Variational Quantum Eigensolver

Quantum Chemistry on Quantum Computers

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Non-Relativistic Time Independent Schrodinger Equation

$$H|\Psi\rangle = \mathsf{E}\,|\Psi\rangle$$

Molecular Hamiltonian in **atomic units**

$$H = -\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I'} - \sum_{i,I} \frac{Z_I}{|r_i - R_I|} + \frac{1}{2}\sum_{i \neq j} \frac{1}{|r_i - r_j|} + \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

Kinetic Energy of electrons

Electron-Nucleus Attraction

Nucleus-Nucleus Repulsion

Kinetic Energy of Nuclei

Electron-Electron Repulsion

$M_I' = Mass\ of\ I^{th}\ Nucleus\ relative\ to\ mass\ of\ electron$

$\nabla^2 = Laplace\ Operator$

$r_i = Position\ vector\ of\ i^{th}\ electron$

$R_I = Position\ vector\ of\ I^{th}\ nucleus$

$Z_I = Atomic\ Number\ of\ I^{th}\ nucleus$

Born Oppenheimer Approximation

The Nuclei are much heavier than the electrons and they move more slowly

→

The electrons can be thought of as moving in a field of fixed nuclei

→

This approximation gives rise to electronic Hamiltonian describing the motion of electrons

Electronic Hamiltonian in atomic units

$$H_{el} = -\sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|r_i - R_I|} + \frac{1}{2}\sum_{i \neq j} \frac{1}{|r_i - r_j|}$$

Schrodinger Equation

$$H_{el}|\psi\rangle = E_{el}|\psi\rangle$$

- It cannot be solved exactly for a system of two or more electrons.
- Our aim is to find the best wavefunction that recovers maximum correlation.
- More sophisticated methods tend to require higher computational resourced.

Hartree Product Wavefunction and Slater Determinants

Independent particle Hamiltonian

$$\mathcal{H} = \sum_i h(i)$$

h(i) is an one electron Hamiltonian that contains electron-electron repulsion in some average way

Let $\{\chi_i\}$ forms the set of eigenfunctions of h(i)

$$h(i)\chi_j(x_1) = \epsilon_j \chi_j(x_1)$$

$$\psi^{HP}(x_1, x_2, x_3, .., x_N) = \chi_i(x_1)\chi_j(x_2)\chi_k(x_3) \dots \dots \chi_N(x_N)$$

But a simple product does not account for the antisymmetric behavior of fermionic wavefunction which requires

$$\psi(x_1, \dots . x_m x_n \dots .) = -\psi(x_1, \dots . x_n x_m \dots .).$$

TWO ELECTRON CASE	N ELECTRON CASE
$\phi(x_1, x_2) = \frac{1}{\sqrt{2}}[\chi_i(x_1)\chi_j(x_2) - \chi_i(x_2)\chi_j(x_1)]$	$\phi(x_1, x_2, .., x_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_N(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \chi_{N-1}(x_N) & \chi_N(x_N) \end{bmatrix}$

Hartree Fock Approximation

The ground state of an N electron system can be approximated by a single slater determinant

$$|\phi_o\rangle = |\chi_i \chi_j \chi_k \cdots\cdots \chi_N\rangle$$

A shorthand notation for slater determinant which includes the normalization factor and only represent the diagonal elements

$minimize\ \langle\phi_o|H|\phi_o\rangle$

- Our aim is to variationally find the best set of spin-orbitals which minimizes the expectation value of the true electronic Hamiltonian which leads to Hartree Fock Equation

$$f(i)\chi(x_i) = \varepsilon\chi(x_i)$$

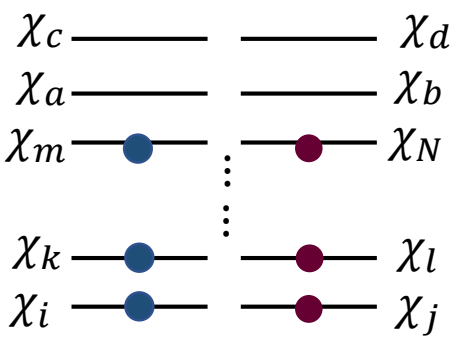
Fock Operator $$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_b (J_b - K_b)$$

$J_b = Coulomb\ Operator$
$K_b = Exchange\ Operator$

Excited Slater Determinants

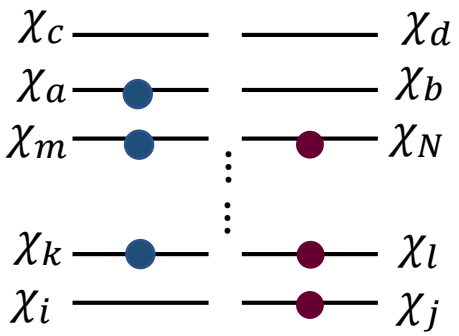
There can be infinite number of solutions of Hartree Fock Equation. In practice, we expand the spatial part of $\{\chi_i\}$ in terms of finite number of known basis functions.

