Quantum Computer Tutorial for Chemist

Youngkyun Ahn, Sowon Kim, Seunghun Choi, Hongseok Choi, Kyungmin Kim

March 13, 2024

0 Introduction

This document is intended to guide basic knowledge of **quantum computer** and **quantum algorithm** for pioneering **electronic structure theory** calculations using quantum computers, especially Quantum Phase Estimation(QPE) and Variational Quantum Eigensolver(VQE).
This document covers terminologies and notations of quantum computer, scheme of electronic structure theory, and some quantum algorithm examples for quantum chemistry.
Since this document is aimed for graduate school newcomer, it requires basic concepts of quantum chemistry and linear algebra.

For any question or suggestion, please contact: Youngkyun Ahn (fib89@kaist.ac.kr), Sowon Kim (sowonkim@kaist.ac.kr), Seungheon Choi (huni1123@kaist.ac.kr), and Hongseok Choi (hongseok2204@kaist.ac.kr).

Contents

0 Introduction **1**

1 Essential Electronic Structure Theory **3**
1.1 Hartree-Fork(HF) approximation . . . 3
1.1.1 The electronic problem . . . 3
1.1.2 Hartree-Fock equation . . . 3
1.1.3 Fock operator . . . 4
1.1.4 The Hartree-Fock process (SCF method) . . . 4
1.1.5 Hartree-Fock limit . . . 5
1.1.6 Interpretation of solutions to the Hartree-Fock equation . . . 5
1.2 Second Quantization . . . 6
1.2.1 Creation and Annihilation operators . . . 6
1.2.2 Hamiltonian represented by second quantization . . . 9
1.3 Configuration Interaction (CI) . . . 9
1.4 Coupled Cluster(CC) . . . 10
1.4.1 Unitary Coupled Cluster (UCC) . . . 11

2 Basics of Quantum Computer **12**
2.1 Qubit . . . 12
2.1.1 Multiple Qubit . . . 13
2.2 Gate & Circuit . . . 14
2.2.1 Pauli Matrix . . . 14

2.2.2 Circuit Representation and Gates . . . 14
2.3 Measurement . . . 17
2.4 Fermionic space to qubit space transformation . . . 18
2.4.1 The wave function in qubits . . . 18
2.4.2 The Jordan-Wigner encoding method . . . 18
2.5 Common Facts about Quantum Computer . . . 19

3 Quantum Phase Estimation(QPE) 20
3.1 Quantum Fourier Transformation(QFT) . . . 20
3.1.1 Theoretical Background . . . 20
3.1.2 Circuit . . . 21
3.1.3 Explanation . . . 22
3.2 Quantum Phase Estimation . . . 23
3.2.1 Theoretical Background . . . 23
3.2.2 Circuit and Explanation . . . 24
3.3 Improving QPE with iteration . . . 25
3.3.1 Theoretical Background . . . 25
3.3.2 Circuit . . . 26

4 Variational Quantum Eignensolver(VQE) 27
4.1 Initialization . . . 27
4.2 Ansatz . . . 28
4.2.1 UCC Ansatz . . . 28
4.3 Measurement . . . 30
4.3.1 $\langle Z \rangle$ Measurement . . . 30
4.3.2 Grouping . . . 31
4.4 Optimization . . . 32

5 Homebuilt VQE manual 33
5.1 Instruction_Colab . . . 33
5.2 Instruction_Local . . . 33

1 Essential Electronic Structure Theory

In this chapter we will summarize a part of the electronic structure theory that is necessary to understand the following chapters. We're only going to cover the basic concepts here. If you want more details, we recommend reading the book in the reference. [1]

1.1 Hartree-Fork(HF) approximation

Finding and describing an approximate solution to the electronic Schrödinger equation is the main issue of electronic structure theory. In this section we will introduce the HF approximation method, which is the starting point for solving the electronic Schrödinger equation for many-electron problems. The HF method uses a mean-field approximation that use average field of the electron correlations, so it does not yield an exact wave function. However, the HF method is used to approximate electronic states, which are then used as the basis for other computational methods (e.g. MP2, CCSD, CI, etc.).

1.1.1 The electronic problem

The solution to a **Schrodinger equation** involving the electronic hamiltonian (Eq. 1.24),

$$\mathcal{H}_{elec}\Phi_{elec} = \mathcal{E}_{elec}\Phi_{elec} \tag{1.1}$$

is the electronic wave function,

$$\Phi_{elec} = \Phi_{elec}(\{\mathbf{r}_i\};\{\mathbf{R}_A\}) \tag{1.2}$$

where $\mathbf{r}_i$ and $\mathbf{R}_A$ is electrons and nuclei described by position vectors.
The total energy for fixed nuclei include the constant nuclear repulsion.

$$\mathcal{E}_{tot} = \mathcal{E}_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \tag{1.3}$$

Solving the equations (1.1) to (1.3) constitute the **electronic problem**. Note that the Hamiltonian we are mainly focused on is the electronic Hamiltonian. ($\mathcal{H} = \mathcal{H}_{elec}$). By solving for these problem, we get the wave function and energy. The wave function, which is the eigenvector of equation (1.1), allows us to obtain about the electronic properties of molecules as well as their energy.

1.1.2 Hartree-Fock equation

The Hartree-Fock approximation method considers the many-electron problem as a one-electon problem and the electron-electron interaction term as the average potential. So in this method, we express the hamiltonian for a many-body electron as a sum of effective one-electron hamiltonians.

$$\mathcal{H}_{HF} = \sum_{i=1}^{N} f(i) \tag{1.4}$$

The effective one-electron operator we use for this is called the **Fock operator**. The eigenvector of the Fock operator is the spin orbital, and the eigenvalue is the energy of the each spin orbital.

$$f(i)\chi(\mathbf{x}_i) = \varepsilon\chi(\mathbf{x}_i) \tag{1.5}$$

where $f(i)$ is Fock operator, $\chi(\mathbf{x}_i)$ is spin orbital for i^{th} electron $\mathbf{x}_i$, and ε is eigenvalue of the operator. We call the equation (1.5) as the **Hartree-Fock equation**.

1.1.3 Fock operator

The Fock operator has the following form

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + v^{HF}(i) \tag{1.6}$$

where $v^{HF}(i)$ is the **average potential** experienced by the i^{th} electron due to the other electrons. This potential $v^{HF}(i)$ is composed of coulomb($\mathcal{J}$) and exchange($\mathcal{K}$) potential.

$$v^{HF}(1) = \sum_b \mathcal{J}_b(1) - \mathcal{K}_b(1) \tag{1.7}$$

The **coulomb potential** is caused by the interaction between one electron and another, and can be interpreted as a probability density of the other electrons that affect it. It is a local potential with a different electron in each orbital.

$$\mathcal{J}_b(1)\chi_a(1) = \int d\mathbf{x}_2 |\chi_b(2)|^2 r_{12}^{-1}\chi_a(1) \tag{1.8}$$

The **exchange potential**, on the other hand, is due to the anti-symmetry of electrons. This potential represents the energy change due to the exchange of electrons and calculates the effect of different orbitals on a single electron, rather than the effect of having one electron in one orbital. In other words, they are non local operators that affect each other.

$$\mathcal{K}_b(1)\chi_a(1) = \int d\mathbf{x}_2 \chi_b(2)^* r_{12}^{-1}\chi_a(2)\chi_a(1) \tag{1.9}$$

1.1.4 The Hartree-Fock process (SCF method)

The Hartree-Fock equation approximates the effect of other electrons as a field in order to find a solution, which means that the resulting solution is nonlinear and must be calculated by iteration. The method of solving the Hartree-Fock equation by calculating the field and updating it by iteration is called the **Self-Consistent Field (SCF) method**. The SCF method is a method that iterates the specific calculations with field until the self-consistency condition is satisfied. In the HF method, the self-consistency condition is that the field $v^{HF}(i)$ no longer change and the spin orbitals are the same as the Fock operator eigenfunctions.
Here is a simple scheme of the SCF process.

1. Make an initial guess at the spin orbitals $\chi(\mathbf{x}_i)$
2. Calculate the average field $v^{HF}(i)$ that affects each electron $\mathbf{x}_i$
3. Solve the eigenvalue equation (1.5) to get a new set of spin orbitals $\chi'(\mathbf{x}_i)$.
4. Using the new spin orbitals, obtain new average field $v^{HF\prime}(i)$
5. Iterate **2** - **4** until self-consistency is reached

In step 3, the new set of spin orbitals $\chi'(\mathbf{x}_i)$ can be obtained from the eigenvectors of the Fock operator $f(i)$. And in step 5, if the field $v^{HF}(i)$ is no longer changing and the spin orbitals are the same as the eigenfunctions of the Fock operator, the self-consistency condition is satisfied.

1.1.5 Hartree-Fock limit

If the initial iuput has a large number of basis sets, it has more flexibility to find a wave function with lower energy. As we increase the number of basis sets, the energy continues to decrease until it reaches a certain limit, which we call the limit as **Hartree-Fock limit**. The wave function at the Hartree-Fock limit is the most accurate wave function that can be obtained by the HF method.

Summary of Hartree-Fock approximation
Purpose : the molecular orbital approximation to solve the electronic problem
Input & output : basis set → orthogonal set of molecular orbitals
Process : replace the multi-electron Hamiltonian with a sum of one-electron operators(Fock operators) → use the variational method to find the wave function with the minimum energy for a given set of orbitals → calculates the correlation between electrons as an average field → solves a nonlinear problem by iteration. (SCF process)
Result : wave function with a single Slater-determinant
This wave function is the **best single-Slater determinant approximation** that can be made with a given basis set.

1.1.6 Interpretation of solutions to the Hartree-Fock equation

The HF solutions be used as a starting point for other advanced approximation methods.
When the wave function is represented by the K spatial orbitals, the number of spin orbitals(generated for each α spin and β spin) is 2K. For N electrons, the eigenvectors corresponding to the energies from the lowest to the N^{th} are called **occupied spin orbitals**, and the remaining 2K-N orbitals are called **virtual spin orbitals**.
The Slater determinant of these orbitals forms the **Hartree-Fock ground state**.

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle \tag{1.10}$$

The lowest energy state is represented by the ground state (1.10), but there are $\binom{2K}{N}-1$ other states. The other states represent other possible determinant from the HF ground state, i.e. they can be described as **excited states** from the occupied orbitals in the ground state to the unoccupied orbitals in the virtual state.
The **singly excited determinant** excited from the occupied orbital, χ_a, to the virtual orbital, χ_r, can be represented as follows.

$$|\Psi_a^r\rangle = |\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_N\rangle \tag{1.11}$$

Also, the **doubly excited determinant** exciteed from the occupied orbitals χ_a, χ_b to the virtual orbitals χ_r, χ_s is represented as follows.

$$|\Psi_{ab}^{rs}\rangle = |\chi_1\chi_2\cdots\chi_r\chi_s\cdots\chi_N\rangle \tag{1.12}$$

All $\binom{2K}{N}$ determinants can thus be classified as either the HF ground state or single, doubly, triply,..., N-tuply excited states. They are important as N-electron basis functions for an expansion of the exact N-electron states of the system. We'll use this excited determinant expression in the next chapter.

We want a more accurate representation of the electronic wave function. The electron correlation

(E_{corr}), which cannot be calculated by the Hartree-Fock method, is expressed as follows

$$E_{corr} = \mathcal{E}_0 - E_0 \tag{1.13}$$

($\mathcal{E}_0$: energy of the system, E_0 : Hartree-Fock limit energy)

In the 1.3 and 1.4, we will introduce more accurate ways of representing wave functions: the **Configuration Interaction (CI)** and **Coupled Cluster (CC)** methods. With these methods, our goal is to find a lower energy by calculating E_{corr}.
The Hartree-Fock method allowed us to represent not only the ground state, but also singly, doubly, and other excitations. The wave function predicted by the HF method is the ground single-Slater determinant, which alone does not give an accurate wave function, but by using the other excitation determinants of the HF method to express the wave function, a more accurate wave function can be obtained.

