta} \end{bmatrix}
\]

\[
= \begin{bmatrix} \cos(\theta) & -i \cdot \sin(\theta) \\ -i \cdot \sin(\theta) & \cos(\theta) \end{bmatrix}.
\]

(3.20)

Since the right side of Eq. (3.20) is equivalent to that of Eq. (3.19), it can be concluded that the circuit in Fig. 3.4 can represent the operation \( e^{-i\theta\sigma^z_0} \).

Similarly, by expanding the Pauli-Y term leveraging the Eq. (3.4) and the Eq. (3.5), it can be obtained that:

\[
e^{-i\theta\sigma^y_0} = \sigma^I + (-i\theta\sigma^y_0) + \frac{(-i\theta\sigma^y_0)^2}{2!} + \frac{(-i\theta\sigma^y_0)^3}{3!} + \frac{(-i\theta\sigma^y_0)^4}{4!} - \cdots
\]

\[
= \sigma^I - i\theta\sigma^y_0 - \frac{\theta^2}{2!}\sigma^I + \frac{i\theta^3}{3!}\sigma^y_0 + \frac{\theta^4}{4!}\sigma^I - \cdots
\]

\[
= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \cdots \right)\sigma^I + i \left(\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} + \cdots \right)\sigma^y_0
\]

\[
= \cos(\theta)\sigma^I - i \cdot \sin(\theta)\sigma^y_0
\]

(3.21)

The resultant operation derived from Eq. (3.21) can be represented with the circuit shown in Fig. 3.5, where the moment 1 and moment 3 are the \( R_x \) gate and the \( R^\dagger_x \) gate, respectively.
Thus the operation represented in circuit of Fig. 3.5 in matrix form can be derived:

\[
(M_3 \times (M_2 \times M_1)) = \left( R_x \times \left( R_z(2\theta) \times R_x^\dagger \right) \right)
\]

\[
= \left( \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \times \left( \begin{bmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{bmatrix} \times \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \right) \right) 
\]

\[
= \frac{1}{2} \begin{bmatrix} e^{-i\theta} + e^{i\theta} & -i \cdot e^{-i\theta} + i \cdot e^{i\theta} \\ i \cdot e^{-i\theta} - i \cdot e^{i\theta} & e^{-i\theta} + e^{i\theta} \end{bmatrix} 
\]

\[
= \begin{bmatrix} \cos(\theta) & -i \sin(\theta) \\ i \sin(\theta) & \cos(\theta) \end{bmatrix}.
\]

Since the right side of Eq. (3.22) is equivalent to that of Eq. (3.21), it can be concluded that the circuit in Fig. 3.5 can represent the operation \( e^{-i\theta \sigma^y_0} \).

### 3.3.2 Two-qubit case and beyond

By following the similar derivation procedure of the exponentiation of the tensor product between Pauli-Z matrices for two qubits, as demonstrated in Sec. 3.2.2, the circuits representing the exponentiation of the tensor product between Pauli-X matrices and between Pauli-Y matrices for two qubits are demonstrated in Fig. 3.6.

Lastly, by following the similar derivation procedure, the pattern can be extended to the n-qubit case for either the Pauli-X or Pauli-Y matrices tensor product exponentiation.

### 3.4 Exponentiation of tensor products between identity matrices

As indicated in the Hamiltonian in Eq. (2.62), the first sub-term is a Pauli-I matrix,
(a) Circuit of exponentiation of the tensor products between Pauli-X matrices for two qubits.

\[ e^{-i\theta (\sigma_3^X \otimes \sigma_0^X)} \]

(b) Circuit of exponentiation of the tensor products between Pauli-Y matrices for two qubits.

\[ e^{-i\theta (\sigma_1^Y \otimes \sigma_0^Y)} \]

Fig. 3.6: Circuit of exponentiation of the tensor products between Pauli-X matrices and between Pauli-Y matrices for two qubits.

and the exponentiation of the term should be \( e^{-i\theta \omega (\sigma_3^X \otimes \sigma_1^X \otimes \sigma_1^Y \otimes \sigma_0^Y)} \Delta t \), which can be further simplified to \( e^{-i\omega (\sigma_3^X \otimes \sigma_1^X \otimes \sigma_1^Y \otimes \sigma_0^Y)} \) according to the relation between \( \theta \) and \( \omega \). In this section, the circuits of exponentiation of the tensor products between Pauli-I matrices for system of qubits are derived.

