VQE algorithm for different molecules

One of the important applications for classical computing is the quantum simulation of chemistry and materials such as properties of materials and molecules, finding molecules structures and predicting chemical reactions rates. To describe the properties of electrons in presence of nuclei (which are considered stationary), the electronic structure Hamiltonian should be solved.

Since physical dimension of quantum systems grows exponentially, finding eigenvalues of certain operators remains a fundamental challenge. To address the challenge, the advent of quantum computing which stems from the Feynman's postulate in the famous paper "Simulating Physics with Computers," published in 1982 (Feynman 1982), is promising.

According that, to simulate quantum systems, one would need to build quantum computers to perform quantum computations, and it is much more efficient than doing it classically for correlated systems. Indeed, one cannot simply scale the calculations on classical computers or apply massive parallelism. But there are serious limitation in computational capabilities of the currently available small quantum devices. A second important aspect is the inefficiency of existing quantum algorithms in terms of the resources that are needed to solve any useful problem on a quantum computer faster than on a classical computer, which is often discussed in terms of the quantum advantage.

Another attractive idea is to use quantum computing on quantum devices to improve quantum technology. The first algorithm that was proposed to solve the Schrödinger equation on a quantum computer was the quantum phase estimation (QPE) (Kitaev 1995; Abrams and Lloyd 1999; 1997). It is a fully quantum algorithm that can extract the phase or eigenvalues of a unitary operator. By using the phase kickback trick and inverse quantum Fourier transform (IQFT), (Shor 1994) QPE obtains the binary representation of the phase or eigenvalue. However, the problem with QPE, and IQFT in particular, is that it requires millions of qubits and gates even for relatively small systems, a requirement far beyond the capabilities of present NISQ hardware.

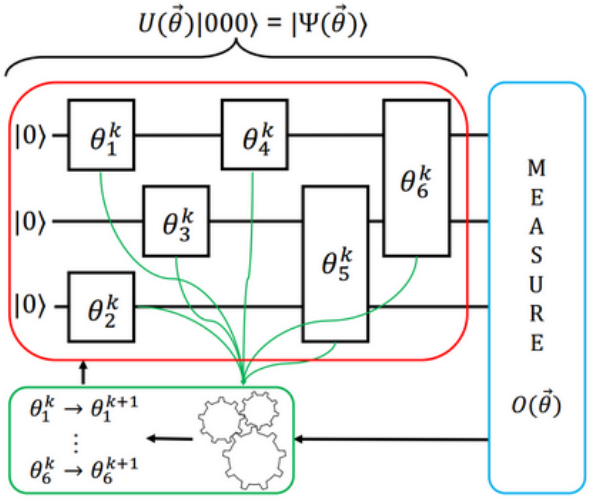
To address this problem, a variational hybrid quantum method VQE was proposed (Peruzzo et al. 2014; McClean et al. 2016; Romero et al. 2018). VQE is designed to utilize both quantum and classical resources to find variational solutions to eigenvalue problems.

Variational Quantum Eigenvector (VQE)

Variational quantum eigensolver is one of the very first examples of variational quantum algorithms. Where these kinds of algorithms are often called hybrid algorithms, as it is integrated of both quantum computers and classical computers.

Here in the VQE algorithm, we use quantum computers to operate on given variable parameters (computes the energy) and classical computers to perform the optimization of the results and then update the resultant values to the parameters and repeat until the find an optimal result.

VQE uses the quantum computer for a state preparation (red box) and measurement subroutine (blue box), and the classical computer to process the measurement results and update the parameters of the quantum computer by optimization algorithm (green box).