1.2 Second Quantization

We have learn that the 'Slater determinant' allows us to express the antisymmetry property of the electron wavefunction. **The second quantization representation**, on the other hand, allows us to express the antisymmetry property as an 'operator'. This representation gives the wavefunction algebraic properties that facilitate a variety of calculations. It can be particularly useful in the multi-electron problem because it allows us to conveniently manipulate the state of the electrons.[1][2]

1.2.1 Creation and Annihilation operators

In the second quantization, we define **creation operator($a^\dagger$)** and **annihilation operator(a)** to represent the wave function as an operator.

For an arbitrary Slater determinant $|\chi_i\chi_k\cdots\chi_l\rangle$, $a_i^\dagger$ and a_i act as follows

$$\begin{aligned} a_i^\dagger|\chi_k\cdots\chi_l\rangle &= |\chi_i\chi_k\cdots\chi_l\rangle \\ a_i|\chi_i\chi_k\cdots\chi_l\rangle &= |\chi_k\cdots\chi_l\rangle \end{aligned} \tag{1.14}$$

In the above expression, $a_i^\dagger$ acts to create electrons in the spin orbital χ_i of the wave function $|\chi_i\chi_k\cdots\chi_l\rangle$, and a_i acts to annihilate electrons in the spin orbital χ_i.

Note the order of $a_i^\dagger$ and a_i : Each operator is applied to the slater determinant in turn, so that the sign of the result is reversed when different operators are applied.

$$\begin{aligned} &a_i^\dagger a_j^\dagger|\chi_k\cdots\chi_l\rangle = a_i^\dagger|\chi_j\chi_k\cdots\chi_l\rangle = |\chi_i\chi_j\chi_k\cdots\chi_l\rangle \\ &a_j^\dagger a_i^\dagger|\chi_k\cdots\chi_l\rangle = a_j^\dagger|\chi_i\chi_k\cdots\chi_l\rangle = |\chi_j\chi_i\chi_k\cdots\chi_l\rangle = -|\chi_i\chi_j\chi_k\cdots\chi_l\rangle \\ &a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 = \{a_i^\dagger, a_j^\dagger\} \end{aligned} \tag{1.15}$$

If the same operators are applied, the wavefunction collapses. For example, if the same creation operators are applied to a wave function, the slater determinant will have two identical columns, resulting in a zero value.

$$a_i^\dagger a_i^\dagger|\chi_k\cdots\chi_l\rangle = a_i^\dagger|\chi_i\chi_k\cdots\chi_l\rangle = |\chi_i\chi_i\chi_k\cdots\chi_l\rangle = 0 \tag{1.16}$$

Also, if the same annihilation operators are applied to a wave function, the wave function will be zero because it is impossible to destroy unoccupied orbital.

$$a_i a_i |\chi_i \chi_k \cdots \chi_l\rangle = a_i |\chi_k \cdots \chi_l\rangle = |\chi_k \cdots \chi_l\rangle = 0 \tag{1.17}$$

$a_i^\dagger$ and a_j satisfy the **anti-commutation relation** with each other.

$$a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} = \{a_i, a_j^\dagger\} \tag{1.18}$$

proof) Anti-commutation relation

1. Consider the operator $a_i a_i^\dagger + a_i^\dagger a_i$ acting on an arbitrary determinant $|\chi_k \cdots \chi_l\rangle$. If spin orbital χ_i is not occupied in this determinant,

$$(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_j \cdots \chi_l\rangle = a_i a_i^\dagger |\chi_k \cdots \chi_l\rangle = a_i |\chi_i \chi_k \cdots \chi_l\rangle = |\chi_k \cdots \chi_l\rangle \tag{1.19}$$

on the other hand, if χ_i is occupied,

$$\begin{aligned}&(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_j \cdots \chi_i \cdots \chi_l\rangle = a_i^\dagger a_i |\chi_k \cdots \chi_i \cdots \chi_l\rangle \\ &= -a_i^\dagger a_i |\chi_k \cdots \chi_i \cdots \chi_l\rangle = -a_i^\dagger |\cdots \chi_k \cdots \chi_l\rangle = |\chi_k \cdots \chi_i \cdots \chi_l\rangle\end{aligned} \tag{1.20}$$

Thus, $a_i a_i^\dagger + a_i^\dagger a_i = 1 = \{a_i, a_i^\dagger\}$

2. Consider the operator $a_i a_j^\dagger + a_j^\dagger a_i$ $(i \neq j)$ acting on an arbitrary determinant $|\chi_k \cdots \chi_l\rangle$. If $\chi_i \notin \{k, \ldots, l\}$ or $\chi_j \in \{k, \ldots, l\}$, each term can be zero because electrons in unoccupied orbitals cannot be destroyed and electrons in occupied orbitals cannot be created.
If $\chi_i \in \{k, \ldots, l\}$ and $\chi_j \notin \{k, \ldots, l\}$, the sum of the terms can be zero because of the anti-symmetry property of determinant.

$$\begin{aligned}&(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \cdots \chi_i \cdots \chi_l\rangle = -(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_i \cdots \chi_k \cdots \chi_l\rangle \\ &= -a_i |\chi_j \chi_i \cdots \chi_k \cdots \chi_l\rangle - a_j^\dagger |\cdots \chi_k \cdots \chi_l\rangle \\ &= a_i |\chi_i \chi_j \cdots \chi_k \cdots \chi_l\rangle - |\chi_j \cdots \chi_k \cdots \chi_l\rangle \\ &= |\chi_j \cdots \chi_k \cdots \chi_l\rangle - |\chi_j \cdots \chi_k \cdots \chi_l\rangle = 0\end{aligned} \tag{1.21}$$

Thus, $a_i a_j^\dagger + a_j^\dagger a_i = 0 = \{a_i, a_i^\dagger\}$ (if $i \neq j$)

Lastly, we define a **vacuum state** $|\ \rangle$ to fully express the properties of the Slater determinant in the creation and annihilation operators. The vacuum state is a state with no electrons, so an arbitrary wave function can be expressed from this state.

$$\begin{aligned}&a_i |\ \rangle = 0 = \langle\ | a_i^\dagger \\ &|\chi_i\rangle = a_i^\dagger |\ \rangle \\ &a_i^\dagger a_k^\dagger \cdots a_l^\dagger |\ \rangle = |\chi_i \chi_k \cdots \chi_l\rangle\end{aligned} \tag{1.22}$$

It also satisfies the **normalized condition** like a wave function.

$$\langle\ |\ \rangle = 1 \tag{1.23}$$

Example 3.1.1) (Szabo P.90)
Show, using the properties of determinants, that

$$(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)|K\rangle = 0$$

for every $|K\rangle$ in the set $|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle$

Summary) Properties of creation & annihilation operators
1. $a_i^\dagger|\chi_k\cdots\chi_l\rangle = |\chi_i\chi_k\cdots\chi_l\rangle$, $a_i|\chi_i\chi_k\cdots\chi_l\rangle = |\chi_k\cdots\chi_l\rangle$
2. $a_i|\ \rangle = 0 = \langle\ |a_i^\dagger$
3. $a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 = \{a_i^\dagger, a_j^\dagger\}$, $a_i a_j + a_j a_i = 0 = \{a_i, a_j\}$
4. $a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} = \{a_i, a_j^\dagger\}$

1.2.2 Hamiltonian represented by second quantization

With the Born-Oppenheimer approximation, we represent the **electronic Hamiltonian** as

$$\mathcal{H}_{elec} = \sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} \tag{1.24}$$

This is the Hamiltonian describing the motion of N electrons in a field of M point charges, where Z_A is the atomic number of the nucleus A and r is the distance between two electrons. The first term is the operator for the kinetic energy of the electrons; the second term is the coulomb attraction between electrons and nuclei; the third term represent the repulsion between electrons.
We can express this as a second quantization representation as

$$\mathcal{H}_{elec} = \sum_{pq} h_{pq}a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs} h_{pqrs}a_p^\dagger a_q^\dagger a_r a_s \tag{1.25}$$

where h_{pq} is a **one-electron integral** and h_{pqrs} is a **two-electron integral**.

$$\begin{aligned} h_{pq} &= \int \phi_p^*(r)\left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{R_I - r}\phi_q(r)\right) \\ h_{pqrs} &= \int \frac{\phi_p^*(r_1)\phi_q^*(r_2)\phi_r(r_2)\phi_s(r_1)}{|r_1 - r_2|} \end{aligned} \tag{1.26}$$

1.3 Configuration Interaction (CI)

The linear combination of all possible determinants that can be obtained from the Hartree-Fock slater determinant makes the N-electron determinant set complete, allowing for an exact representation of any N-electron wave function.

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{a<b<c,r<s<t} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle \tag{1.27}$$

By summing over $a < b$ and summation over $r < s$ means summing over all unique pairs of occupied $(\chi_a, \chi_b, ...)$ and virtual $(\chi_r, \chi_s, ...)$ spin orbitals. The wave function with all the configurations to represent the exact state is called the **Full Configuration Interaction (FCI)** wave function.
Given that there are 2K total spin orbitals and N electrons, the number of possible determinants is ${}_{2k}C_n$, so the wave function representing the FCI through this set of orbitals will have ${}_{2k}C_n$ different N-electron wave functions.
In simple symbolic form, this looks like this

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_S|\Psi_S\rangle + c_D|\Psi_D\rangle + c_T|\Psi_T\rangle + \cdots \tag{1.28}$$

where $|S\rangle$ is a term representing a single excitation, $|D\rangle$ is a double, then a triple .... and so on. The FCI matrix to calculate the energy using this is expressed as follows

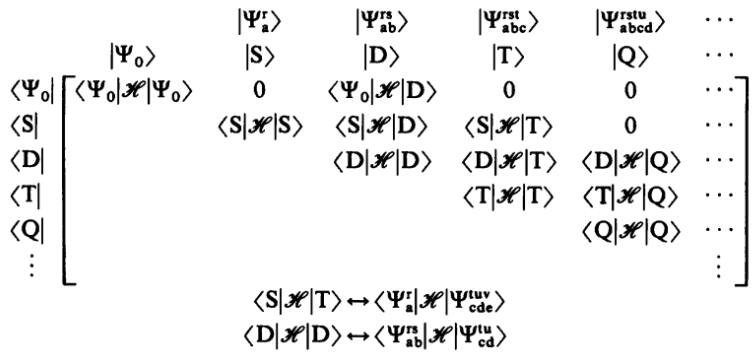


Figure 1: The Full CI matrix

Full Configuration Interaction is the most accurate way to find the wave function for a given orbital set, but it is very computationally intensive. Instead of the full CI, we can use **doubly excited configuration interaction(DCI)** and **singly and doubly excited CI(SDCI)**.

Looking at the (Figure 1), there is no coupling between the ground state and the singly excited state, so the single excitation is not used directly to find the correlation energy of the ground state. So we create a DCI that only considers the doubly excitation term when thinking of the least excitation linear combination.

$$|\Phi_{DCI}\rangle = |\Psi_0\rangle + \sum_{c<d,t<u} c^{tu}_{cd}|\Psi^{tu}_{cd}\rangle \tag{1.29}$$

Also, the SDCI for a singly and doubly excited term is

$$|\Phi_{SDCI}\rangle = |\Psi_0\rangle + \sum_{ra} c^r_a|\Psi^r_a\rangle + \sum_{c<d,t<u} c^{tu}_{cd}|\Psi^{tu}_{cd}\rangle \tag{1.30}$$

1.4 Coupled Cluster(CC)

Since the CI method only uses specific excitation terms, it is limited in its ability to approximate an infinite system. We will see how this method uses the concept of coupled clusters to represent more pictures.