3.4.1 One-qubit case

Firstly, in case only one qubit is applied with the exponentiation of the Pauli-I matrix, again, assume the qubit is the 0\(^{th}\) one for simplicity. The simplified operation corresponding to this scenario is \( e^{-i\theta \sigma_0^I} \).
By expanding the term directly leveraging the Eq. (3.4) and the Eq. (3.5), it can be obtained that:

\[
e^{-i\theta\sigma^I_0} = \sigma^I + (-i\theta\sigma^z_0) + \frac{(-i\theta\sigma^z_0)^2}{2!} + \frac{(-i\theta\sigma^z_0)^3}{3!} + \frac{(-i\theta\sigma^z_0)^4}{4!} - \cdots
\]

\[
= \sigma^I - i\theta\sigma^z - \frac{\theta^2}{2!}\sigma^I + \frac{i\theta^3}{3!}\sigma^z + \frac{\theta^4}{4!}\sigma^I - \cdots
\]

\[
= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \cdots\right)\sigma^I + i\left(\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} + \cdots\right)\sigma^z_0
\]

\[
= \cos(\theta)\sigma^I - i \cdot \sin(\theta)\sigma^z_0
\]

(3.23)

As shown in Fig. 3.7, if the matrix derived in Eq. (3.23) is named the \( R_I \) gate, it can be used to represent the operation \( e^{-i\theta\sigma^I_0} \).

![Fig. 3.7: Circuit of exponentiation of the Pauli-I matrix for one qubit.](image)

### 3.4.2 Two-qubit case and beyond

In the case of two qubits being applied with the exponentiation of tensor product between Pauli-I matrices, for instance, the 0\(^{th}\) and the 1\(^{st}\) qubit, then the simplified operation corresponding to this scenario is \( e^{-i\theta\sigma^I_0 \otimes \sigma^I_0} \).
By expanding the term leveraging the Eq. (3.4) and the Eq. (3.5), it can be obtained that:

\[
e^{-i\theta(\sigma_1^I \otimes \sigma_0^I)} = \sigma^I \otimes \sigma^I + (-i\theta \sigma_1^I \otimes \sigma_0^I) + \left(\frac{-i\theta \sigma_1^I \otimes \sigma_0^I}{2!}\right)^2 + \left(\frac{-i\theta \sigma_1^I \otimes \sigma_0^I}{3!}\right)^3 + \cdots
\]

\[
= \sigma^I \otimes \sigma^I - i\theta \sigma_1^I \otimes \sigma_0^I - \frac{\theta^2}{2!} \sigma^I \otimes \sigma^I + \frac{i\theta^3}{3!} \sigma_1^I \otimes \sigma_0^I + \frac{\theta^4}{4!} \sigma^I \otimes \sigma^I - \cdots
\]

\[
= \left(1 - \frac{\theta^2}{2} + \frac{\theta^4}{4!} - \cdots\right) \sigma^I \otimes \sigma^I + i \left(-\theta + \frac{\theta^3}{3} - \frac{\theta^5}{5!} + \cdots\right) \sigma_1^I \otimes \sigma_0^I
\]

\[
= \cos(\theta) \sigma^I \otimes \sigma^I - i \sin(\theta) \sigma_1^I \otimes \sigma_0^I
\]

\[
= \cos(\theta) \cdot \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} - i \sin(\theta) \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\]

\[
= \begin{bmatrix} e^{-i\theta} & 0 & 0 & 0 \\ 0 & e^{-i\theta} & 0 & 0 \\ 0 & 0 & e^{-i\theta} & 0 \\ 0 & 0 & 0 & e^{-i\theta} \end{bmatrix}
\]

The resultant operation derived from Eq. (3.24) can be represented with either the circuits shown in Fig. 3.8.

