

# Simulation of Molecules with Variational Quantum Eigensolvers

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**Abstract**—Universal quantum computers were originally proposed to efficiently simulate quantum many-body systems. They could potentially revolutionize protein folding simulation, our search for high-temperature superconductors, new drugs, and new materials. Monte Carlo methods are often used to tackle these problems on classical computers. However, the runtimes of these methods grow exponentially with the number of particles simulated. Recently, noisy intermediate stage quantum computers have developed the capacity to address increasingly larger problems. Using a variational quantum eigensolver, we can determine various structural properties of simple molecules. We have described these standard techniques to perform the simulation of fermionic hamiltonians. This is achieved through a hardware efficient variational quantum eigensolver that is run on the IBMQ available quantum computers and simulators. The fermions are efficiently encoded into qubits using the Jordan Wigner transformation. Using these techniques developed recently, we were able to attempt the calculation of the bond length and the ground state energy of  $H_2$ . We also studied the effects of using different ansatz and differing circuit depths on our results. We found a very good agreement between noiseless simulation and classical numerical eigensolver. However, with realistic noise, VQE yielded inaccurate results. The Two-Local ansatz yielded superior results than the UCC ansatz. Due to the high level of noise, we found that lower circuit depths performed better.

**Index Terms**—Quantum Computing, Quantum Chemistry, Variational Quantum Eigensolver

## I. INTRODUCTION

Quantum computing has the potential of revolutionizing computation by solving problems exponentially faster than what would be possible on a classical computer. Richard Feynman originally proposed quantum computing as a way to efficiently simulate quantum many-body systems [1]. Quantum chemistry has been one field that has struggled with computational complexity [2]. Determining molecular structure often heavily relies upon finding the ground state energy of a particular fermionic hamiltonian as seen below:

$$H|\Psi\rangle = E_0|\Psi\rangle \quad (1)$$

Where  $H$  is the hamiltonian,  $E_0$  is the ground state energy, and  $|\Psi\rangle$  is the wavefunction. Such an eigenvalue problem is not considered tractable, even for a quantum computer. However, if the hamiltonian is local, like the hamiltonians seen in physics, then it may be solved efficiently on a quantum computer [3]. Solving such eigenvalue

problems can be important for problems outside quantum chemistry such as new material and new drug discovery[4].

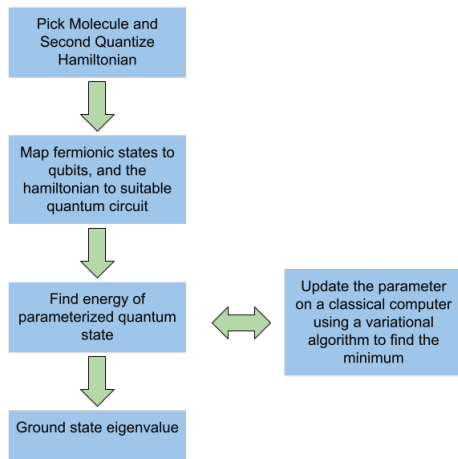


Figure 1. Flowchart of steps to simulating a hamiltonian using VQE.

Having an efficient way to encode quantum states as qubits is essential to any quantum algorithm. The Jordan Wigner transformation allows us to represent a fermionic hamiltonian compactly in terms of Pauli Matrices, and fermionic states are represented very simply in terms of qubits. This compact fermion-to-qubit mapping makes this eigenvalue problem more accessible to quantum computers. The Quantum Phase Estimation (QPE) algorithm allows us to find the eigenvalues of a unitary operator in a time-efficient manner. This has been used to successfully simulate molecules in the past [5]. However, this algorithm requires long coherence times for accurate results [6]. Alternatively, the Variational Quantum Eigensolver (VQE) is an algorithm that uses a hybrid approach to solving the eigenvalue problem [7][8]. It uses a quantum circuit to prepare parameterized initial states and measure their energies. This circuit can produce an entangled state and measure it in a time-efficient manner. This quantum circuit is the main reason for the speed advantage of VQE over classical algorithms. These circuits are often composed of layers of entanglement blocks and parameterized single-qubit rotations [9]. After the energy of the initial state is evaluated, some minimization routine [10] is used to find the ground state energy. This process of simulating arbitrary

fermionic hamiltonians has recently made these quantum simulations feasible on open source quantum computers. We will review and explain this general procedure and implement it to characterize a Hydrogen molecule. The procedure is summarized in Figure 1.