Now we will introduce a method to include not only double excitations here, but also quadruples, hextuples, ..., 2nth-tuples by using exponenetial operator. This is called the **coupled cluster** approximation .
It is expressed as

$$|\Phi_{CCA}\rangle = \exp(\mathcal{T}_2)|\Psi_0\rangle \tag{1.31}$$

where $\mathcal{T}_2$ is $\frac{1}{4}\sum_{abrs} c^{rs}_{ab} a^\dagger_r a^\dagger_s a_b a_a$. We call the operator $\mathcal{T}$ the **cluster** of the wave function.
Since expanding the exponential can be written as $\exp(x) = 1 + x + (\frac{1}{2})x^2 + \cdots$, we can also expand

the wave function represented by CCA.

$$
\begin{aligned}
|\Phi_{CCA}\rangle &= (1 + \frac{1}{4}\sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a + \frac{1}{32}\sum_{abcd,rstu} c_{ab}^{rs} c_{cd}^{tu} a_r^\dagger a_s^\dagger a_b a_a a_t^\dagger a_u^\dagger a_d a_c + \cdots)|\Psi_0\rangle \\
&= |\Psi_0\rangle + \frac{1}{4}\sum_{abrs} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \frac{1}{32}\sum_{abcd,rstu} c_{ab}^{rs} c_{cd}^{tu}|\Psi_{abcd}^{rstu}\rangle + \cdots
\end{aligned}
\tag{1.32}
$$

Similarly, single terms can be stacked on top of an exponential. In this case, the single cluster is $\mathcal{T}_1 = \sum_{ar} c_a^r a_r^\dagger a_a$. This can be expressed as $|\Phi_{CCA}\rangle = \exp(\mathcal{T}_1 + \mathcal{T}_2)|\Psi_0\rangle$, which is the CCSD method.

This method allows more configuration to be included, but may be less accurate on small systems because each parameter is dependent of the others.

1.4.1 Unitary Coupled Cluster (UCC)

To represent the general cluster operator, we can write $\mathcal{T} = \mathcal{T}_1 + \mathcal{T}_2 + \cdots$.

$$
\begin{aligned}
\mathcal{T}_1 &= \sum_{ar} c_a^r a_r^\dagger a_a \\
\mathcal{T}_2 &= \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a
\end{aligned}
\tag{1.33}
$$

Combining the cluster operator and its complex conjugate operator over the exponential produces a unitary operator.

$$
|\psi\rangle = e^{\mathcal{T}-\mathcal{T}^\dagger}|\Psi_0\rangle \tag{1.34}
$$

which gives us a unitary representation of the operator. This representation is called a **unitary coupled cluster**.

A simple proof of why the operator (1.34) is unitary is as follows.

$$
\begin{aligned}
&e^{\mathcal{T}-\mathcal{T}^\dagger} = \exp(\sum_{ar} c_a^r a_r^\dagger a_a + \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a + \cdots) \cdot \exp(-\sum_{ar} c_a^r a_r a_a^\dagger + \sum_{abrs} c_{ab}^{rs} a_r a_s a_b^\dagger a_a^\dagger - \cdots) \\
&= \exp(\sum_{ar} c_a^r a_r a_a^\dagger + \sum_{abrs} c_{ab}^{rs} a_r a_s a_b^\dagger a_a^\dagger + \cdots) \cdot \exp(-\sum_{ar} c_a^r a_r^\dagger a_a - \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a - \cdots) = e^{\mathcal{T}^\dagger-\mathcal{T}} \\
&\therefore e^{\mathcal{T}-\mathcal{T}^\dagger} = e^{\mathcal{T}^\dagger-\mathcal{T}}
\end{aligned}
\tag{1.35}
$$

The operator to create wave function from the initial wave function is called **ansatz**. If the ansatz is unitary, it can be used in quantum computer algorithms. In our VQE calculation, which we will discuss later, we will use the unitary coupled cluster ansatz.

Example 4.2.1)
Proof the equation (1.35) for cluster operator $\mathcal{T} = \mathcal{T}_1 + \mathcal{T}_2$, number of electrons $N = 2$, number of spin orbitals $2K = 4$

2 Basics of Quantum Computer

양자 단위에서 일어나는 현상을 고전 컴퓨터로 재현하는 일은 너무 많은 computational cost를 소모하는 탓에 풀기 어렵습니다. Richard P. Feynman은 이런 문제를 양자적인 성질을 띄는 물질을 연산 단위로 사용함으로 해결할 수 있다고 주장했습니다. 실제로 양자 컴퓨터는 구조적으로 고전 컴퓨터와 연산의 방식이 다르고, 고전 컴퓨터에서는 polynomial time 안에 풀 수 없다고 여겨지는 문제들이 양자 컴퓨터로는 풀 수 있음이 밝혀지기도 했습니다.
Electronic structure theory에서 다루는 문제들 중 분자의 ground state energy를 정확하게 계산하는 문제 역시 고전 컴퓨터로 풀기 어려운 문제 중 하나로, 양자 컴퓨터를 활용하여 풀 수 있을 것이라고 전망하여 많은 학자들이 연구하고 있습니다.
해당 단원에서는 양자컴퓨터의 구성원소인 qubit, gate, circuit과 그것의 기술 방법에 대해 다룹니다.

도움이 될 자료) Youtube: How to make a Quantum Bit - Veritasium
Wikipedia: Quantum logic gate
HORIZON 칼럼: 믿기 힘든 양자[7]: 두 상태 이야기
HORIZON 칼럼: 믿기 힘든 양자[8]: 위상의 귀환
HORIZON 칼럼: NISQ 시대의 양자 컴퓨터

2.1 Qubit

고전 컴퓨터의 연산 단위인 bit가 0 혹은 1 두 상태 중 하나로 표현된다면, 양자 컴퓨터의 기본적인 연산 단위인 **qubit**은 두 상태 0과 1의 superposition으로 표현됩니다. Qubit은 양자역학의 대표적인 예시인 two-state problem으로 표현할 수 있으며, **Z basis**인 **ket** $|0\rangle$과 $|1\rangle$을 사용하여 다음과 같이 쓸 수 있습니다:

$$|\psi\rangle = a\,|0\rangle + b\,|1\rangle\,, \qquad a, b \in \mathbb{C}, \quad \langle\psi|\psi\rangle = |a|^2 + |b|^2 = 1$$

이 때 $\mathbb{C}$ 는 복소수 집합입니다. 우리는 $|\psi\rangle$가 normalized되어 있다는 조건과, $|\psi\rangle$의 global phase $e^{i\Phi}$은 임의로 정할 수 있다는 성질을 사용하여 $|\psi\rangle$를 다음과 같이 표현하기도 합니다:

$$|\psi\rangle = \cancel{e^{i\Phi}}\left\{\cos\frac{\theta}{2}\,|0\rangle + \sin\frac{\theta}{2}e^{i\phi}\,|1\rangle\right\}$$

Qubit을 vector로 표현할 때에는 다음처럼 표기합니다:

$$|0\rangle = \begin{pmatrix}1\\0\end{pmatrix}, |1\rangle = \begin{pmatrix}0\\1\end{pmatrix}, |\psi\rangle = \begin{pmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}e^{i\phi}\end{pmatrix}$$

Qubit 하나는 자유도가 2개이기 때문에, 같은 자유도를 가진 구 표면 위의 한 점으로 표현할 수 있습니다. 이를 **Bloch sphere**라고 합니다. 후술하겠지만, qubit의 개수가 증가하면 자유도가 기하급수적으로 증가하기 때문에 모든 qubit을 Bloch sphere로 기술할 때에는 유의해야 합니다.

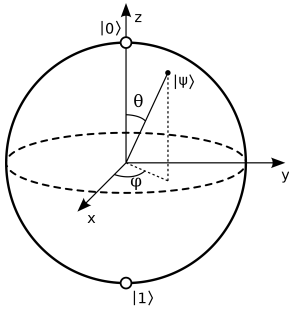


Figure 2: Bloch Sphere, Wikipedia, Bloch Sphere

Bra는 **ket**의 complex conjugate입니다.

$$\langle\psi| = |\psi\rangle^\dagger = \begin{pmatrix} a \\ b \end{pmatrix}^\dagger = \begin{pmatrix} a^* & b^* \end{pmatrix}$$

Z basis가 아닌, **X basis**나 **Y basis**으로 표현할 때는 다음처럼 표기합니다:

$$\textbf{X basis: } |+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, |-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\textbf{Y basis: } |+i\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}, |-i\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

2.1.1 Multiple Qubit

Quantum computer는 보통 여러 qubit으로 이루어져 있습니다. 두 개의 qubit으로 이루어진 state는 다음과 같이 표현합니다:

$$|\psi\rangle = c_{00}|00\rangle + c_{01}|01\rangle + c_{10}|10\rangle + c_{11}|11\rangle$$

만약 두 qubit이 서로 독립인 경우에는 각 qubit들의 **tensor product**로 표현할 수도 있습니다:

$$|\psi_1\rangle = |\alpha\rangle \otimes |\beta\rangle = \begin{pmatrix} \alpha_0 \\ \alpha_1 \end{pmatrix} \otimes \begin{pmatrix} \beta_0 \\ \beta_1 \end{pmatrix} = \begin{pmatrix} \alpha_0 \cdot \begin{pmatrix} \beta_0 \\ \beta_1 \end{pmatrix} \\ \\ \alpha_1 \cdot \begin{pmatrix} \beta_0 \\ \beta_1 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} \alpha_0\beta_0 \\ \alpha_0\beta_1 \\ \alpha_1\beta_0 \\ \alpha_1\beta_1 \end{pmatrix}$$

$$= \alpha_0\beta_0|00\rangle + \alpha_0\beta_1|01\rangle + \alpha_1\beta_0|10\rangle + \alpha_1\beta_1|11\rangle$$

Qubit들이 서로 독립으로 존재할 것이라는 인식을 하기 쉬운데, 여러 qubit들이 **entangle**되어있을 경우 tensor product로 표현할 수 없습니다.
편의상 ket간의 tensor product를 축약하여 하나의 ket으로 표기하기도 합니다(bra도 동일합니다).

$$|0\rangle \otimes |1\rangle \equiv |01\rangle, |\alpha\rangle \otimes |\beta\rangle \equiv |\alpha\beta\rangle$$

필요한 경우 ket 안에 있는 수를 2진법 정수로 취급하여 표기하기도 합니다 (e.g. $|110\rangle \equiv |6\rangle$). 이렇게 표기할 경우 ket 안의 정수가 matrix representation의 index와 같아집니다.

2.2 Gate & Circuit

Quantum algorithm은 주어진 qubit에 의도한 **operation**을 가하고 그 현상을 관찰하는 작업을 일컫습니다. Quantum algorithm을 이해하기 위해서는 operation을 배치하는 방법과, 만들어진 operation을 알맞게 interpret하는 방법을 알아야 합니다. 이 section에서는 operation을 배치하는 법과, 그것을 읽는 방법에 대해 다룹니다.

2.2.1 Pauli Matrix

Pauli matrix는 spin state basis를 eigenstate로 가지는 2×2 matrix의 basis들로, 다음과 같습니다:

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

가령 Z의 eigenvector는 $|0\rangle$과 $|1\rangle$이고, X의 eigenvector는 $|+\rangle$과 $|-\rangle$인 셈입니다. Pauli matrix는 Hermitian이고, unitary합니다. Pauli Matrix는 spin momentum을 설명하는 데 핵심적이기 때문에, 앞으로 다룰 operation에서 자주 등장합니다.