Fig. 3.8: Circuit of exponentiation of the tensor products between Pauli-I matrices for two qubits.
Use the left circuit as a proofing example:

\[ M_3 \times (M_2 \times M_1) \]

\[ = CNOT \times ((\sigma I \otimes R_{I}(2\theta)) \times CNOT) \]

\[ = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \times \begin{bmatrix} e^{-i\theta} & 0 & 0 & 0 \\ 0 & e^{-i\theta} & 0 & 0 \\ 0 & 0 & e^{-i\theta} & 0 \\ 0 & 0 & 0 & e^{-i\theta} \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \]

\[ = \begin{bmatrix} e^{-i\theta} & 0 & 0 & 0 \\ 0 & e^{-i\theta} & 0 & 0 \\ 0 & 0 & e^{-i\theta} & 0 \\ 0 & 0 & 0 & e^{-i\theta} \end{bmatrix} \]

where the right side of Eq. (3.25) is equivalent to that of the Eq. (3.24).

(a) Circuit of exponentiation of the tensor products between Pauli-I matrices for three qubits.

(b) Circuit of exponentiation of the tensor products between Pauli-I matrices for four qubits.

Fig. 3.9: Circuits of exponentiation of the products between Pauli-I matrix for more than two qubits.

Furthermore, by following the similar derivation procedure, circuits of exponentiation...
of the tensor products between Pauli-I matrix for three-qubit and four-qubit cases can be easily obtained, as summarized in Fig. 3.9, where $I \equiv \sigma^I$. Most importantly, the pattern can be extended to the n-qubit case as well.

### 3.5 Exponentiation of tensor products between hybrid matrices

With the methods of establishing the circuits of the tensor products exponentiation between the same type of Pauli matrices, including Pauli-X, -Y, -Z and -I, the circuit with hybrid types of Pauli matrix can also be established easily.

For example, to represent the operation $e^{-i\theta(\sigma^y_1 \sigma^x_0)}$ with the quantum circuit, the circuit shown in Fig. 3.10 is the one, where in the first moment and the last moment, the Hadamard gates are applied on the 0th qubit because the exponentiation of the Pauli-X gate is applied on the qubit, while the $R_x$ gate is applied on the 1st qubit in the first moment and the $R_x^\dagger$ gate in the last moment because the exponentiation of the Pauli-Y gate is applied on the qubit. By following a similar logic, the circuits of the exponentiation of each sub-term in the Hamiltonian summarized in Eq. (2.62) is summarized in Fig. 3.11 and Fig. 3.12.

![Fig. 3.10: Circuit of exponentiation of the tensor products between Pauli-Y and Pauli-X matrices for two qubits.](image)

### 3.6 Hamiltonian circuit

Finally, the circuit of the Hamiltonian derived in Eq. (2.62) that can be leveraged to simulate the dynamics of the Hydrogen molecule system is established, as shown in Fig. 3.13. Because the whole circuit is too long, it has been cut into four section, and the original circuit can be obtained by concatenating each section by sequence.
Sub-Hamiltonian Based Operation | Circuits
--- | ---
$e^{-i\theta_1 (1_3 \otimes 1_2 \otimes 1_1 \otimes 1_0)}$ | ![Circuit for $e^{-i\theta_1 (1_3 \otimes 1_2 \otimes 1_1 \otimes 1_0)}$]
$e^{-i\theta_2 (\sigma_0^z)}$ | ![Circuit for $e^{-i\theta_2 (\sigma_0^z)}$]
$e^{-i\theta_3 (\sigma_1^z)}$ | ![Circuit for $e^{-i\theta_3 (\sigma_1^z)}$]
$e^{-i\theta_4 (\sigma_2^z)}$ | ![Circuit for $e^{-i\theta_4 (\sigma_2^z)}$]
$e^{-i\theta_5 (\sigma_0^z \sigma_1^z)}$ | ![Circuit for $e^{-i\theta_5 (\sigma_0^z \sigma_1^z)}$]
$e^{-i\theta_6 (\sigma_0^z \sigma_2^z)}$ | ![Circuit for $e^{-i\theta_6 (\sigma_0^z \sigma_2^z)}$]
$e^{-i\theta_7 (\sigma_1^z \sigma_3^z)}$ | ![Circuit for $e^{-i\theta_7 (\sigma_1^z \sigma_3^z)}$]
$e^{-i\theta_8 (\sigma_0^x \sigma_1^z \sigma_2^z \sigma_3^z)}$ | ![Circuit for $e^{-i\theta_8 (\sigma_0^x \sigma_1^z \sigma_2^z \sigma_3^z)}$]