## II. SECOND QUANTIZATION

Here we will outline a procedure for turning the hamiltonian of any molecule into a second quantized form, which allows for a more natural fermion-to-qubit mapping. The relevant forces involved in the hamiltonian of a molecule are the electromagnetic forces. The hamiltonian of an arbitrary molecule is given below:

$$H = -\sum_I \frac{\nabla_I^2}{2M_I} - \sum_i \frac{\nabla_i^2}{2m_i} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} + \sum_I \sum_{J>I} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (2)$$

Here  $I$  indices the nuclei and  $i$  indices the electrons.  $Z, M, R$  are charges, masses, and radii of nuclei, respectively.  $m$  and  $r$  are the masses and radii of the electrons, respectively. Since the mass of the nuclei is much larger than the electrons we can apply the Born-Oppenheimer approximation and assume that nuclei are static. We obtain the following hamiltonian:

$$H_{bo} = -\sum_i \frac{\nabla_i^2}{2m_i} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} \quad (3)$$

Now we will now turn  $H_{bo}$  in terms of creation ( $a$ ) and annihilation operators ( $a^\dagger$ ). An arbitrary state of a fermionic system can be put in one-to-one correspondence with states of the form  $|n\rangle = |n_1, n_2, \dots, n_N\rangle$ , where there are  $N$  possible energy orbitals, and each  $n_i$  is either 0 or 1, representing whether each orbital is occupied or not. We note that these states need to be anti-symmetrized to form fermionic states. We also note these states have a very natural representation as qubits. The creation and annihilation operators act on such a state in the following way:

$$a_i |\dots n_i \dots n_N\rangle = n_i (-1)^{\sum_{j<i} n_j} |\dots, n_i \oplus 1, \dots, n_N\rangle$$

$$a_i^\dagger |\dots n_i \dots\rangle = (1 - n_i) (-1)^{\sum_{j<i} n_j} |\dots, n_i \oplus 1, \dots, n_N\rangle$$

These act very similarly to the  $\sigma^x$  state act on a spin qubit. These operators obey certain anticommutation relations, which are essential to describing the heisenberg uncertainty relations of these states. These are given by:

$$\{a_i, a_j^\dagger\} = \delta_{ij} \mathbb{I} \quad (4)$$

$$\{a_i, a_j\} = 0 \quad (5)$$

$$\{a_i^\dagger, a_j^\dagger\} = 0 \quad (6)$$

Where  $\{a, b\} = ab + ba$ . We can use these operators to write our Hamiltonian in a different form:

$$H_{sc} = \sum_{ij} h_{ij} a_i a_j^\dagger + \sum_{pqrs} h_{pqrs} a_p a_q a_r^\dagger a_s^\dagger \quad (7)$$

The first term here defines 'one-body interactions' such as the kinetic energy, and the second terms define 'two-body interactions', such as the electromagnetic interactions. The coefficient for the one-body interactions are given by the one-body integrals:

$$h_{ij} = \int \phi_i^*(r) \left( -\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{R_I - r} \right) \phi_j(r) dr$$

Where  $\phi_i$  are the wavefunctions of the orbital in the  $i$ -th state. The two-body coefficients are given by the two-body interactions:

$$h_{pqrs} = \int \int \phi_p^*(r_1) \phi_q^*(r_2) \frac{1}{r_1 - r_2} \phi_r(r_2) \phi_s(r_1) dr_1 dr_2 \quad (8)$$

These integrals can be efficiently computed on a classical computer using a variety of methods. We will be using the PySCF library, which is made specifically for computing these terms.

## III. FERMION-TO-QUBIT MAPPING

To effectively simulate these fermionic systems, we need a compact fermion-to-qubit mapping. An arbitrary fermionic state is given by:

$$S^- |n_1 \dots n_N\rangle = \sum_{\sigma \in S_N} (-1)^{\text{sgn}(\sigma)} |\sigma(n_1) \dots \sigma(n_N)\rangle \quad (9)$$

Where  $S_N$  is the permutation group of  $N$  elements.  $\text{sgn}$  is the sign of the permutation, which can be  $\pm 1$ . We will use the non-anti-symmetrized version to represent our fermionic states. There are several ways we can perform a fermion-to-qubit mapping.