Using time independent Schrodinger equation help us to find the ground state energy of molecules:

$$\mathrm{H}|\vec{\psi}\rangle = \mathrm{E}|\vec{\psi}\rangle$$

The expectation values of this Hamiltonian are going to be eigenvalues. In this case, the ground state energy will be the smallest eigenvalue:

$$\langle\vec{\psi}|\mathrm{H}|\vec{\psi}\rangle \geq \mathrm{E}_0$$

We are going to approximate E_0 which is unknown by minimizing $\langle\psi|H|\vec{\psi}\rangle$. It can be done by parametrizing the wave function:

$$\text{Min}\ (\theta)\ \rightarrow\ \langle\vec{\psi}(\theta)|H|\vec{\psi}(\theta)\rangle$$

This is the main optimization that we have in the Variational Quantum Eigenvalues. However, we need some information, such as how to map the Hamiltonian and the wave function, before implementing this on real hardware. To address the problem we use second quantization formalism. Finally, we are able to map the state to qubit and apply our molecule Hamiltonian to get expectation value.

A simple use case of the VQE is to compute the interatomic distance of elements of a molecule. So, we can change the interatomic distance and use the VQE to compute the lowest energy at each distance. Then the distance that gives the lowest energy, yields the actual interatomic distance.

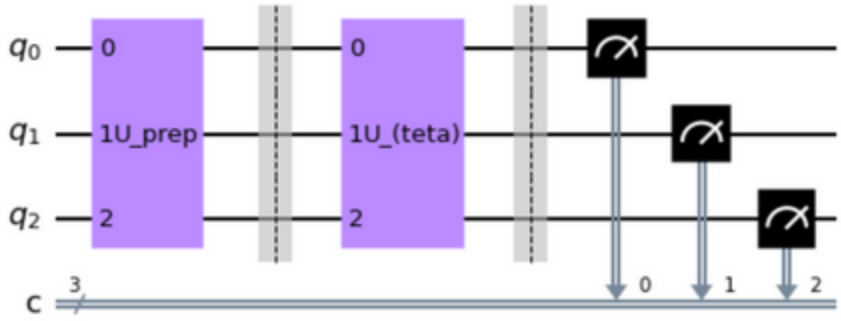
So, a variation of circuits consists of the following process.

- The first thing we want to do is prepare some initial state psi and as usual, this is often a ground state or a zero state or some fixed reference state.
- Then we execute parametrized unitary transformation which breaks down to a sequence of gates.
- So, the architecture of the circuit is fixed but the parameters fed to the gates are not fixed, and then to convert quantum information back to classical information we want to measure some particular observables.
- Then, we use the classical computers to optimize the results and then feedback the results into the variable parameters and compute with present values. Repeat the process until we find the optimal result.

VQE Circuit

The circuit in Quantum Computer consists of three parts.

1. The first step in preparation
2. The second step is Ansätze
3. The third step is the measurement



1.Preparation part

The qubit register is initialized in the zero state $|\bar{0}\rangle$. (in this circuit $|000\rangle$.)

$$\left|\psi_{ref}\right\rangle = U_{prep}|\bar{0}\rangle$$

U_{prep} is consists of a non-parameterized set of gates to generate mean-field or multi-reference state $\left|\psi_{ref}\right\rangle$. This state is in the first barrier.

2. Ansatze part

$$|\psi(\theta)\rangle = U(\theta)\left|\psi_{ref}\right\rangle$$

$U(\theta)$ contains a series of parametrized gates. $|\psi(\theta)\rangle$ states in second barrier. We call $|\psi(\theta)\rangle$ ansatz and $U(\theta)$ ansatz circuit, however, we can call both of them ansatz in brief. "Ansatz space" is The set of all possible states that can be created by the circuit $U(\theta)$.

3.Measurment part

Whenever we generate an ansatz, we should measure the Hamiltonian H. H is a linear combination of Pauli operators (I, X, Y and Z).

$$H = \sum_j h_j P_j = \sum_j h_j \prod_i \sigma_i^j$$

H is the Hamiltonian and σ_i^j is Pauli gates. Then we can measure the energy in this step $E(\theta_k)$ by this equation:

$$E(\theta_k) = \sum_{j}^{N} h_j \langle \psi(\theta_k) | \prod_i \sigma_i^j | \psi(\theta_k) \rangle$$

Ansatz

An Ansatz is initial guess of the structure or the architecture of the program, so therefore an efficient Ansatz can provide us optimum results. It can be fixed or varied depending on the program. It is a fundamental ingredient of the program.