Fig. 3.11: Circuits for Sub-Hamiltonians (a).
Fig. 3.12: Circuits for Sub-Hamiltonians (b).
(a) The first section of the Hamiltonian circuit.

(b) The second section of the Hamiltonian circuit.

(c) The third section of the Hamiltonian circuit.

(d) The fourth section of the Hamiltonian circuit.

Fig. 3.13: Circuit of the Hamiltonian.
The parameter $\theta_i$ in the circuit are defined as follows:

$$\theta_i = \omega_i \cdot \Delta t, \quad i = 1, 2, \cdots, 15,$$

and the overlap integral parameters $\omega_i$ can be obtained from the Eq. (2.62):

$$\omega_1 = \frac{3}{2} \left( \frac{h_{ii}}{4} + \frac{h_{0110}}{4} + \frac{h_{0330}}{4} + \frac{h_{1221}}{4} + \frac{h_{2332}}{4} + \frac{h_{0220} - h_{0202}}{4} + \frac{h_{1331} - h_{1313}}{4} \right), \quad (3.27a)$$

$$\omega_2 = -\left( \frac{h_{00}}{2} + \frac{h_{0110}}{4} + \frac{h_{0330}}{4} + \frac{h_{0220} - h_{0202}}{4} \right), \quad (3.27b)$$

$$\omega_3 = \frac{h_{0110}}{4}, \quad (3.27c)$$

$$\omega_4 = -\left( \frac{h_{22}}{2} + \frac{h_{1221}}{4} + \frac{h_{2332}}{4} + \frac{h_{0220} - h_{0202}}{4} \right), \quad (3.27d)$$

$$\omega_5 = -\left( \frac{h_{11}}{2} + \frac{h_{0110}}{4} + \frac{h_{1221}}{4} + \frac{h_{1331} - h_{1313}}{4} \right), \quad (3.27e)$$

$$\omega_6 = \frac{h_{0220} - h_{0202}}{4}, \quad (3.27f)$$

$$\omega_7 = \frac{h_{2332}}{4}, \quad (3.27g)$$

$$\omega_8 = \frac{h_{0132}}{4}, \quad (3.27h)$$

$$\omega_9 = \frac{h_{0132} - h_{0312}}{8}, \quad (3.27i)$$

$$\omega_{10} = \frac{h_{1221}}{4}, \quad (3.27j)$$

$$\omega_{11} = \frac{h_{1331} - h_{1313}}{4}, \quad (3.27k)$$

$$\omega_{12} = -\left( \frac{h_{33}}{2} + \frac{h_{0330}}{4} + \frac{h_{2332}}{4} + \frac{h_{1331} - h_{1313}}{4} \right), \quad (3.27l)$$

$$\omega_{13} = \frac{h_{0132} + h_{0312}}{8}, \quad (3.27m)$$

$$\omega_{14} = \frac{h_{0132} + h_{0312}}{8}, \quad (3.27n)$$

$$\omega_{15} = \frac{h_{0330}}{4}. \quad (3.27o)$$

In summary, the circuit of the exponentiation of the Hydrogen molecule Hamiltonian is built from scratch, and it can be used to simulate the system. Importantly, by understanding the fundamentals of the second-quantization and the Bravyi-Kitaev transformation (BKT),
the Hamiltonian for other chemistry system can also be derived. In addition, by following the logic of the quantum circuit derivations demonstrated in this chapter, the simulation circuit for a system of qubits of any size can be developed, and simulations for chemistry molecules other than the hydrogen molecule are also viable.