2.2.2 Circuit Representation and Gates

Quantum algorithm을 이해하는 데에는, system에 가해지는 operation의 순서가 중요합니다(이는 operation이 non-commute하기 때문입니다). 일련의 operation을 직관적으로 표현하기 위해 우리는 **circuit**이라고 부르는 diagram을 사용합니다:

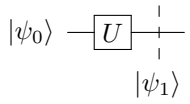


Figure 3: Example of a single qubit quantum circuit

Circuit위의 가로줄은 각각 qubit 하나를 상징합니다. Circuit 위에 표현된 operation은 **gate**이라고 부릅니다. Qubit state의 vector representation과 마찬가지로, operation들은 모두 matrix representation으로 표현할 수 있습니다. 이 때 모든 operation은 반드시 **unitary**해야 합니다. Figure 3을 수식으로 표현하면 아래와 같습니다:

$$|\psi_1\rangle = U\,|\psi_0\rangle$$

Figure 4은 two qubit circuit의 한 예시입니다:

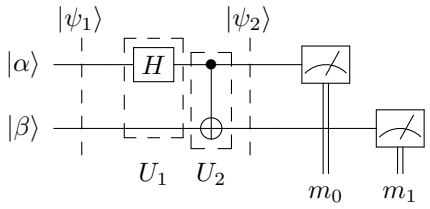


Figure 4: Example of a two qubit quantum circuit

위 circuit에 사용된 gate는 Table 1을 참조하기 바랍니다.

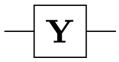
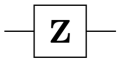
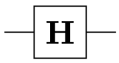
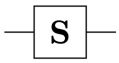
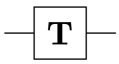
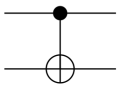
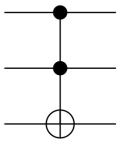
Operator	Gate(s)	Matrix
Pauli-X (X)		$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$
Pauli-Y (Y)		$\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$
Pauli-Z (Z)		$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$
Hadamard (H)		$\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$
Phase (S, P)		$\begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix}$
π/8 (T)		$\begin{bmatrix} 1 & 0 \\ 0 & e^{i\pi/4} \end{bmatrix}$
Controlled Not (CNOT, CX)		$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$
Controlled Z (CZ)		$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$
SWAP		$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$
Toffoli (CCNOT, CCX, TOFF)		$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$

Table 1: List of quantum logic gates

Multi qubit circuit에서 gate를 표현할 때에는 tensor product을 사용합니다. 다음은 $|\psi_1\rangle$과 U_1을 수식으로 표현한 것입니다:

$$\begin{aligned} |\psi_1\rangle &= |\alpha\rangle \otimes |\beta\rangle \\ U_1 &= H \otimes I \\ &= \left\{ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \right\} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned}$$

두 개 이상의 qubit에 동시에 작용하는 gate는 작은 단위의 gate들의 tensor product로 표현되지 않습니다. $|\alpha\rangle$와 $|\beta\rangle$가 전부 $|0\rangle$일 때 U_2와 $|\psi_2\rangle$룰 수식으로 표현하면 다음과 같습니다:

$$U_2 = |0\rangle \langle 0|_c \otimes I_t + |1\rangle \langle 1|_c \otimes X_t = \begin{pmatrix} I & O \\ O & X \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$$

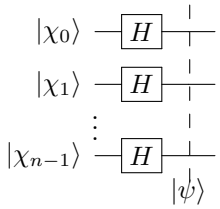
래첨자 c와 t는 control qubit과 target qubit을 뜻합니다.
위 예시에서 U_2 gate는 Controlled X (혹은 CX, CNOT) gate라고 불립니다. Controlled U gate는 control qubit(점으로 표현합니다)의 상태에 따라 target qubit(gate 모양으로 표현합니다)에 U gate 시행 여부가 결정되는 multi-qubit gate 입니다. 위 예시에서는 control qubit인 $|\alpha\rangle$이 $|1\rangle$일 때 target qubit인 $|\beta\rangle$에 X gate가 시행됩니다.
$|\psi_2\rangle$는 Bell state라고 불리며, 두 qubit의 tensor product로 표현할 수 없는 **entangled state**의 대표적인 예시입니다.

$$\begin{aligned} &\nexists\ |\phi_0\rangle, |\phi_1\rangle \text{ such that} \\ |\psi_2\rangle &= \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) \\ &= |\phi_0\rangle \otimes |\phi_1\rangle \end{aligned}$$

많이 쓰이는 quantum gate들의 목록을 보려면 Table 1를 참조하십시오.

Example 1)
$N > 2$인 N에 대해서, N 개의 Bloch sphere로 N qubit을 표현할 수 없음을 Degree of freedom을 활용하여 설명하여라.

Example 2)



a) $|\chi_{all}\rangle = |0\rangle$일 때, $|\psi\rangle = \frac{1}{\sqrt{2^n}} \sum_{j=0}^{2^n-1} |j\rangle$ 임을 보여라.
b) $|\chi_{n-1}\rangle = |1\rangle, |\chi_{else}\rangle = |0\rangle$일 때, $|\psi\rangle$을 $\Sigma\ j$ 에 관한 식으로 표현하여라.
c) $|\chi_{all}\rangle = |1\rangle$일 때, $|\psi\rangle$을 $\Sigma\ j$ 에 관한 식으로 표현하여라.

hint) n=2일 때부터 보인 뒤, 일반화를 시도하십시오.
이 예제는 3.1를 이해하는데 도움이 될 예제이므로 풀어보기를 권장합니다.

2.3 Measurement

양자의 특성상, 한 번 system을 관측하면 그 system은 관측된 state로 확정되고 이외의 state들은 모두 collapse합니다. 그러니 우리가 관찰하고 싶은 어떤 state가 여러 state의 중첩으로 표현된다면, 한 차례의 관측만으로는 여러 중첩을 모두 표현할 수 없을 것입니다. 우리는 관측하고 싶은 state를 구현한 circuit을 $N\,(\geq 1000)$ 회 시행하여, 각각의 measurement를 수합해 state의 각 state의 확률을 계산합니다. 수식으로 $|j\rangle$의 확률 $P\,(|j\rangle)$은 다음과 같습니다:

$$|\psi\rangle = \sum_{j=0}^{2^N-1} c_j\,|j\rangle\,, \quad P\,(|j\rangle) = c_j^* c_j$$

Fig 4의 예시를 들면:

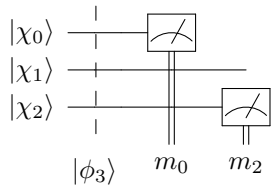
$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\,|00\rangle + \frac{1}{\sqrt{2}}\,|11\rangle$$

$$P\,(|00\rangle) = P\,(|11\rangle) = \frac{1}{2}, \quad (|01\rangle) = P\,(|10\rangle) = 0$$

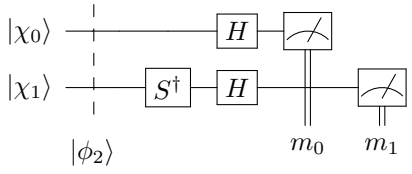
위 measurement로 우리는 각 state의 모든 coefficient를 알 수는 없지만, 적절한 물리량에 대한 기댓값을 얻는 것은 가능합니다. 아래는 Fig 4에서 $\langle Z\otimes Z\rangle$를 계산하는 식입니다:

$$\begin{aligned}\langle\psi_2|\,Z\otimes Z\,|\psi_2\rangle &= \left\langle \psi_2 \middle| \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\otimes\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \middle| \psi_2\right\rangle \\ &= c_{00}^* c_{00} - c_{01}^* c_{01} - c_{10}^* c_{10} + c_{11}^* c_{11} = \frac{1}{2} - 0 - 0 + \frac{1}{2} = 1\end{aligned}$$

Example 3)
N qubit state $|\phi_N\rangle = \sum_{j=0}^{2^N-1} c_j\,|j\rangle$에 대해 다음 기댓값을 c_j에 관한 식으로 표현하여라.
a) $\langle\phi_3|Z\otimes I\otimes Z|\phi_3\rangle$
b) $\langle\phi_2|X\otimes I|\phi_2\rangle$
c) $\langle\phi_2|X\otimes Y|\phi_2\rangle$
d) $P\,(|a\ 0\ b\rangle) + P\,(|a\ 1\ b\rangle) = P\,(|a\ \_\ b\rangle)$ 로 표기하기로 하자.
다음 circuit은 $|\chi_1\rangle$을 측정하지 않는다. 아래 circuit에서 수집한 data로도 a)의 기댓값을 계산할 수 있음을 보여라:



e) 우리는 측정을 통해 $p\,(j) = c_j^* c_j$ 만 얻을 수 있다. b)와 c)의 기댓값을 얻기 위해서는 circuit을 다르게 구성해야 한다. 다음 circuit을 통해서 c)를 계산할 수 있음을 보여라:



2.4 Fermionic space to qubit space transformation

The wave function and hamiltonian can be represented in terms of **fermionic operators**. (The creation and annihilation operator). Now let's look at how these things are transformed in a quantum computer. In this chapter, we will introduce how to efficiently encode the fermionic operator on a quantum computer. [3]

2.4.1 The wave function in qubits

Before introducing the encoding method, we first see how a wave function can be represented in qubits. By representing the wave function as an **occupation number (ON) vector**, we ensure that qubits and orbitals have a one-to-one correspondence.

The ON vector is defined as follows.

$$|\mathbf{k}\rangle = |k_1, k_2, \ldots, k_M\rangle, k_p = \begin{cases} 1, & \text{if } \phi_p \text{ occupied} \\ 0, & \text{if } \phi_p \text{ unoccupied} \end{cases} \tag{2.1}$$

The k_p is the **occupation number**, which is 1 if the spin orbital is occupied by an electron and 0 otherwise. We can make each of these occupation numbers correspond to a qubit. If the spin orbital is occupied, the state of a qubit is $|1\rangle_p$ and if it is unoccupied, $|0\rangle_p$.

For example, if the wave function $|\phi_1\phi_2\rangle$ is represented by four qubits, it can be written as $|1100\rangle$. And this corresponds to four qubits as $|1\rangle$, $|1\rangle$, $|0\rangle$, $|0\rangle$.