Plugging of expanded spin orbitals $\{\chi_i\}$ in the Hartree Fock equation gives rise to matrix equations (Roothan Equantion) which are used to determine the combining coefficient.



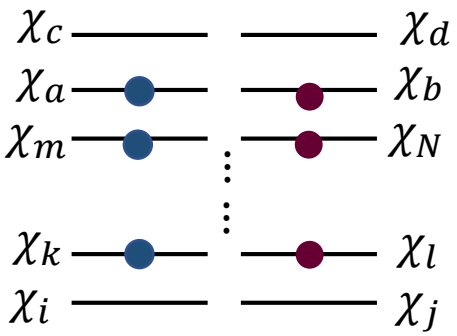
$|\chi_i\chi_j\chi_k \dots\dots \chi_N\rangle$

Hartree Fock Determinant ($|\phi_o\rangle$)



$|\chi_a\chi_j\chi_k \dots\dots \chi_N\rangle$

Singly Excited Determinant ($|\phi_i^a\rangle$)



$|\chi_a\chi_b\chi_k \dots\dots \chi_N\rangle$

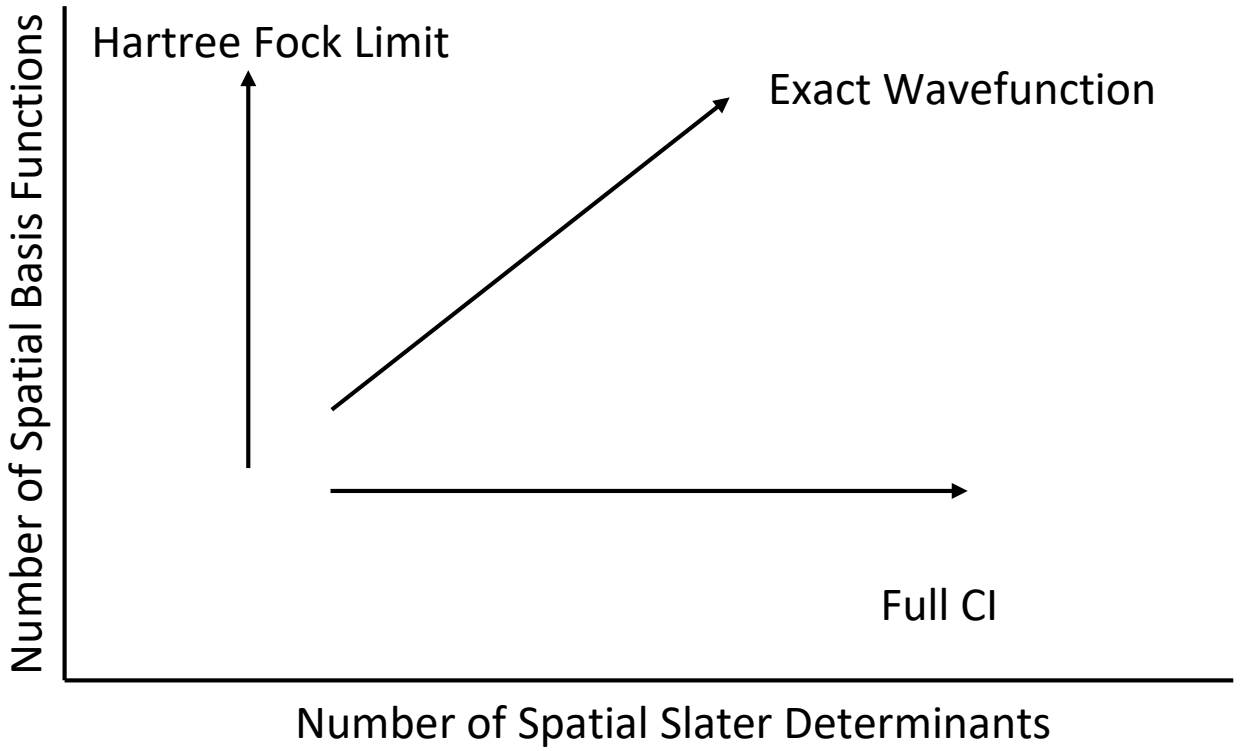
Doubly Excited Determinant ($|\phi_{ij}^{ab}\rangle$)