3.7 Quantum circuit application example: phase estimation algorithm

One of the applications of the Hamiltonian circuits in Fig. 3.13 is to simulate the state energies of the Hydrogen molecule system, and there are in general two approaches. One approach is to leverage the Phase Estimation Algorithm (PEA) through the quantum processors, and another one is to use the linear algebra packages through the classical computers. However, the goal of both approaches is to find the eigenvalue of the Hamiltonian at a given system bond length.

While the approach with the classical computer is used in most of the simulations nowadays, the quantum approach is of importance to realize pure quantum computing. The core intuition of the PEA algorithm is to convert the state of a qubit from $Z$–axis to $X – Y$ plane in the Bloch sphere so that the relative phase of the qubit can be measured at any moment of time [27]. Then, by collecting the relative phase information in a period, the angular frequency of the qubit state around the $Z$–axis can be found, which is directly related with the system’s ground state energy.

![Fig. 3.14: Core circuit for one-qubit Phase Estimation Algorithm (PEA).](image)

Take a single qubit as an example, its core PAE circuit is shown in Fig. 3.14, which
is composed of four moments. In most quantum computing, the default state of a qubit is $|0\rangle$. Therefore, the initial state of the qubit in the circuit is assumed to be by default. The first moment is a Hadamard gate, which serves for the purpose of projecting the state of the qubit from the $Z$–axis to the $X$ – $Y$ plane in the corresponding Bloch sphere. Then, the second moment is a $R – 1$ gate, and its mathematical expression is:

$$R_1(\theta) = \begin{bmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{bmatrix}.$$  (3.28)

The purpose of the $R_1$ gate on the qubit is to have the qubit evolve around the $Z$–axis for $\theta$ radius, which is also called the relative phase. The moment 3 is another Hadamard gate, which converts the state of the qubit back to its original $Z$ basis. Last, the qubit is measured on the $Z$ basis as indicated at the moment 4, and the $Z$ basis measurement is mathematically expressed as:

$$M_z = \begin{bmatrix} 0 & 1 \end{bmatrix}.$$  (3.29)

Therefore, the mathematical expression of the whole circuit operation can be calculated from:

$$U = M_4 \times (M_3 \times (M_2 \times M_1))$$

$$= \begin{bmatrix} 0 & 1 \end{bmatrix} \times \left( \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \times \left( \begin{bmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{bmatrix} \times \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \right) \right)$$

$$= \frac{1}{2} \left[ 1 - e^{i\theta} \ 1 + e^{i\theta} \right],$$

where $U$ represents the whole circuit. The probability of having a measurement of $|1\rangle$ is:

$$\Pr (|\psi'_0\rangle = |1\rangle) = |U |\psi_0\rangle|^2$$

$$= \left| \frac{1}{2} \left[ 1 - e^{i\theta} \ 1 + e^{i\theta} \right] \times \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right|^2 = \left| \frac{1}{2} \left( 1 - e^{i\theta} \right) \right|^2,$$  (3.31)

where $|\psi_0\rangle$ is the initial qubit state, and $|\psi'_0\rangle$ is the final qubit state.

Eq. (3.31) can be further simplified by leveraging the Euler’s formula, the double-angle
identity equation and the formula for calculating the magnitude of a complex number, as summarized in Eq. (3.32)

\[
e^{i\theta} = \cos(\theta) + i\sin(\theta), \quad (3.32a)
\]

\[
e^{-i\theta} = \cos(\theta) - i\sin(\theta), \quad (3.32b)
\]

\[
\sin(2\theta) = 2\sin(\theta)\cos(\theta), \quad (3.32c)
\]

\[
\cos(2\theta) = \cos^2(\theta) - \sin^2(\theta) = 1 - 2\sin^2(\theta) = 2\cos^2(\theta) - 1, \quad (3.32d)
\]

\[
|a + b \cdot i| = \sqrt{a^2 + b^2}. \quad (3.32e)
\]