### A. Jordan Wigner Transformation

In the Jordan Wigner transformation, the orbital occupation levels are mapped to qubits as follows:

$$\begin{pmatrix} q_1 \\ \vdots \\ q_N \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} n_1 \\ \vdots \\ n_N \end{pmatrix}$$

Here  $q$  represents a qubit and  $n$  is the occupation state. One can see from before that the creation annihilation operators can be mapped to pauli operators in some way. The exact mapping is given by:

$$a_i^\dagger \mapsto \left( \prod_{j<i} \sigma_j^z \right) \sigma_i^- \quad (10)$$

where  $\sigma^- = \sigma^x - i\sigma^y$ .

$$a_i \mapsto \left( \prod_{j<i} \sigma_j^z \right) \sigma_i^+ \quad (11)$$

where  $\sigma^+ = \sigma^x + i\sigma^y$ . These mappings also preserve the canonical anticommutation relations in equations (4)-(6), and thus preserve the physics of the system. One issue with this mapping is that it is  $O(N)$ -local, whereas the original hamiltonian was fully local.

### B. Bravyi-Kitaev mapping

There is a superior fermion-to-qubit mapping that gives an  $O(\log N)$ -local hamiltonian called the Bravyi-Kitaev mapping [11]. For 2 state system, the encoding is given by:

$$\begin{pmatrix} q_1 \\ q_2 \end{pmatrix} = \begin{pmatrix} n_1 \oplus n_2 \\ n_2 \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$$

Here multiplication and addition is over the finite field  $\mathbb{Z}_2$ . We label this first matrix as  $\beta_1$ . We can define a general  $2^N \times 2^N$  matrix recursively.

$$\beta_N = \left( \begin{array}{c|ccc} & 1 & \cdots & 1 \\ & 0 & \cdots & 0 \\ & \vdots & \ddots & \vdots \\ \beta_{N-1} & 0 & \cdots & 0 \\ \hline \mathbf{0} & & & \beta_{N-1} \end{array} \right) \quad (12)$$

The new  $O(\log N)$ -local creation and annihilation operators are mapped as follows:

$$a_i \mapsto \frac{1}{2} \prod_{j \in U(i)} \sigma_j^x \times \left( \sigma_i^x \prod_{j \in P(i)} \sigma_j^z + i \sigma_i^y \prod_{j \in R(i)} \sigma_j^z \right) \quad (13) \quad a)$$

$$a_i^\dagger \mapsto \frac{1}{2} \prod_{j \in U(i)} \sigma_j^x \times \left( \sigma_i^x \prod_{j \in P(i)} \sigma_j^z - i \sigma_i^y \prod_{j \in R(i)} \sigma_j^z \right) \quad (14)$$

The functions  $U(i), P(i), R(i)$  can be systematically found using partially ordered binary strings [12].

An alternative method is known as the parity transformation is also commonly used, but is less efficient than Bravyi-Kitaev, and less straightforward than the Jordan Wigner transformation. Though the Bravyi-Kitaev method is more efficient for larger molecules, for our purposes the Jordan Wigner transformation will suffice.

## IV. VARIATIONAL QUANTUM EIGENSOLVER

### A. Variational Principle

The variational principle states that the expectation value of any hermitian operator always has a minimum, which is given by its lowest eigenvalue. In the case of the hamiltonian we get:

$$\langle \psi | H | \psi \rangle \geq \lambda_0 = E_0 \quad (15)$$

for some arbitrary state in our Hilbert space  $|\psi\rangle$ . This allows us to solve for the lowest eigenvalue by simply minimizing this expression. Since our Hilbert space is finite ( $\mathcal{H} = \mathbb{C}^{2^n}$ ), this is a computationally feasible task. However, exploring this entire space is inefficient, so this usually requires us to restrict to a certain subspace. This requires us to make an 'ansatz' or guess a 'variational form'.