In the context of variational circuits, an ansatz usually describes a subroutine consisting of a sequence of gates applied to specific wires. Similar to the architecture of a neural network, this only defines the base structure, while the types of gates and/or their free parameters can be optimized by the variational procedure.

Many variational circuit ansatzes have been proposed by the quantum computing community. The strength of an ansatz depends on the desired use-case, and it is not always clear what makes a good ansatz.

One can distinguish three different base structures, namely a layered gate ansatz, an alternating operator ansatz, and a tensor network ansatz.

Layered gate ansatz:

A layer is a sequence of gates that is repeated. The number of repetitions of a layer forms a hyperparameter of the variational circuit.

We can often decompose a layer further into two overall unitaries A and B. Block A contains single-wire gates applied to every subsystem or wire. Block B consists of both single-wire gates as well as entangling gates.

Layered gate ansatz can differ in three regards:

• Whether only A, only B, or both A and B are parametrized

• Which types of gates are used in A and B.

• Whether the gates in Block BB are arranged randomly, fixed, or determined by a hyperparameter

Such layered ansatz appears in both discrete and continuous-variable quantum computing models.

Alternating operator ansatz:

The alternating operator ansatz was first introduced by Farhi, Goldstone and Gutmann (2014) as the Quantum Approximate Optimization Algorithm (QAOA), and later used for machine learning (Verdon, Broughton, Biamonte (2017)) and other domain-specific applications (Fingerhuth et al. (2018)).

Again, we use layers of two blocks. The difference is that this time the unitaries representing these blocks are defined via Hamiltonians A and B which are evolved for a short time Δt.

The idea of this ansatz is based on analogies to adiabatic quantum computing, in which the system starts in the ground state of A and adiabatically evolves to the ground state of B. Quickly alternating (i.e., stroboscopic) applications of AA and BB for very short times Δt can be used as a heuristic to approximate this evolution.

Tensor network ansatz:

Amongst the architectures that do not consist of layers, but a single fixed structure, are gate sequences inspired by tensor networks (Huggins et al. (2018), Du et al. (2018)). The simplest one is a tree architecture that consecutively entangles subsets of qubits.

Another tensor network is based on matrix product states. The circuit unitaries can be decomposed in different ways, and their size corresponds to the "bond dimension" of the matrix product state — the higher the bond dimension, the more complex the circuit ansatz.

Few of the mostly used Ansatz are:

Hardware efficient ansatz

The parametrized quantum circuit of the hardware efficient ansatz consists of a sequence of single qubit rotation gates and "entangling" 2-qubit gates. One example of the circuits for the ansatz is shown in below Fig (the case of 4-qubit systems). Note that each single qubit rotation gate, $\left|\psi_{unitary-UCCSD}\right\rangle = U(\theta)\,|HF\rangle$, has an angle θ as a parameter. The number of repetitions of the single qubit rotations and 2-qubit gates (here we choose controlled Z gates) are called depth, denoted as D in

the figure. The structure of the circuit is easy to implement in real NISQ devices (especially ones composed of superconducting qubits) because the 2-qubit gates are applied only to adjacent qubits. More details are found in the reference below.

Hardware efficient ansatz consist of repeated, required parametrized gates which are easy to implement on the quantum hardware. Quantum computers which have short coherence times and constrained gate topologies use Hardware Efficient ansatz. They are having been used to generally find the ground state energies of small molecules. Few of drawbacks of the Hardware Efficient ansatz are, it is inefficient in our case as we sample too much Hilbert space unnecessarily because we are looking only for one state, resulting in complexity to optimize. It cannot be used for larger systems, as they do not consider values of chemical system being simulated.

Using Hardware Efficient Ansatz with random initial values makes the energy gradient essentially zero among most directions of Hilbert space, which makes classical optimisation extremely difficult. With a greater number of qubits, this effect becomes exponentially more prominent. Therefore, for problems in quantum computational chemistry, randomly initialised Hardware Efficient Ansatz are not used.