2.4.2 The Jordan-Wigner encoding method

The Jordan-Wigner encoding is a method of transforming the fermionic operator into a linear combination of Pauli operators that can be measured directly on a quantum computer. [4]

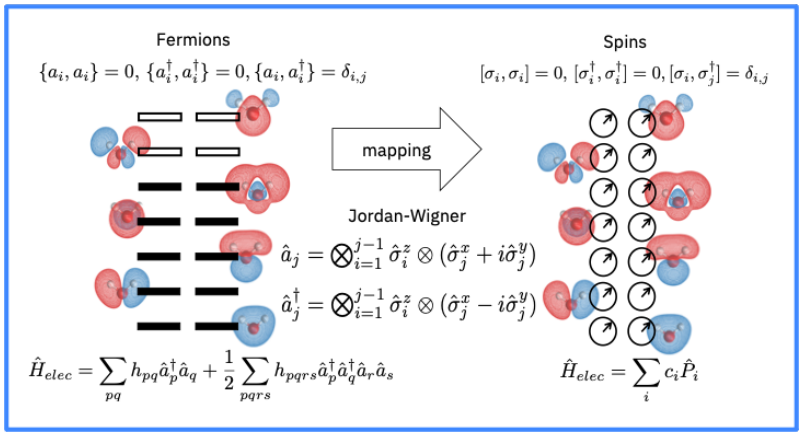


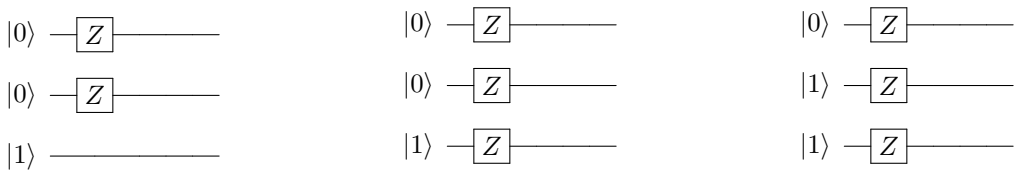
Figure 5: The mapping from fermions to qubits

If we do not consider the anti-commutation relation, the fermionic operators acting on the j-th qubit can be represented as follows: the creation operator changes the qubit state $|0\rangle$ into $|1\rangle$, and the annihilation operator changes the qubit state $|1\rangle$ into $|0\rangle$. This action can be directly

transformed as a Pauli operator.

$$\begin{aligned} \hat{a}_j^\dagger \to |1\rangle\langle 0|_j &= \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = \frac{X_j - iY_j}{2} \\ \hat{a}_j \to |0\rangle\langle 1|_j &= \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = \frac{X_j + iY_j}{2} \end{aligned} \tag{2.2}$$

where X_j and Y_j are Pauli operators acting on the j-th qubit.
However, these transformation cannot preserve an anti-commutation property of fermionic operators, because there is no sign change. To preserve that we add the Pauli string (linear combination of the Pauli operator), $Z_0 \otimes \cdots \otimes Z_{j-1}$. Note that $Z_0 \otimes \cdots \otimes Z_{j-1}$ has an eigenvalue of +1 if there are an even number of occupied orbitals up to the jth qubit, and -1 if it is odd. This represent the sign scription of fermionic operators.



(a) $|001\rangle \to |001\rangle$ (b) $|001\rangle \to -|001\rangle$ (c) $|011\rangle \to |011\rangle$

Figure 6: Example of applying the $Z_0 \otimes \cdots \otimes Z_{j-1}$ operator

Finally, we have the following result.

$$\begin{aligned} \hat{a}_j^\dagger &\to \frac{X_j - iY_j}{2} \otimes Z_0 \otimes \cdots \otimes Z_{j-1} \\ \hat{a}_j &\to \frac{X_j + iY_j}{2} \otimes Z_0 \otimes \cdots \otimes Z_{j-1} \end{aligned} \tag{2.3}$$

The Jordan-Wigner Encoding is a method that encodes locally for each orbital occupation. There are other encoding methods as well, the parity method, which encodes based on the parity of the orbitals, and the Bravy-Kitaev method, which encodes by considering both occupation and parity.

Example 3.2.1)
Suppose the fermionic operator is

$$1 + a_1^\dagger a_0$$

Using the Jordan-Wigner method, represent it as a linear combination of Pauli strings.

2.5 Common Facts about Quantum Computer

임의의 unitary matrix가 있을 때, 그것을 시행하는 multi-qubit gate를 반드시 만들 수 있음이 증명되어있습니다. 그런 점에서 양자 컴퓨터는 거대한 unitary matrix calculator라고 볼 수 있습니다. 거대한 행렬 연산이 고전 컴퓨터의 가장 큰 병목이었다면, 양자 컴퓨터는 (설계를 잘 한다면) 훨씬 효율적이고 빠르게 연산할 수 있다는 점이 양자컴퓨터의 특징입니다.
현재 양자 컴퓨터는 여러 기술적인 한계를 맞고 있습니다. Qubit의 개수도 20 $\sim$ 30개 정도이고, gate들의 오차도 무시할 수 없는 수준입니다. 이런 양자 컴퓨터를 Noisy Intermediate-Scale Quantum computer(**NISQ**) 라고 부릅니다. NISQ에서 구현할 수 있는 양자 알고리즘은 상당히 제한되어 있습니다. 동시에 3개 이상의 qubit을 entangle하는 연산은 오차가 심해 2 qubit gate들의 조합으로 대체해야 하고, Circuit depth(multi qubit gate의 개수를 일컫습니다) 역시 너무 커지면 오차가 지수적으로 증가하므로 이 점에 유의하며 양자 알고리즘을 설계해야 합니다.

3 Quantum Phase Estimation(QPE)

Electronic structure theory involves the calculation of energy and configuration for a stationary system. While full configuration interaction (full-CI) calculation is known for its highest accuracy, it has been proven intractable for classical computers. Consequently, the primary challenge in this field is to perform this calculation with lower computational costs.

Quantum phase estimation, which we will cover in this section, is the quantum algorithm supposed by John von Neumann. QPE offers the advantage of computing eigenvalues with desired precision (in terms of significant figures), thereby providing high computational accuracy. Specifically, it enables us to calculate the eigenvalue of a Hamiltonian, allowing us to determine the energy of a given system. However, implementing the QPE algorithm in NISQ devices poses a challenge due to its significant circuit depth. As a result, the practical implementation of QPE remains challenging at present.

Handout QFT
Handout QPE
Qiskit: Quantum Fourier Transform
Qiskit: Quantum Phase Estimation
Youtube: **But what is a Fourier Transform? A visual introduction - 3B1B**
Youtube: **What is a Discrete Fourier Transform? - Grant Sanderson**
Youtube: Fast Fourier Transform explained - Veritasium

3.1 Quantum Fourier Transformation(QFT)

QFT is the first algorithm you need to know to understand QPE. It's a qubit-mapped illustration of the Discrete Fourier transform. **In that sense, learning about Discrete Fourier Transform with supporting resources will be important** to understand this chapter[5][6].

3.1.1 Theoretical Background

We can write Discrete Fourier Transform as follows:

$$\tilde{v}_j = \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{-\frac{2\pi i}{N} kj} v_k \equiv \sum_k U_{jk} v_k \tag{3.1}$$
$$\vec{\tilde{v}} = \mathbf{U}\vec{v}$$

The equation denotes rotation of vector $\vec{v} = (v_0, v_1, \cdots, v_{N-1})$ to $\vec{\tilde{v}} = (\tilde{v}_0, \tilde{v}_1, \cdots, \tilde{v}_{N-1})$ by operating unitary matrix transformation $\mathbf{U}$. The same operation can also be performed by basis rotation $\hat{x}_k$ to new basis $\hat{y}_j$, which is opposite-direction rotation to $\vec{v} \rightarrow \vec{\tilde{v}}$. In this case, vector $\vec{v}$ should be fixed under basis rotation.

$$\hat{y}_j = \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{\frac{2\pi i}{N} kj} \hat{x}_k = \sum_k \hat{x}_k U^*_{kj} \tag{3.2}$$

Imagine the state $|\psi\rangle$ consisting of n qubits. We can consider it as a normal vector belonging to $\mathbb{C}^{2^n}$ space.

$$|\psi\rangle = \begin{pmatrix} c_0 \\ c_1 \\ \vdots \\ c_{2^n-1} \end{pmatrix} = \sum_{k=0}^{2^n-1} c_k |k\rangle \tag{3.3}$$

By substituting $|k\rangle$ at (3.3) to $\hat{x}_k$ at (3.2), rotated basis $|\tilde{j}\rangle$ corresponding to $\hat{y}_j$(3.2) can be written as follows(3.4):

$$\begin{aligned}
|\tilde{j}\rangle &= \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{\frac{2\pi i}{N} jk} |k\rangle \qquad\qquad (let\, N = 2^n) \\
&= \frac{1}{\sqrt{2^n}} \sum_{x_0,\cdots,x_{n-1}}^{\{0,1\}} e^{\frac{2\pi i}{2^n} j\left(2^{n-1}x_0 + 2^{n-2}x_1 + \cdots + x_{n-1}\right)} |x_0 x_1 \cdots x_{n-1}\rangle \\
&= \frac{1}{\sqrt{2^n}} \sum_{x_0,\cdots,x_{n-1}}^{\{0,1\}} e^{\frac{2\pi i}{2} jx_0} e^{\frac{2\pi i}{2^n} j(2^{n-2}x_1 + \cdots + x_{n-1})} |x_0\rangle \otimes |x_1 \cdots x_{n-1}\rangle \\
&= \left\{ \frac{1}{\sqrt{2}} \sum_{x_0}^{\{0,1\}} e^{\frac{2\pi i}{2} jx_0} |x_0\rangle \right\} \otimes \left\{ \frac{1}{\sqrt{2}^{n-1}} \sum_{x_1,\cdots,x_{n-1}}^{\{0,1\}} e^{\frac{2\pi i}{2^n} j(2^{n-2}x_1 + \cdots + x_{n-1})} |x_1 \cdots x_{n-1}\rangle \right\} \\
&= \left\{ \frac{1}{\sqrt{2}} \left(|0\rangle + e^{\frac{2\pi i}{2} j} |1\rangle \right) \right\} \otimes \left\{ \frac{1}{\sqrt{2}^{n-1}} \sum_{x_1,\cdots,x_{n-1}}^{\{0,1\}} e^{\frac{2\pi i}{2^n} j(2^{n-2}x_1 + \cdots + x_{n-1})} |x_1 \cdots x_{n-1}\rangle \right\} \\
&= \bigotimes_{m=0}^{n-1} \left\{ \frac{1}{\sqrt{2}} \left(|0\rangle + e^{2\pi i \frac{j}{2^{m+1}}} |1\rangle \right) \right\}
\end{aligned} \tag{3.4}$$

See equation (3.4). We can find that if we substitute $|0\rangle \sim |2^n - 1\rangle$ in the place of the basis $\hat{x}_k$ of the Discrete Fourier Transform expression, the result will naturally be reduced to a tensor product of n qubits.

3.1.2 Circuit

Figure 7 is a quantum circuit representation of the equation (3.4). Before describing the QFT circuit, let's first define the CR_n gate:

$$\begin{aligned}
&\text{let} \quad R_n \equiv \begin{pmatrix} 1 & 0 \\ 0 & e^{\frac{2\pi i}{2^n}} \end{pmatrix} = R_Z \left(\frac{2\pi}{2^n} \right) \\
&\text{then} \quad CR_n \equiv |0\rangle\langle 0|_c \otimes I_t + |1\rangle\langle 1|_c \otimes R_{n,t} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{\frac{2\pi i}{2^n}0} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & e^{\frac{2\pi i}{2^n}1} \end{pmatrix} \equiv I_c \otimes R_Z \left(\frac{2\pi}{2^n} \chi_c \right)_t
\end{aligned} \tag{3.5}$$

In (3.5), the CR_n gate appears to impose an $R_Z\left(2\pi\chi_c/2^n\right)$ transformation on the target qubit only, without changing the control qubit (the two qubits are not independent; since χ_c is the state of the control gate!).
QFT circuit can be illustrated as:

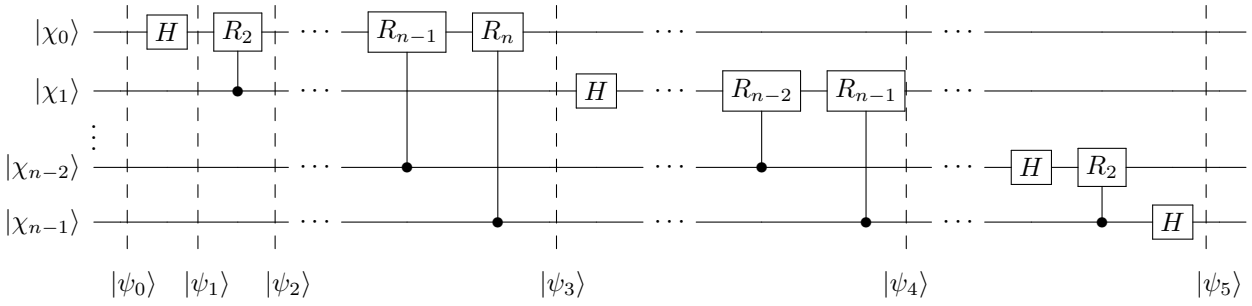


Figure 7: Circuit of QFT

Let's check the state in the middle of the circuit:

$$|\psi_0\rangle = |\chi_0\chi_1\cdots\chi_{n-1}\rangle \equiv |X\rangle \tag{3.6}$$

$$|\psi_1\rangle = \{H|\chi_0\rangle\} \otimes |\chi_1\cdots\chi_{n-1}\rangle$$
$$= \frac{1}{\sqrt{2}}\left\{|0\rangle + e^{\frac{2\pi i}{2}\chi_0}|1\rangle\right\} \otimes |\chi_1\cdots\chi_{n-1}\rangle \tag{3.7}$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\left(R_Z\left(\frac{2\pi}{2^n}\chi_1\right)\left\{|0\rangle + e^{\frac{2\pi i}{2}\chi_0}|1\rangle\right\}\right) \otimes |\chi_1\cdots\chi_{n-1}\rangle$$

$$\vdots \tag{3.8}$$

$$= \frac{1}{\sqrt{2}}\left\{|0\rangle + e^{\frac{2\pi i}{2}\chi_0}e^{\frac{2\pi i}{2^2}\chi_1}|1\rangle\right\} \otimes |\chi_1\cdots\chi_{n-1}\rangle \tag{3.9}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2}}\left\{|0\rangle + e^{\frac{2\pi i}{2^n}(\chi_0 2^{n-1}+\chi_1 2^{n-2}+\cdots+\chi_{n-1}2^0)}|1\rangle\right\} \otimes |\chi_1\cdots\chi_{n-1}\rangle$$
$$= \frac{1}{\sqrt{2}}\left\{|0\rangle + e^{\frac{2\pi i}{2^n}X}|1\rangle\right\} \otimes |\chi_1\cdots\chi_{n-1}\rangle \tag{3.10}$$

In this case, $X = \chi_0 2^{n-1}+\chi_1 2^{n-2}+\cdots+\chi_{n-1}2^0$. See $|\psi_3\rangle$; we can find that the first qubit becomes a similar form to the last line of eq.(3.4).

$$|\psi_4\rangle = \frac{1}{\sqrt{2}^2}\left\{|0\rangle + e^{\frac{2\pi i}{2^n}X}|1\rangle\right\} \otimes \left\{|0\rangle + e^{\frac{2\pi i}{2^{n-1}}(\chi_1 2^{n-2}+\chi_2 2^{n-3}+\cdots+\chi_{n-1}2^0)}|1\rangle\right\} \otimes |\chi_2\cdots\chi_{n-1}\rangle$$
$$= \frac{1}{\sqrt{2}^2}\left\{|0\rangle + e^{\frac{2\pi i}{2^n}X}|1\rangle\right\} \otimes \left\{|0\rangle + e^{\frac{2\pi i}{2^{n-1}}(X-\chi_1 2^{n-1})}|1\rangle\right\} \otimes |\chi_2\cdots\chi_{n-1}\rangle$$
$$= \frac{1}{\sqrt{2}^2}\left\{|0\rangle + e^{\frac{2\pi i}{2^n}X}|1\rangle\right\} \otimes \left\{|0\rangle + e^{\frac{2\pi i}{2^{n-1}}X}|1\rangle\right\} \otimes |\chi_2\cdots\chi_{n-1}\rangle \tag{3.11}$$

Thus, one part of the circuit can convert a qubit to a Fourier basis.

$$|\psi_5\rangle = \mathcal{QFT}|X\rangle = \frac{1}{\sqrt{2}^2}\left\{|0\rangle + e^{\frac{2\pi i}{2^n}X}|1\rangle\right\} \otimes \left\{|0\rangle + e^{\frac{2\pi i}{2^{n-1}}X}|1\rangle\right\} \otimes \cdots \otimes \left\{|0\rangle + e^{\frac{2\pi i}{2}X}|1\rangle\right\}$$
$$= \bigotimes_{m=0}^{n-1}\left\{|0\rangle + e^{\frac{2\pi i}{2^{n-m}}X}|1\rangle\right\} \tag{3.12}$$

Let's compare equation(3.4) with equation(3.12). We can see that the two are the same equation, except that the domain of the tensor product has been flipped from m + 1 to n - m (this can also be equalized by adding swap gate to Figure 7's $|\psi_5\rangle$).

3.1.3 Explanation

The main point of QFT lies in the conversion between Z axis basis and the Fourier basis. The Fourier basis is depicted on the equator of the Bloch sphere, guided by the intuition that the

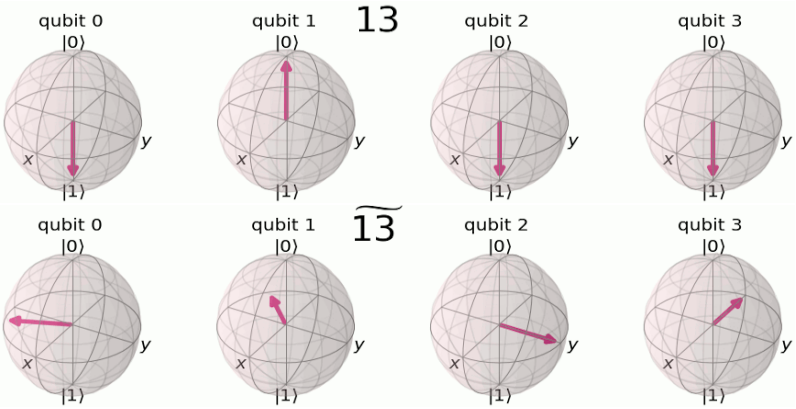


Figure 8: Z axis basis(up) and Fourier basis(down) of qubits

rotated phase angles return to their original positions with the periodicity of 2π. Figure 8 is a visualized example of qubit state $|X\rangle = |13\rangle$. You can see the visualized material of the above transformation in Chapter 2.1 of Qiskit Tutorial - Quantum Fourier Transform.

As discussed in Chapter 2.5, every quantum circuit represents a unitary operation, ensuring reversibility. Hence, the inverse Quantum Fourier Transform operation ($\mathcal{QFT}^\dagger$) is also possible, enabling the transformation of the Fourier basis to the Z-axis basis. The $\mathcal{QFT}^\dagger$ operation holds significant importance in Quantum Phase Estimation (QPE), which will be described later in this section.

Example 4)
Calculate $\mathcal{QFT}_3 |5\rangle$ on a 3 qubit circuit system.

Example 5)
Perform the QFT circuit by using Qiskit.

3.2 Quantum Phase Estimation

Quantum phase estimation(QPE) is a qunatum algorithm calculating the eigenvalue of the desired operation. Inspired by the fact that QFT supports translation between the z-axis basis and the Fourier basis, the objective is to map the eigenvalue to the Fourier basis and subsequently decode it back to the Z-axis basis[7].

3.2.1 Theoretical Background

Lemma 1. The eigenvalue of unitary matrix U can always expressed in terms of $e^{i\theta}$.
proof. When $|\psi\rangle$ is an eigenket of U,

$$\begin{aligned} U|\psi\rangle &= c|\psi\rangle \\ \langle\psi|\psi\rangle &= \langle\psi|U^\dagger U|\psi\rangle = c^\dagger c\langle\psi|\psi\rangle \\ \therefore c^\dagger c &= 1, c = e^{i\theta} \end{aligned}$$

For this reason, we call the eigenvalue c's exponential part θ as a **phase** in the context of a unitary operator.

3.2.2 Circuit and Explanation

Let's define the following operations on the desired operator H (in the case of electronic structure theory, the Hamiltonian of a given system) and its eigenket $|\phi_i\rangle$.

$$\begin{aligned} &H\,|\phi_i\rangle = \lambda_i\,|\phi_i\rangle \\ &\text{let } U_H = e^{i\tau H} \\ &\text{then, } U_H\,|\phi_i\rangle = e^{i\tau\lambda_i}\,|\phi_i\rangle \end{aligned} \tag{3.13}$$

$$\begin{aligned} CU_H &\equiv |0\rangle\langle 0|_c \otimes I_t + |1\rangle\langle 1|_c \otimes U_{H,t} \\ &= I \otimes \left(e^{i\tau H}\right)^{\chi_c} \end{aligned} \tag{3.14}$$

It's similar to eq (3.5). However, note that the target qubit can also be a multi-qubit gate since H is defined as a unitary operation of arbitrary size.

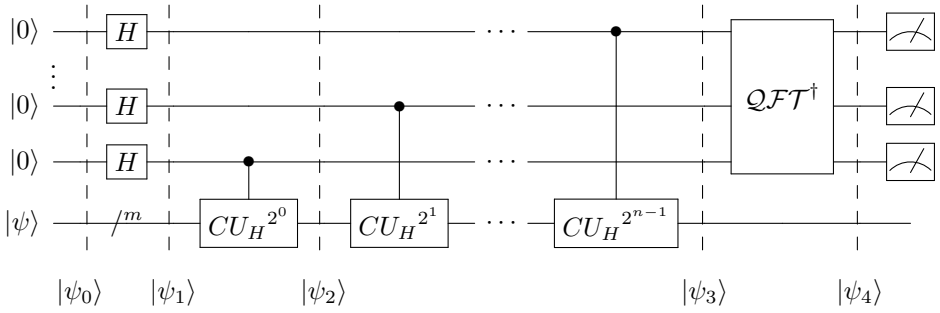


Figure 9: Circuit of QPE, working

In the above circuit, ${CU_H}^k$ means that the CU_H gate has been implemented k times. In the above circuit, the n measurement qubits have a control term added to them, and the state of each measurement qubit determines whether the operation U_H is performed on the $|\psi\rangle$ qubit as a target. Let's check the state in the middle of the circuit:

$$|\psi_0\rangle = |0\rangle|0\rangle\cdots|0\rangle|\psi\rangle \tag{3.15}$$

$$|\psi_1\rangle = \frac{1}{\sqrt{2}^n}\left(|0\rangle + |1\rangle\right)^{\otimes n}|\psi\rangle \tag{3.16}$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}^n}(|0\rangle + |1\rangle)^{\otimes n-1} \otimes \left(|0\rangle + e^{2\pi i\theta\cdot 2^0}\,|1\rangle\right)|\psi\rangle \tag{3.17}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2}^n}\left(|0\rangle + e^{2\pi i\theta\cdot 2^{n-1}}\,|1\rangle\right) \otimes \cdots \otimes \left(|0\rangle + e^{2\pi i\theta\cdot 2^1}\,|1\rangle\right) \otimes \left(|0\rangle + e^{2\pi i\theta\cdot 2^0}\,|1\rangle\right)|\psi\rangle \tag{3.18}$$

$$= \frac{1}{\sqrt{2^n}}\sum_{x=0}^{2^n-1} e^{2\pi ix\theta}|x\rangle|\psi\rangle \tag{3.19}$$

$$|\psi_4\rangle = QFT^{-1}\left[\frac{1}{\sqrt{2^n}}\sum_{x=0}^{2^n-1} e^{2\pi ix\theta}|x\rangle\right]|\psi\rangle \tag{3.20}$$

$$= \frac{1}{\sqrt{2^n}}\sum_{x=0}^{2^n-1} e^{2\pi ix\theta}QFT^{-1}\left[|x\rangle\right]|\psi\rangle \tag{3.21}$$

$$= \frac{1}{\sqrt{2^n}}\sum_{x=0}^{2^n-1} e^{2\pi ix\theta}\frac{1}{\sqrt{2^n}}\sum_{y=0}^{2^n-1} e^{-\frac{2\pi i}{2^n}yx}|y\rangle|\psi\rangle \tag{3.22}$$

Thus, the final state will be:

$$|\psi_f\rangle = \frac{1}{2^n}\sum_{y=0}^{2^n-1}\left[\sum_{x=0}^{2^n-1} e^{-\frac{2\pi i}{2^n}(y-2^n\theta)x}\right]|y\rangle\otimes|\psi\rangle \tag{3.23}$$

The state is expressed with the qubit basis $|y\rangle$, which is the Z-axis basis obtained by inverse QFT. Now, we can define an error δ with condition $2^n\theta = a + 2^n\delta$, where a is a closest integer to $2^n\theta$. Hence, with error term, equation (3.23) can be rewritten as:

$$|\psi_f\rangle = \frac{1}{2^n}\sum_{y=0}^{2^n-1}\left[\sum_{x=0}^{2^n-1} e^{-\frac{2\pi i}{2^n}(y-a)x}e^{2\pi i\delta x}\right]|y\rangle\otimes|\psi\rangle \equiv \sum_{y=0}^{2^n-1} c_y|y\rangle\otimes|\psi\rangle \tag{3.24}$$

Finally, we can measure the value in the form of probability. The probability of finding $|y\rangle = |a\rangle$ is

$$Pr(a) = |\langle a|\psi\rangle|^2 \tag{3.25}$$

$$= \left|\langle a|\frac{1}{2^n}\sum_{y=0}^{2^n-1}\sum_{x=0}^{2^n-1} e^{-\frac{2\pi i}{2^n}(y-a)x}e^{2\pi i\delta x}|y\rangle\right|^2 \tag{3.26}$$

$$= \left|\frac{1}{2^n}\sum_{x=0}^{2^n-1} e^{2\pi i\delta x}\right|^2 \tag{3.27}$$

When δ=0 in equation (3.27), you can easily see that $Pr(a)$=1.