If there are k number of basis functions, we get 2k number of spin-orbitals. The total number of determinants possible with N number of electrons is $\binom{2k}{N}$

Expansion of exact wave function in slater determinant basis

$$|\psi\rangle = C_o|\phi_o\rangle + \sum_{i,a} C_i^a|\phi_i^a\rangle + \sum_{i,j,a,b} C_{ij}^{ab}|\phi_{ij}^{ab}\rangle + \sum_{i,j,k,a,b,c} C_{ijk}^{abc}|\phi_{ijk}^{abc}\rangle + \cdots$$

One can obtain the Hamiltonian matrix $H_{\mu\nu} = \langle\phi_\mu|H|\phi_\nu\rangle$; μ, ν representing an excitation label. The lowest eigenvalue after diagonalizing the matrix will give the exact energy in a given basis. This procedure is described as **Configuration Interaction(CI)**



The Second Quantized Formalism

An elegant alternate way of dealing with many body systems where the antisymmetric nature of many-body wavefunction and slater determinants is transferred to some operators

Creation Operator($\hat{a}^\dagger$)	Annihilation Operator($\hat{a}$)
$\hat{a}_p^\dagger \lvert\chi_q\chi_r\chi_s \dots\rangle = \lvert\chi_p\chi_q\chi_r\chi_s \dots\rangle$	$\hat{a}_p \lvert\chi_p\chi_q\chi_r\chi_s \dots\rangle = \lvert\chi_q\chi_r\chi_s \dots\rangle$
$\hat{a}_p^\dagger \lvert\chi_p\chi_q\chi_r\chi_s \dots\rangle = 0$	$\hat{a}_p \lvert\chi_q\chi_r\chi_s \dots\rangle = 0$

$\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = 0 \qquad \{\hat{a}_p, \hat{a}_q\} = 0 \qquad \{\hat{a}_p^\dagger, \hat{a}_q\} = \delta_{pq}$ ⟹

Anticommutation relation obeyed by the creation and annihilation operator

We can generate Excited State Slater Determinants by the action of string of creation-annihilation operators on the Hartree Fock State

$$\hat{a}_a^\dagger \hat{a}_i \lvert\phi_o\rangle = \hat{a}_a^\dagger \hat{a}_i \lvert\chi_i\chi_j\chi_k \dots\dots\chi_N\rangle = \lvert\chi_a\chi_j\chi_k \dots\dots\chi_N\rangle = \lvert\phi_i^a\rangle$$

$$\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \lvert\phi_o\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \lvert\chi_i\chi_j\chi_k \dots\dots\chi_N\rangle = \lvert\chi_a\chi_b\chi_k \dots\dots\chi_N\rangle = \lvert\phi_{ij}^{ab}\rangle$$

Operators such as the Hamiltonian can also be written in second quantized form

$$H = \sum_{pq} \langle p|h|q\rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

Exact wavefunction expansion and Quantum Computing

The expansion of exact wave wavefunction in the slater determinant basis can be written as:

$$|\psi\rangle = \left(1 + \hat{C}_1 + \hat{C}_2 + \cdots\right)|\phi_o\rangle$$

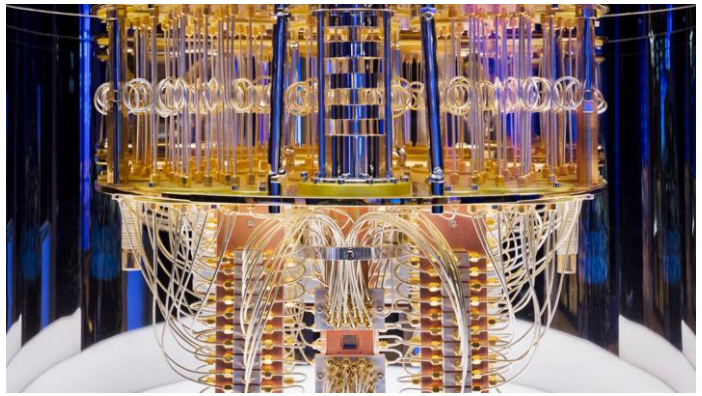
$$\hat{C}_1 = \sum_{i,a} C_i^a \hat{a}_a^\dagger \hat{a}_i \qquad \hat{C}_2 = \sum_{i,j,a,b} C_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$$

The exact wavefunction can be obtained by the action of an parameterized operator on a reference state

$$|\psi(\theta)\rangle = U(\theta)|\phi_o\rangle$$

The linear parameterization lacks size extensivity at truncated level. Hence, other ansatzes such as the Coupled Cluster ansatz are used.