### B. Variational Forms

To restrict ourselves subspace we start with parametrizing a unitary operator  $U(\vec{\theta})$  with:

$$U(\vec{\theta}) |\psi\rangle = |\psi(\vec{\theta})\rangle$$

$$\langle \psi(\vec{\theta}) | H | \psi(\vec{\theta}) \rangle = E(\vec{\theta})$$

Classically, preparing the wave function into arbitrary entangled state can have an exponential computational cost. On quantum computer they can be prepared efficiently with a quantum circuit like the one shown in Figure 2.

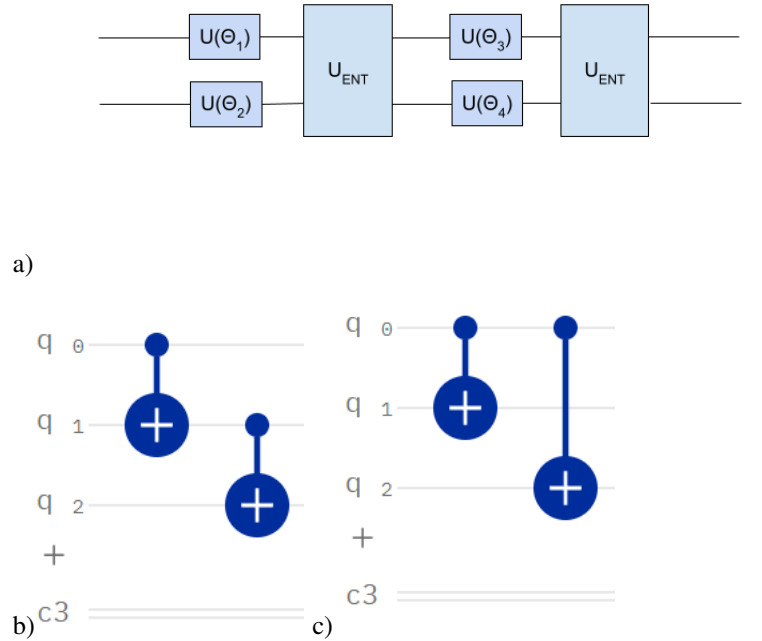


Figure 2. Example variational form circuit. a) 2 qubit variational form circuit with depth 2. b)  $U_{ENT}$  block with linear entanglement. c)  $U_{ENT}$  block with full entanglement.

The  $U_{ENT}$  blocks in Fig. 2 entangle the multiple qubits and usually take on a hardware-specific form. In Fig 2b, 2c we show different implementations of the entanglement block. The  $U(\theta)$  gates are usually implemented as a series of rotations. The goal of these circuits is to have as general of a state as possible with as few parameters as possible. The depth of the ansatz can increase accuracy, but deeper circuits would also propagate more error due to noise. Using an ansatz that might have some physical intuition behind it may yield more accurate results. After preparing the state, its energy can be found efficiently through a series of measurements. Using equations (7),(10),(11), we can see in general our hamiltonian will look like:

$$H_{qubit} = \sum_{i,j,k,l=0}^3 c_{ijkl} \sigma_1^i \otimes \sigma_2^j \otimes \sigma_2^k \otimes \sigma_4^l \quad (16)$$

We use the convention that  $\vec{\sigma} = \{\mathbb{I}, \sigma^x, \sigma^y, \sigma^z\}$ . Our arbitrary state will have the form:

$$\sum_{n_1 \dots n_N=0}^1 d_{\vec{n}} |\vec{n}\rangle$$

So then we measure the energy and get a function that depends only on the probabilities of each qubit, since the Pauli matrix expectation values will always give either 0,1 or -1, from a pure state. The qiskit-nature ElectronStructureMoleculeDriver computes these values for us, and the measurements are automated.

After choosing a variational form and measuring its energy, we then apply an optimization algorithm.

### C. Optimization

Optimization is often done through standard methods such as gradient descent and stochastic gradient descent. However, these algorithms are sensitive to the dimension of the search space, because they have to sample more space to approximate the gradient. The simultaneous perturbation stochastic approximation (SPSA) approximates the gradient using two measurements, regardless of dimension. Despite this less accurate approximation of the gradient, the SPSA algorithm achieves similar results to conventional gradient descent [10].