3.3 Improving QPE with iteration

Iterative quantum phase estimation (IQPE) is an algorithm designed to complement the accuracy problem of QPE. IQPE has the advantage of being unconstrained by the number of qubits. Even with a limited qubit number, you can achieve any desired level of accuracy by increasing the number of trials. Ultimately, the algorithm can provide the exact solution of the desired eigenvalue.

3.3.1 Theoretical Background

In the section of QPE, we already remarked that an eigenvector of the arbitrary unitary operator U can be illustrated as $U|\psi\rangle = e^{i\theta} = e^{2\pi i\phi}$. Because of the periodicity, the range should be limited to $0 \le \phi < 1$. Now we can define a new operator for IQPE,

$$\hat{V}_k = [e^{-2\pi i\phi_{k-1}}\hat{V}_{k-1}]^2$$

when $\hat{V}_0 = U$. We will see how this operator can be applied to phase estimation.
At the first trial for k=0, let's assume a condition $2^n\phi \ge 2^n\phi_0$ so that $2^n\phi_0$ becomes a lower bound integer for the true value ϕ. Now we get the relation

$$\phi \ge \phi_0$$

At the second trial for k=1, let us operate $\hat{V}_1$ to $|\psi\rangle$ to get an eigenvalue. Then we get $\hat{V}_1|\psi\rangle = [e^{-2\pi i\phi_0}U]^2|\psi\rangle = e^{2\pi i(\phi-\phi_0)\cdot 2}|\psi\rangle$. Same as we did in the first trial, we can also take a lower bound value ϕ_1 to the phase of $\hat{V}_1$. By rearranging the formula $(\phi-\phi_0)\cdot 2 \ge \phi_1$,

$$\phi \ge \phi_0 + \frac{1}{2}\phi_1$$

This can be carried out iteratively, taking only the lower bound ϕ_k value for each operation and applying it to the formula below. The more the number of trials k increases, the closer the right side value is to the true value ϕ.

$$\phi \geq \phi_0 + \frac{1}{2}\phi_1 + \frac{1}{2^2}\phi_2 + ... + \frac{1}{2^k}\phi_k \tag{3.28}$$

3.3.2 Circuit

Figure 10 is a quantum circuit of iterative QPE. The overall structure seems similar to the QPE circuit, however, the controlled-U gate is replaced with a controlled-$\hat{V}_k$ gate.
IQPE repeats the whole circuit while incrementing the value of trial k from 0 to desired value. We will obtain the proper eigenvalue ϕ_k during each trial k and successively add it to the lower bound. As shown in Equation (3.28), the lower bound increases as the number of trials increases, leading to a value closer to the true value.

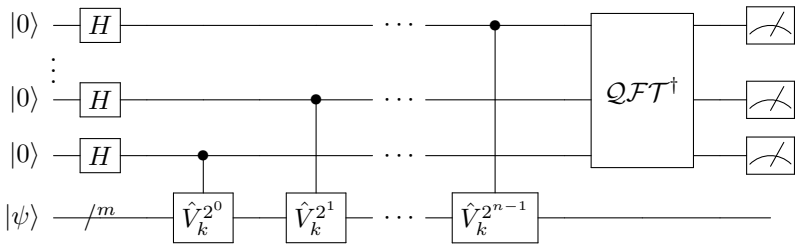


Figure 10: Circuit of iterative QPE, where $\hat{V}_k = [e^{-2\pi i\phi_{k-1}}\hat{V}_{k-1}]^2$.

4 Variational Quantum Eignensolver(VQE)

According to the variational principle, for arbitrary trial function, the following equation is true.

$$\langle\psi|\, H\, |\psi\rangle \geq E_0 \tag{4.1}$$

If we can make an exact function by making appropriate changes to the trial function, we can obtain the ground energy of the molecular system. Therefore, if you can set the appropriate variation, it means that you can apply the variational method effectively. It was confirmed that the variation can be implemented using various gates in quantum algorithms(called ansatz), and based on this, a quantum algorithm that approximates the ground state called variational quantum eigensolver(VQE) was studied.[3]

VQE is divided into 4 major procedure, setting initial state, changing initial state to trial state, measuring and optimizing. First, we set ground state as initial state, then, we set a trial function by operating the given ansatz which depends on a parameter θ in the initial state. It computes the expectation value of a physical quantity from measurement process. Then, through a classical optimization process, it reduces the expectation value to the minimum value by updating the parameter(ansatz) and trial function and by iterating the measurement. We are focus on an explanation about overall procedure excepted for optimization.

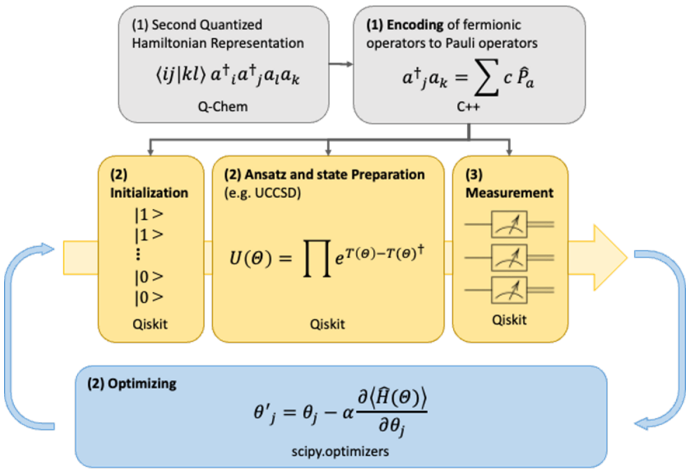


Figure 11: VQE overall scheme

4.1 Initialization

We need to represent the electronic wavefunction in terms of qubits to calculate the ground state energy for the molecule of interest. The important points are to figure out the number of orbitals and the number of electrons in the molecular system, and to choose a wavefunction than can well describe the ground state. Therefore, in generally, Hartree-Fock ground state is chosen as an initial state. (1.10) In the case of an inappropriate initial state(if not satisfy the above two conditions), it will converge to an incorrect result, so setting the initial state properly is the first thing to consider in VQE.

Let's understand the initialization process through H_2 molecule example. The molecule has a system of 4 orbitals and 2 electrons.(2 occupied, 2 unoccupied) So we have to set the initial state to two $|1\rangle$(occupied) and two $|0\rangle$(unoccupied). (2.1) From the four qubits set to $|0\rangle$, the initial state is set by operating X gates on the first and second qubits.

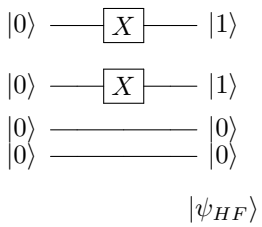


Figure 12: setting initial state of H_2 molecule

4.2 Ansatz

Ansatz selection is important part of eigensolver and the main purpose of this is to change a given initial state into a trial function. It mixes from the initial state to the superposed state using various gates such as control gate and rotation gate. Although the characteristic of ansatz may vary depending on the purpose of calculation, two things should be basically satisfied. It should be possible to describe all state of interest and also make the trial state converge to exact state. A typical example is UCC ansatz, which can conveniently express the excited state of electrons. However, since the number of iteration required for convergence increases if the expressibility is high, it is important to choose an appropriate ansatz between expression and training.

$$|\psi\rangle = U(\theta)\,|\psi_{HF}\rangle \tag{4.2}$$

4.2.1 UCC Ansatz

We introduced UCC as an ansatz which can parameterize conveniently the excited electron state. When these are single-electron excitations and double electron excitations, resulting in UCC Single and Double(UCCSD), also can be extended to high order. Thanks to its unitary through the exponential of an anti-Hermitian operator, it can be implemented as a quantum algorithm. (1.33)

Let's learn how it is constructed on the circuit by following the process below using UCCSD ansatz as an example. It is a central part of the UCCSD ansatz to encode the fermion operator into Pauli words, the tensor product of the Pauli matrices. This is exactly same as the encoding process learned above.

From 1.34, 2.3, UCCSD ansatz can be represented by Pauli matrix using JW encoding.

$$\begin{aligned} U(\theta) &= \exp(\sum_{a,r} \theta_a^r (a_r^\dagger a_a - a_a^\dagger a_r) + \sum_{a,b,r,s} \theta_{ab}^{rs} (a_r^\dagger a_s^\dagger a_b a_a - a_a^\dagger a_b^\dagger a_s a_r)) \\ &= \exp(\sum_j \theta_j A_j) \\ &= \exp(\sum_j i c_j P_j)(P = p_1 \otimes p_2 \otimes \cdots \otimes p_n, p \in \{I, X, Y, Z\}) \end{aligned} \tag{4.3}$$

The next step, called Trotterization, is the process of approximating the exponentialized Pauli

word to a product form. The approximation is needed because it is not ensured that $e^{A+B} = e^A e^B$ when A, B is matrix. We convert the UCC ansatz into a series of parameterized quantum gates which can directly be implemented on a quantum computer.

$$\exp(\sum_j ic_j P_j) \approx \prod_j (e^{ic_j \frac{P_j}{n}})^n \tag{4.4}$$

Then, rewrite exponentialized matrix. It is defined by expansion of Taylor series.

$$e^A = A^0 + A^1 + \frac{1}{2}A^2 + ... \tag{4.5}$$

Using this equation, we can represent $e^{iZ\theta}$ and $e^{iZZ\theta}$ to matrix form, the result is below. We know that $e^{iZ\theta}$ is rotation operator which rotate by θ phase around the Z axis.

$$\begin{aligned} e^{iZ\theta} &= \begin{pmatrix} e^{i\theta} & 0 \\ 0 & e^{-i\theta} \end{pmatrix} = R_Z(\theta) \\ e^{iZZ\theta} &= \begin{pmatrix} e^{i\theta} & 0 & 0 & 0 \\ 0 & e^{-i\theta} & 0 & 0 \\ 0 & 0 & e^{-i\theta} & 0 \\ 0 & 0 & 0 & e^{i\theta} \end{pmatrix} \end{aligned} \tag{4.6}$$

Since the matrix is unitary, it can be represented on the circuit.