The dimension of the Hilbert space formed by the many body basis increases exponentially with the increase in size of the molecule!!

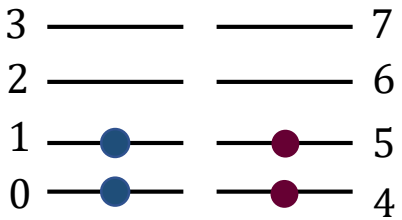


- Quantum Computers provide an excellent platform for storing and manipulating many body wavefunctions.
- Using only n qubits, we can generate a space of 2^n basis functions.
- The wavefunction can be expanded in this basis and properties can be calculated by measuring the expectation values with respect to desired operators.

Encoding Operators and Determinants in terms of Qubit states and Gates

To be able to simulate exact wavefunction, we must encode the slater determinants and second quantized operators in terms of qubit states and qubit gates.

The Slater Determinants can be expressed in ***Occupation Number basis***:



$$|f_7 f_6 \dots \dots \dots f_0\rangle \quad f_i \in \{0,1\}$$

0 is for unoccupied; 1 for occupied

Action of Creation and Annihilation operators:

- Creation/annihilation operator changes the occupation number to 1/0 if it was in 0/1 and otherwise.
- The pre-factor takes care of the anti-commutation relation.

$$\hat{a}_j^\dagger |f_{n-1} \dots f_{j+1} 0 f_{j-1} \dots f_0\rangle = (-1)^{\sum_s^{j-1} f_s} |f_{n-1} \dots f_{j+1} 1 f_{j-1} \dots f_0\rangle$$

$$\hat{a}_j^\dagger |f_{n-1} \dots f_{j+1} 1 f_{j-1} \dots f_0\rangle = 0$$

$$a_j |f_{n-1} \dots f_{j+1} 1 f_{j-1} \dots f_0\rangle = (-1)^{\sum_s^{j-1} f_s} |f_{n-1} \dots f_{j+1} 0 f_{j-1} \dots f_0\rangle$$

$$a_j |f_{n-1} \dots f_{j+1} 1 f_{j-1} \dots f_0\rangle = 0$$

Jordan Wigner Transformation

one to one relation

Qubit states $|0\rangle$ and $|1\rangle$ correspond to unoccupied and occupied state respectively

$$|f_{n-1}f_{n-2}\cdots\cdots\cdots f_0\rangle \longrightarrow |q_{n-1}\rangle \otimes |q_{n-2}\rangle \otimes \cdots \otimes |q_o\rangle \qquad f_j = q_j \in \{0,1\}$$

One qubit Creation and Annihilation

They can be constructed to have the required action on the qubit states

$$\hat{Q}^+|0\rangle = |1\rangle, \qquad \hat{Q}^+|1\rangle = 0, \qquad \hat{Q}^-|1\rangle = |0\rangle, \qquad \hat{Q}^-|0\rangle = 0.$$

$$\hat{Q}^+ = |1\rangle\langle 0| = \frac{1}{2}(\sigma^x - i\sigma^y), \qquad \hat{Q}^- = |0\rangle\langle 1| = \frac{1}{2}(\sigma^x + i\sigma^y).$$

Preserving the parity

The creation and annihilation operators must preserve proper parity which is a result of the anticommutation rules

$$a_j^\dagger \equiv \hat{Q}_j^+ \otimes Z_{j-1}^{\rightarrow}$$

$$a_j \equiv \hat{Q}_j^- \otimes Z_{j-1}^{\rightarrow}$$

Jordan Wigner Transformation is the most commonly used method. The occupation information is saved locally by the parity is saved globally