Therefore, Eq. (3.31) can be further simplified as below:

\[
\left| \frac{1}{2} \left(1 - e^{i\theta}\right) \right|^2 = \left| \frac{1}{2} \left(1 - (\cos(\theta) + i\sin(\theta))\right) \right|^2
\]

\[
= \left| \frac{1}{2} \left(1 - \left(1 - 2\sin^2\left(\frac{\theta}{2}\right)\right) - 2i\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)\right) \right|^2
\]

\[
= \left| \sin^2\left(\frac{\theta}{2}\right) - i\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right) \right|^2
\]

\[
= \left| \sin\left(\frac{\theta}{2}\right) \right|^2 \cdot \left| \sin\left(\frac{\theta}{2}\right) - i\cos\left(\frac{\theta}{2}\right) \right|^2
\]

\[
= \sin^2\left(\frac{\theta}{2}\right). \quad (3.33)
\]

This indicates the final state of the qubit \(|\psi'_0\rangle\) has the probability of \(\sin^2\left(\frac{\theta}{2}\right)\) to collapse to the state \(|1\rangle\) after applying the circuit \(U\) on its initial state of \(|0\rangle\). In addition, by following a similar derivation procedure, it can be proved that the final state of the qubit \(|\psi'_0\rangle\) has the probability of \(\cos^2\left(\frac{\theta}{2}\right)\) to collapse to the state \(|1\rangle\) after applying the circuit \(U\) if its initial state is \(|1\rangle\). In either case, a sinewave function directly related to the relative phase of the qubit can be obtained. At different bond lengths of the Hydrogen molecule system, the frequency of the sinewave is unique, which can lead to the solution to the corresponding state energy of the molecular system.
CHAPTER 4
Numerical Results and Discussions

The Hamiltonian energy circuit of the Hydrogen molecule system derived in this study can be used for many tasks, including exploring the orbital dynamics of the Hydrogen molecule or finding the system state energy at a certain bond length. To testify the validity of the derived circuit, the Hamiltonian circuit is used to calculate the ground and the first-excited state energies of the Hydrogen molecule at different bond lengths, as well the ground state energy of the lithium hydride molecule at different bond lengths, and the corresponding codes are summarized in https://github.com/Yili-Zhang/STAT_Thesis_Code. Moreover, the simulated results are qualitatively and quantitatively compared with the results from previous publications. Due to the time limit, the Phase Estimation Algorithm is not used in the simulation, and the classical computer is used during the simulation to solve for the corresponding Hamiltonian’s eigenvalues.

4.1 Ground state energies of the hydrogen molecule system

By leveraging the Eq. (2.62), the circuit in Fig. 3.13 and the Google Cirq library [28], the ground state energies of the Hydrogen molecule system at different bond lengths can be simulated and calculated as shown in Fig. 4.1.

In the simulation, the ground state energy at 17 bond lengths is generated, ranging from 0.5 to 1.6 Å (angstroms). In Fig. 4.1, the X-axis represents the bond lengths (in the unit of Å), which are half of the distance between the two atomic clouds in the Hydrogen molecule. The Y-axis represents the ground state energy of the Hydrogen molecule at the corresponding bond length. The blue circle scatters represent the energy curve generated in this study based on the second-quantization and the Bravyi-Kitaev transformation (BKT), while the orange star scatters represent the energy curve generated based on the dataset from the Tab. II of Kolos et al. study in 1968 [2].
By qualitatively comparing the ground state energies at different bond lengths from this study with that from Kolos et al. study, as shown in Fig. 4.1, both ground state energy curves of the Hydrogen molecule are the similar trend. The slight shift between the energy curves of the two studies is likely to be caused by the different approaches to deriving the Hamiltonians, where the Hamiltonian from the Kolos et al. study is calculated by accumulating and integrating the wave functions in the Hydrogen molecule, which is similar to the first-quantization method, while the Hamiltonian from this study is derived from the second-quantization.