Unitary coupled cluster (UCC) ansatz

UCC ansatz is a cousin of the coupled-cluster method in quantum chemistry and often applied to calculation of a molecular system by quantum computers. The most common choice is the UCC singles and doubles ansatz (unitary CCSD), defined as:

$$U(\theta) = \exp\left(T(\theta) - T^{\dagger}(\theta)\right), T(\theta) = \sum_{ij} \theta_{ij} a_i^{\dagger} a_j + \frac{1}{2} \sum_{ijkl} \theta_{ijkl}\, a_i^{\dagger} a_j^{\dagger} a_k a_l$$

Where |HF⟩ is the Hartree-Fock state of the system. This ansatz often gives a good approximation of the ground state of a given molecular Hamiltonian because it nicely captures the essence of the electron correlations in the molecule.

Classical Optimisation

Classical optimization is one of the main processes of VQE, as we cannot optimize the Hamiltonian values without Classical optimization algorithms. Classical optimization algorithms are mainly divided into two parts:

1. Direct search method

2. Gradient based method

Direct search algorithms require more function evaluations but are considered more robust to noise than gradient based methods.

VQE iterations

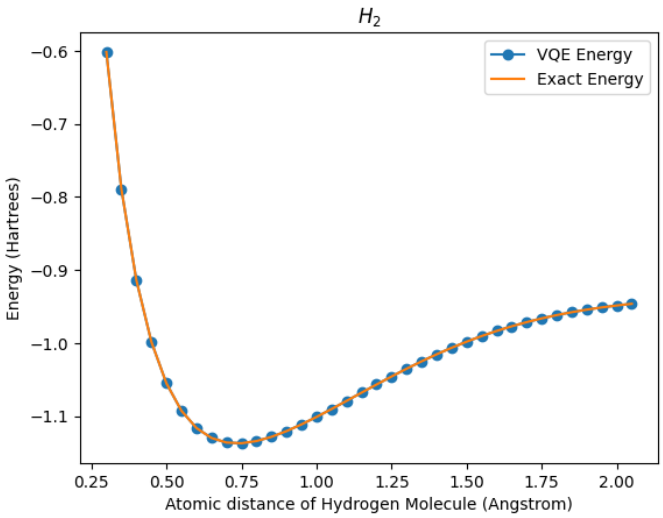
After getting the result from the circuit, we will use the classical computer to update parameters θ_{k+1}. So we can prepare a new ansatz $|\psi(\theta_{k+1})\rangle$. In every iteration, we will get lower energy. We will repeat the iteration until the result will converge to a minimum.

How to find the ground state of H_2

We exploring the Variational Quantum Eigensolver (VQE) algorithm for estimating the ground state energy for H_2 molecule. Where the two atoms are configured to be at a distance of 0.735 angstroms. The molecular input specification is processed by the PySCF driver. This driver produces an Electronic Structure Problem which gathers all the problem information required by Qiskit Nature. The second-quantized operators contained in that problem can be mapped to qubit operators with a Qubit Mapper.

For actually finding the ground state solution, the Variational Quantum Eigensolver (VQE) algorithm is used. Its main three components are the estimator primitive (Estimator), wavefunction ansatz (UCCSD), and optimizer (L_BFGS_B). The UCCSD component is the only one provided directly by Qiskit Nature and it is usually paired with the HartreeFock initial state and an all-zero initial point for the optimizer.

The entire problem is then solved using a Ground State Eigensolver which wraps both, the Parity Mapper and VQE. Since an Electronic Structure Problem is provided to it (which was the output of the PySCFDriver) it also returns an Electronic Structure Result.



Then we apply the VQE method to the bigger molecules such as $H_3, H_4, \mathrm{Li}-\mathrm{H}$ and $\mathrm{Be}-H_2$ and we find that the exact energy and VQE energy have the same values. It means that VQE is a reliable method to obtain eigenvalues of the system. It is interesting to note that if noiseless quantum computer is available in future, VQE algorithm will have exact result.