Parity Basis

Counting Parity

The j[th] qubit contains information of the parity of all occupied orbitals up to j

$$|f_{n-1}f_{n-2}\cdots\cdots\cdots f_0\rangle \longrightarrow |p_{n-1}\rangle \otimes |p_{n-2}\rangle \otimes \cdots \otimes |p_o\rangle \quad p_j = \sum_{s=0}^{j} f_s \ (mod\ 2)$$

$$|0101\rangle \rightarrow |0011\rangle$$

We don't have to apply Z gates to all qubit's with lower index. A single Z gate at (j-1)[th] qubit gives the parity of the new state after application of the creation/annihilation operator at j[th] qubit

- Unlike Jordan-Wigner, we cannot directly apply $Q^{\pm}$ to represent creation/annihilation. Application of Q^{+} or Q^{-} will depend on (J-1)[th] qubit state.
- If **(j – 1)[th]** qubit ⇒ $|0\rangle$, then qubit **j** will correspond to the occupation of orbital j; using $a_j^{\dagger}$ will require acting Q^{+} on j[th] qubit.
- If **(j – 1)[th]** qubit ⇒ $|1\rangle$, then qubit **j** will have opposite to that of its occupation, and we will need to act Q^{-} on qubit j to simulate $a_j^{\dagger}$ (and vice versa for the annihilation operator).

Action of Creation and Annihilation operators in Parity Basis

$$\hat{\mathcal{P}}_j^{\pm} \equiv \hat{Q}_j^{\pm} \otimes |0\rangle\langle 0|_{j-1} - \hat{Q}_j^{\mp} \otimes |1\rangle\langle 1|_{j-1}$$

$$a_j^{\dagger} \equiv X_{j+1}^{\leftarrow} \otimes \hat{\mathcal{P}}_j^{+} \qquad a_j \equiv X_{j+1}^{\leftarrow} \otimes \hat{\mathcal{P}}_j^{-}$$

Variational Quantum Eigen solver

- The variational quantum eigen solver is a variational algorithm that intends to find the optimum parameters that parameterize the wavefunction.
- The trial wavefunction is obtained by the action of a parameterized ansatz on a reference function which is usually taken to be the Hartree-Fock State.
- The expectation value with respect to the Hamiltonian is minimized using any of the available numerical optimization techniques.

Reference often taken to be Hartree Fock Determinant

$$|\Psi(\theta)\rangle = \hat{U}(\theta)|\phi_o\rangle$$

Parameterized Trial Wavefunction

Unitary Ansatz

We have to find the optimum set of parameters for which the trial wave function is very close to the actual wavefunction

Variational optimization of Hamiltonian Expectation Value

$$\min_{\theta}\langle \boldsymbol{\phi_o}|\hat{\boldsymbol{U}}^{\dagger}(\boldsymbol{\theta})\hat{\boldsymbol{H}}\hat{\boldsymbol{U}}(\boldsymbol{\theta})|\boldsymbol{\phi_o}\rangle$$

- The circuit to determine the required expectation value is constructed using a Quantum Computer.
- A classical optimizer is employed to optimize the output expectation value with respect to the parameters
- The numerical variational optimization scheme absorbs some of the noise giving accurate results in the currently available Noisy Intermediate Scale Quantum(NISQ) Devices.

VQE Illustration

(1a) Hamiltonian representation *(e.g. second quantized Hamiltonian)*

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$

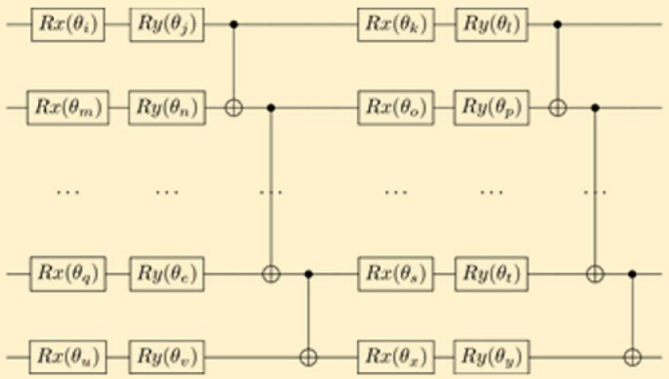
(1b) Encoding of fermionic operators to Pauli operators

$$\hat{H} = \sum_a w_a \hat{P}_a$$

(1d) Initialization *(e.g. Hartree Fock)*

$$|\psi\rangle_{HF} = \begin{matrix} |1\rangle \\ |1\rangle \\ \cdots \\ |0\rangle \\ |0\rangle \end{matrix}$$