## V. EXPERIMENT

We used the IBMQ quantum computers to simulate  $H_2$  molecules. We did 4 simulations: normal simulator UCC ansatz, noisy simulator UCC ansatz, noisy simulator Two-Local ansatz with depth 2, noisy simulator Two-Local ansatz with depth 3. The UCC and Two-Local ansatz are show in Fig. 7,8 of the appendix, respectively. We used code provided by Qiskit and implemented it into an algorithm to find the bond length and ground state energy for the Hydrogen molecule[13]. Simulations were done both on the QASM simulator and with a simulator coupled with noise from the IBMQ Lima computer. These results were compared with results from a classical algorithm (NumpyMinEigensolver). We measured the standard error between the classical and quantum simulations.

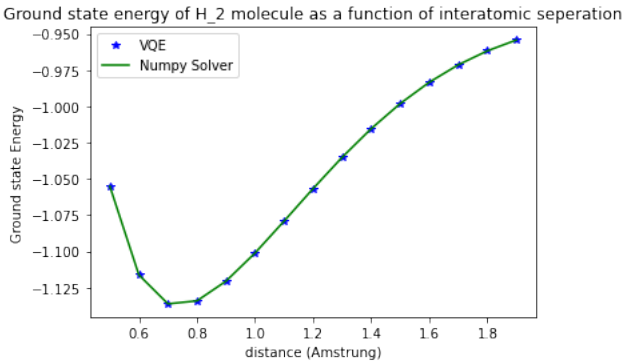


Figure 3. Ground state energy as a function of distance of a diatomic hydrogen molecule, solved by a NumpyMinEigensolver and a VQE solver simulates on the QASM simulator. The standard error was 0.00

Ground state energy of H<sub>2</sub> molecule as a function of interatomic separation

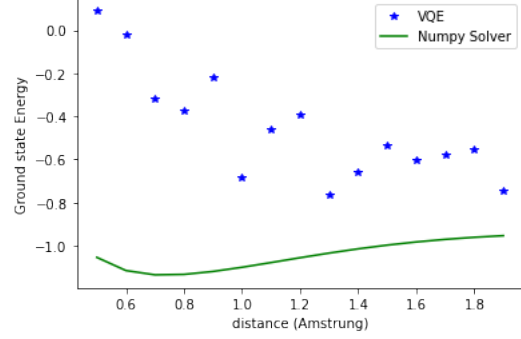


Figure 4. Ground state energy as a function of distance of a diatomic hydrogen molecule, solved by a NumpyMinEigensolver and a VQE solver, with UCC ansatz, simulated on the QASM simulator coupled with noise from IBMQ Lima. The standard error was 0.0894

Ground state energy of H<sub>2</sub> molecule as a function of interatomic separation

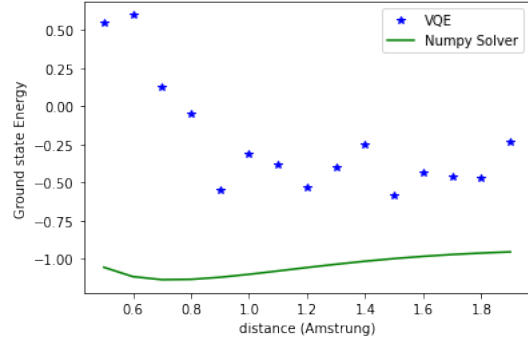


Figure 5. Ground state energy as a function of distance of a diatomic hydrogen molecule, solved by a NumpyMinEigensolver and a VQE solver, Two-Local ansatz with depth 2, simulated on the QASM simulator coupled with noise from IBMQ Lima. The standard error was 0.074

Ground state energy of H<sub>2</sub> molecule as a function of interatomic separation

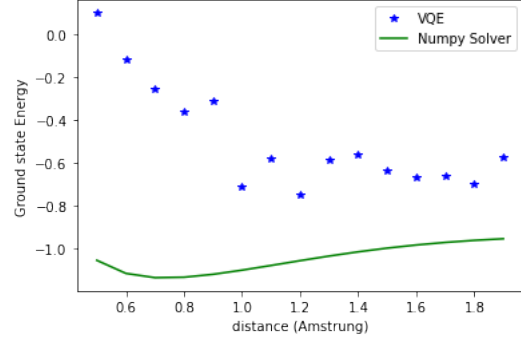


Figure 6. Ground state energy as a function of distance of a diatomic hydrogen molecule, solved by a NumpyMinEigensolver and a VQE solver, Two-Local ansatz with depth 3, simulated on the QASM simulator coupled with noise from IBMQ Lima. The standard error was 0.104