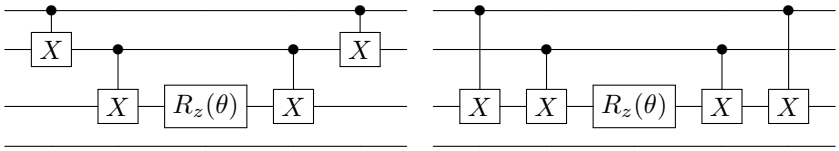


Figure 13: Ladder implement(left) and Star implement(right) of $e^{iZZZI\theta}$

Then how should we express the X and Y operators? We have dealt with a similar problem in the previous measurement section. It needs to transform the basis of X and Y operator to the basis of Z operator. It can be performed by placing H and S gates on the circuit. The X and Y operator are transformed to the Z operator through the H gate and S, H gate, respectively. (2.3)

$$\begin{aligned} e^{cX} &= H \cdot e^{cZ} \cdot H \\ e^{cY} &= \{HS^\dagger\}^\dagger \cdot e^{cZ} \cdot HS^\dagger \end{aligned} \tag{4.7}$$

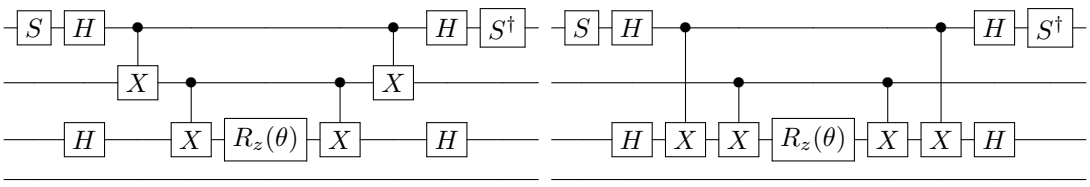


Figure 14: Ladder implement(left) and Star implement(right) of $e^{iYZXI\theta}$

4.3 Measurement

The Hamiltonian can be represented with linear combination of Pauli words using Jordan-Wigner Encoding method. We can express the expectation value of the Hamiltonian by finding the expectation value of the Pauli words. It is defined as a linear combination as shown the equation below. (1.25, 2.3)

$$\begin{aligned} \mathcal{H}_{elec} &= \sum_i c_i P_i (P = p_1 \otimes p_2 \otimes \cdots \otimes p_n, p \in \{I, X, Y, Z\}) \\ \langle \mathcal{H}_{elec} \rangle &= \sum_i c_i \langle P_i \rangle = \sum_i c_i \langle \psi | P_i | \psi \rangle \end{aligned} \tag{4.8}$$

As mentioned in chapter 1.3 (2.3), the probability is expressed by the coefficient of the statevector. However, since we cannot track each statevector in real, we have to be obtain the probability by measuring each qubits. The process of capturing a single state is called a shot, and the probability of each state is obtained through enough N times of shot.

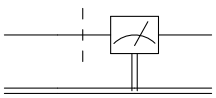
4.3.1 $\langle Z \rangle$ Measurement

Among the Pauli matrices, the measurement of the Z operator can be expressed as the difference between the probabilities of $|0\rangle$ and $|1\rangle$ state because the matrices are diagonal. Additionally, the expectation value of I operator must be 1. It means that I operator is independent to measurement process. 2.3

$$\begin{aligned} \langle Z \rangle = \langle \psi | Z | \psi \rangle &= \begin{pmatrix} c_0^* & c_1^* \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = c_0^* c_0 - c_1^* c_1 = P(|0\rangle) - P(|1\rangle) \\ \langle I \rangle = \langle \psi | I | \psi \rangle &= \begin{pmatrix} c_0^* & c_1^* \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = c_0^* c_0 + c_1^* c_1 = P(|0\rangle) + P(|1\rangle) = 1 \\ \langle ZZ \rangle = \langle \psi | ZZ | \psi \rangle &= \begin{pmatrix} c_{00}^* & c_{01}^* & c_{10}^* & c_{11}^* \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c_{00} \\ c_{01} \\ c_{10} \\ c_{11} \end{pmatrix} \\ &= c_{00}^* c_{00} - c_{01}^* c_{01} - c_{10}^* c_{10} + c_{11}^* c_{11} = P(|00\rangle) - P(|01\rangle) - P(|10\rangle) + P(|11\rangle) \end{aligned} \tag{4.9}$$

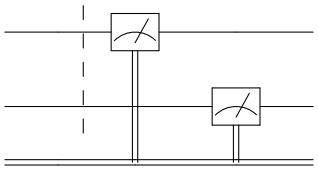
Assume the following two examples.

1. a total of 2048 shots, 0 state is 1023 and 1 state is 1025.



$$P(|0\rangle) = \frac{1023}{2048}, P(|1\rangle) = \frac{1025}{2048}$$
$$\langle Z \rangle = P(|0\rangle) - P(|1\rangle) = -\frac{2}{2048}$$

2. a total of 2048 shots, 00 state is 255, 01 state is 769, 10 state is 767 and 11 state is 257.



$$P(|00\rangle) = \frac{255}{2048}, P(|01\rangle) = \frac{769}{2048}, P(|10\rangle) = \frac{767}{2048}, P(|11\rangle) = \frac{257}{2048}$$
$$\langle ZZ \rangle = P(|00\rangle) - P(|01\rangle) - P(|10\rangle) + P(|11\rangle) = -\frac{1024}{2048}$$

However, it needs to transform the basis of X and Y operator to the basis of Z operator for measurement of X and Y operator, since the probabilities can not express expectation value by simply summation. (2.3)

$$\langle ZIXY \rangle = \langle \psi | ZIXY | \psi \rangle = \langle \psi' | ZIZZ | \psi' \rangle \tag{4.10}$$

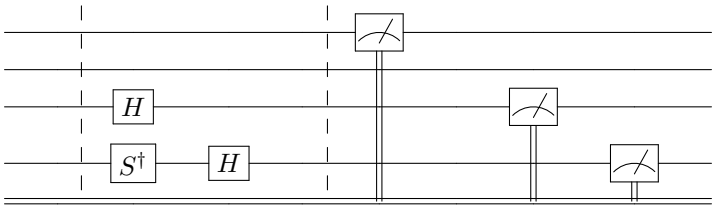


Figure 15: ZIXY measure

We deal with a method to calculate the expectation value of 4 Pauli operators. Based on this, we can reconstruct the expectation value of complex Pauli matrices constituting the Hamiltonian as an equation of probabilities.

4.3.2 Grouping

In a real quantum computer system, since the measurement cost is proportional to the number of measurements, methods to reduce it through post processing are proposed. One of them is grouping. Some of numerous Pauli words have the same circuit diagram. Since this depends on the X and Y operators, it is satisfy when the order of X and Y operators in Pauli words is same. The expectation value of Pauli words belonging to a group is expressed as a combination of probabilities obtained through the same measurement. For example, IZXI, ZIXY, ZZXI, ZIIY are belong to [ZZXY] group.

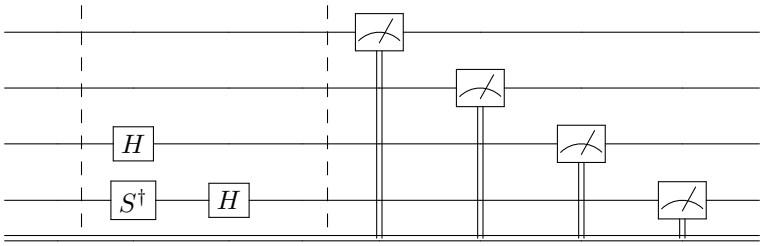


Figure 16: ZZXY group

4.4 Optimization

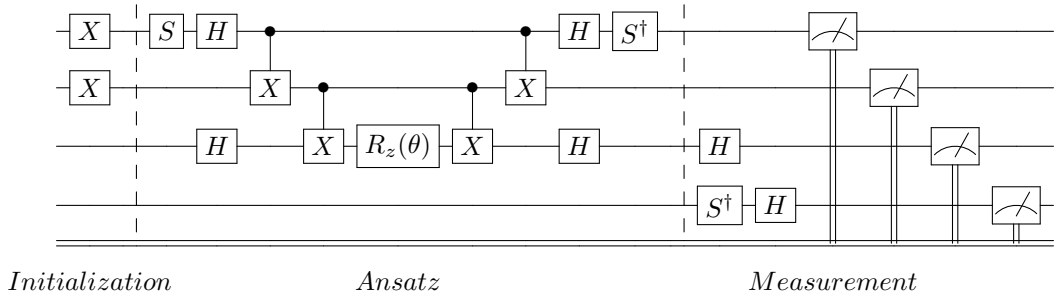


Figure 17: VQE scheme

Review the above overall VQE Scheme. We obtained the Hamiltonian energy of trial state through the 3 procedures. However, it is not minimum energy we want, so it needs to optimize trial state to exact state. This is same as determining the $i+1$ th parameter($\theta^{(i+1)}$) of ansatz with i th ($\theta^{(i)}$) and the result, and iteratively performed until the Hamiltonian energy converges to the minimum. There are two major categories of optimization, gradient-based optimizers and gradient-free optimizers.[8] Gradient based optimizers require evaluation of gradient for optimization, and examples include Gradient Descent (GD), Broyden-Fletcher-Goldfard-Shanno (BFGS) and Simultaneous Perturbation Stochastic Approximation (SPSA). The opposite is called a gradient-free optimizer, and representative Constrained Optimization BY Linear Approximation (COBYLA) and POWELL exist. In fact, optimization is a field outside of our interest, so there will be no big problem even if we just check the above.

5 Homebuilt VQE manual

We prepared a full VQE code on a Google colab™ `.ipynb` file you can run through.

5.1 Instruction_Colab

First, you should clone the contents in Y.K.Ahn's Google drive directory. Download the full contents at Google Drive File and upload the whole contents to your own Google Drive. Run `tutorial.ipynb` and f ㅋ ollow the instruction.

5.2 Instruction_Local

References

[1] Attila Szabo and Neil S Ostlund. *Modern quantum chemistry: introduction to advanced electronic structure theory*. Courier Corporation, 2012.

[2] Trygve Helgaker, Poul Jorgensen, and Jeppe Olsen. *Molecular electronic-structure theory*. John Wiley & Sons, 2013.

[3] Jules Tilly et al. "The Variational Quantum Eigensolver: A review of methods and best practices". In: *Physics Reports* 986 (2022). The Variational Quantum Eigensolver: a review of methods and best practices, pp. 1–128. ISSN: 0370-1573. DOI: https://doi.org/10.1016/j.physrep.2022.08.003. URL: https://www.sciencedirect.com/science/article/pii/S0370157322003118.

[4] *Electronic sturcture*. URL: https://qiskit.org/documentation/stable/0.24/tutorials/chemistry/01_electronic_structure.html.

[5] *Quantum Fourier Transform*. 2021. URL: https://learn.qiskit.org/course/ch-algorithms/quantum-fourier-transform.

[6] *Discrete Fourier Transform*. 2021. URL: https://www.youtube.com/watch?t=773&v=g8RkArhtCc4&feature=youtu.be.

[7] *Quantum Phase Estimation*. 2021. URL: https://learn.qiskit.org/course/ch-algorithms/quantum-phase-estimation.

[8] Harshdeep Singh, Sonjoy Majumder, and Sabyashachi Mishra. "Benchmarking of different optimizers in the variational quantum algorithms for applications in quantum chemistry". In: *The Journal of Chemical Physics* 159.4 (July 2023), p. 044117. ISSN: 0021-9606. DOI: 10.1063/5.0161057. eprint: https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0161057/18065624/044117_1_5.0161057.pdf. URL: https://doi.org/10.1063/5.0161057.