(2a) Ansatz and state preparation *(e.g. Hardware efficient)*



(2b) Rotation to measurement basis

$$\hat{P}_a = U_a^\dagger (Z^{\otimes N}) U_a$$
$$\hat{P}_b = U_b^\dagger (Z^{\otimes N}) U_b$$
$$\hat{P}_c = U_c^\dagger (Z^{\otimes N}) U_c$$
$$\cdots$$

(2c) Measurement of Pauli strings

$$\langle \psi(\boldsymbol{\theta}) | U_a^\dagger (Z^{\otimes N}) U_a | \psi(\boldsymbol{\theta}) \rangle$$
$$\langle \psi(\boldsymbol{\theta}) | U_b^\dagger (Z^{\otimes N}) U_b | \psi(\boldsymbol{\theta}) \rangle$$
$$\langle \psi(\boldsymbol{\theta}) | U_c^\dagger (Z^{\otimes N}) U_c | \psi(\boldsymbol{\theta}) \rangle$$
$$\cdots$$

(2d) Observables computation (e.g. expectation value, gradient etc.)

$$\langle \hat{H}(\boldsymbol{\theta}) \rangle = \sum_a w_a \langle \psi(\boldsymbol{\theta}) | \hat{P}_a | \psi(\boldsymbol{\theta}) \rangle$$

$$\frac{\partial \langle \hat{H}(\boldsymbol{\theta}) \rangle}{\partial \theta_j} = \langle \hat{H}(\boldsymbol{\theta}_{\neq j}, \theta_j + \frac{\pi}{2}) \rangle - \langle \hat{H}(\boldsymbol{\theta}_{\neq j}, \theta_j - \frac{\pi}{2}) \rangle$$

(3) Parameters update *(e.g. gradient descent)*

$$\theta_j' = \theta_j - \alpha \frac{\partial \langle \hat{H}(\boldsymbol{\theta}) \rangle}{\theta_j}$$

Quantum computing subroutines

Traditional computing subroutines

Pros and Cons of VQE

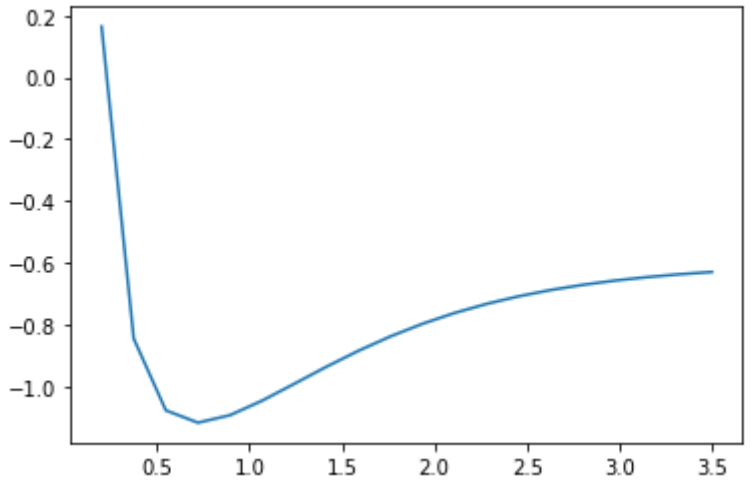
ADVANTAGES

- VQE requires shallower circuit depths than those required by other algorithms such as Quantum Phase Estimation and hence is very suitable for NISQ devices with limited coherence time.
- Being variational, it is resilient to noise which plague currently available quantum devices.
- It provides a large flexibility in terms of availability of various ansatzes and optimizers.
- Various adaptive approaches towards ansatz construction can create even shallower circuit depths required for VQE measurements.

DISADVANTAGES

- The true cost of VQE is related to the complexity of the optimization technique employed. In general, the VQE optimization landscape is difficult and the optimization consumes a large number of measurement evaluations.
- The optimization trajectory could get stuck in barren plateaus having vanishing gradient.
- In a noisy simulation, the iterative convergence is slow.

1. Calculate the SCF Energy for H_2 for H-H bond length in the range [0.2-3.5] (take 10 grid points points) and plot the energy vs bond-length curve



2. Consider the Hartree-Fock state of H_4 in occupation number basis(8 qubit, 4 electrons system in sto-3g basis). Write it in terms of qubit state using Jordan-Wigner and Parity encoding. Measure the state and verify.

3. Construct the superposition state $\frac{1}{\sqrt{2}}\left(|0101\rangle + |1010\rangle \right)$ Using Jordan Wigner mapping.

4. Print the Hamiltonian in Jordan Wigner and Parity encoding