Fig	$E_0$ (Hartree)	Bond Length(A)	error
3	-1.137	0.74	0.000
4	-0.78	1.32	0.089
5	-0.53	0.91	0.074
6	-0.79	1.24	0.104

Table I. Summary of results for  $H_2$ .

## VI. DISCUSSION

In these experiments, we tested the practicality of the VQE algorithms on modern NISQ computers and compared them to classical results that we know to be accurate. We found that our simulated VQE with no noise was in perfect agreement with theory. However, this agreement with theory went away with the addition of quantum noise to the simulation. This is likely due to errors causing the evaluation of the energy to be less accurate and thus the optimization algorithm would have optimized based on inaccurate information, resulting in finding the incorrect minima.

We found that the two-Local ansatz was generally more accurate than the UCC ansatz for this particular hamiltonian. This may be a coincidence since the difference in accuracy was not large.

We found that adding more circuit depth lead to a less accurate result because the noise from the quantum computer was magnified as they went through deeper circuits. The error increased from 0.074 Hartree to 0.104 Hartree when the circuit depth went from 2 to 3. On a less noisy quantum computer, the results of the depth 3 system may have been more accurate, as it would be able to search more of the Hilbert space.

## VII. CONCLUSION AND FUTURE OUTLOOK

In this lab, we reviewed recent methods for simulating quantum chemistry using quantum computers. We described how the hamiltonian of an arbitrary molecule could be second quantized. The Jordan Wigner mapping and Bravyi-Kitaev mapping were discussed and compared. We then discussed VQEs, their ansatz, and optimization routine. After applying these on a real quantum computer we found that the noise level was far too high to accurately simulate a Hydrogen molecule. However, the simulations without noise showed promise, and indicate that these problems may be solvable in the future exponentially faster than they are now. One method that may help us get more accurate results even with this level of noise is by using Zero-Noise Extrapolation[14].

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## VIII. APPENDIX

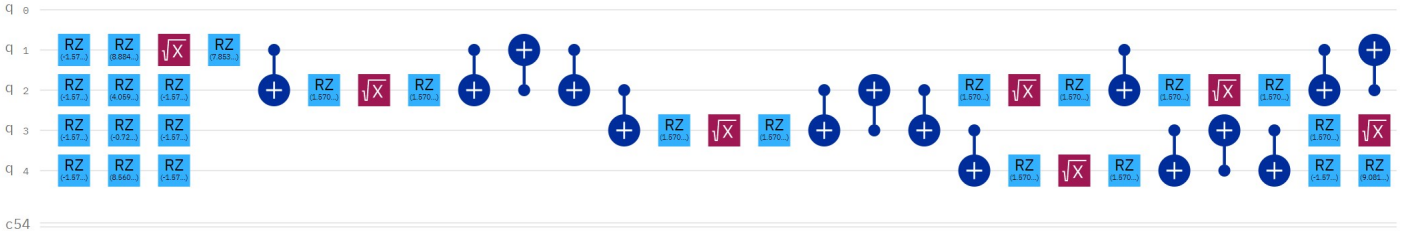


Figure 7. UCC Variational form circuit used in our computations

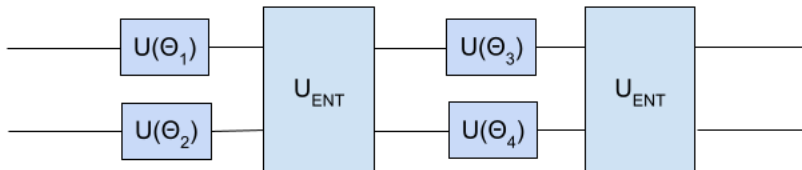


Figure 8. Two-Local Variational form circuit, when  $U_{ENT}$  is a linear CNOT entanglement.

GitHub code: [Link to my code is on GitHub](#)