By quantitatively comparing the two studies, firstly, the bond length corresponding to the lowest ground state energy in this study is found to be 0.750 Å, while the one from the Kolos et al. study is 0.701 Å. The absolute difference between them is 0.049 Å, as summarized in Tab. 4.1. In addition, as shown in the table, the lowest ground state energy in this study is found to be $-1.13711707$ Hartrees, while the one in the Kolos et al. study is $-1.17447482$ Hartrees. The absolute difference between them is 0.03735775 Hartrees.
Table 4.1: Comparisons between minimum ground state energies and corresponding bond lengths in two studies.

<table>
<thead>
<tr>
<th>Bond length of min. energy</th>
<th>Min. ground energy state</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Å]</td>
<td>[Hartree]</td>
</tr>
<tr>
<td>This study</td>
<td>0.750</td>
</tr>
<tr>
<td>Kolos et al. study</td>
<td>0.701</td>
</tr>
<tr>
<td>Absolute difference</td>
<td>0.049</td>
</tr>
</tbody>
</table>

Thus, it can be claimed that both the minimum ground state energy difference and the corresponding bond length difference are relatively small. Furthermore, as shown in Tab. 4.2, the average absolute difference over the whole ground state energies between the two studies is 0.04524362 Hartrees, while the average relative absolute difference is 4.02%, which are within reasonable small ranges.

Table 4.2: Average absolute and relative differences of ground state energies between this and the Kolos et al. studies.

<table>
<thead>
<tr>
<th>Average absolute difference</th>
<th>Average relative absolute difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Hartree]</td>
<td>[%]</td>
</tr>
<tr>
<td>0.04524362</td>
<td>4.02</td>
</tr>
</tbody>
</table>

So far, it can be concluded that from both the qualitative and quantitative comparisons between the results from this study and that from the Kolos et al. study in 1968, the circuit built from the derivations of the second-quantization and the Bravyi-Kitaev transformation (BKT) can accurately simulate the ground state energy of the Hydrogen molecule at different system bond lengths.

4.2 Excited state energies of the hydrogen molecule system

Furthermore, with the same circuit, by updating the overlying integral parameters in the Hamiltonian from the ground state values to the first-excited state values, the first-excited state energy curve of the Hydrogen molecule can be simulated as well, as indicated
in Fig. 4.2. In the figure, 40 bond lengths are generated ranging from 0.2 Å to 3.5 Å. The blue circle scatters represent the ground state energy curve generated based on the circuit built from this study, while the orange diamond scatters represent the first-exited state energy curve generated from this study as well. By qualitatively comparing the results in Fig. 4.2 with that in Fig. 3 from the study of Colless et al. [29], it can be observed the curve trend and the order of magnitudes of the ground and first-exited state energies are very similar between two studies. Thus, it can be concluded that the circuit built from this study can work well for the first-exited state of the Hydrogen molecule system.

Fig. 4.2: Ground state energy and excited state energy curves for the hydrogen molecule.
4.3 Ground state energies for the Lithium hydride $LiH$

In a similar manner, we can calculate the ground state energies of the $LiH$ with different bond lengths, as shown in Figure 4.3.

![Ground State Energy Levels of LiH at Different Bond Lengths](image)

Fig. 4.3: Ground state energy and excited state energy curves for the $LiH$. 
CHAPTER 5

Conclusion and Future Work

In summary, in this study, how the Schrodinger’s Equation and the Phase Estimation Algorithm are used to estimate the Hydrogen molecule’s state energy is explained, and the Hamiltonian of the Hydrogen molecule built from the rigorous derivations on second-quantization and Bravyi-Kitaev transformation (BKT) are demonstrated in detail. Then the circuit for simulating the energy dynamics of the Hydrogen molecule system is derived and established step by step, and the simulation on ground and first-exited state energies of the Hydrogen molecule system at different bond lengths are carried out. According to the qualitative and quantitative analysis of the simulation results, it can be concluded that the circuits built from the derivations work properly for Hydrogen molecule system, and the similar derivation process and methods can be extended into other quantum chemical system in future studies.
REFERENCES


