

Variational Algorithms for Ground State Calculations of Simple Molecules

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Outline

- Electronic Structure of Molecules
- Variational Principle
- Variational Monte Carlo
- Quantum Computing Approach
- Variational Quantum Algorithm

How to calculate electronic structure

Molecular Orbital

To calculate the hydrogen molecule (H_2) orbital, we employ the **LCAO (Linear Combination of Atomic Orbitals)** approximation.

We define the molecular wavefunction $|\psi_{H_2}\rangle$ as:

$$|\psi_{H_2}\rangle = c_1 |H_{1s}^{(1)}\rangle + c_2 |H_{1s}^{(2)}\rangle$$

$$|\psi\rangle = c_1 |\phi_1\rangle + c_2 |\phi_2\rangle$$



How to Calculate Electronic Structure

Solve Time-Independent Schrödinger Equation (TISE)

We substitute our LCAO ansatz into the time-independent Schrödinger Equation:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

We project the equation onto the basis state:

$$\langle \phi_i | \hat{H} | \Psi \rangle = E \langle \phi_i | \Psi \rangle \quad (1)$$

This step transforms the operator equation into a system of linear equations:

$$c_1 \langle \phi_1 | \hat{H} | \phi_1 \rangle + c_2 \langle \phi_1 | \hat{H} | \phi_2 \rangle = E (c_1 \langle \phi_1 | \phi_1 \rangle + c_2 \langle \phi_1 | \phi_2 \rangle) \quad (2)$$

$$c_1 \langle \phi_2 | \hat{H} | \phi_1 \rangle + c_2 \langle \phi_2 | \hat{H} | \phi_2 \rangle = E (c_1 \langle \phi_2 | \phi_1 \rangle + c_2 \langle \phi_2 | \phi_2 \rangle) \quad (3)$$

Characteristic Equation

Matrix Representation

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$$\begin{bmatrix} \varepsilon & t \\ t & \varepsilon \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

- ▶ $H_{ii} = \langle \phi_i | \hat{H} | \phi_i \rangle = \varepsilon$: **On-site Energy of an isolated atom**
- ▶ $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = t$: **Hopping Energy** (Resonance Integral)
- ▶ $S_{ij} = \langle \phi_i | \phi_j \rangle$: **Overlap Integral**, Assumed orthogonality for simplification
($S_{i,j} \approx 0, S_{i,i} \approx 1$)

Characteristic Equation

For the system of linear equations to have a non-trivial solution (where coefficients $c_1, c_2 \neq 0$), the determinant of the coefficient matrix must vanish:

$$\det(\mathbf{H} - E\mathbf{S}) = 0$$

Substituting our Tight-Binding parameters (ε and t) and assuming orthogonality ($S \approx I$):

$$\begin{vmatrix} \varepsilon - E & t \\ t & \varepsilon - E \end{vmatrix} = 0$$

This yields two possible Energy Eigenvalues:

$$E = \varepsilon \pm t$$

Molecular Energy Levels

Eigenvalue Solutions ($t < 0$)

Anti-Bonding State (E_-)

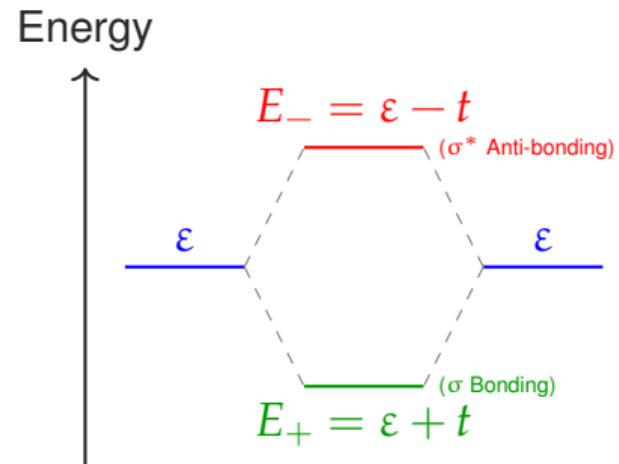
$$E_- = \varepsilon - t \approx -11.6\text{eV}$$

This state has a higher energy (**unstable**)

Bonding State(E_+)

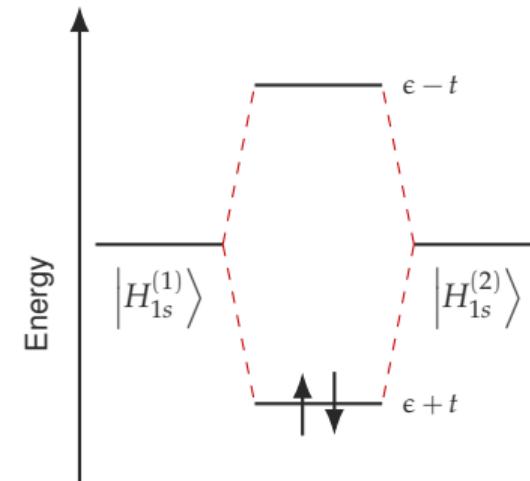
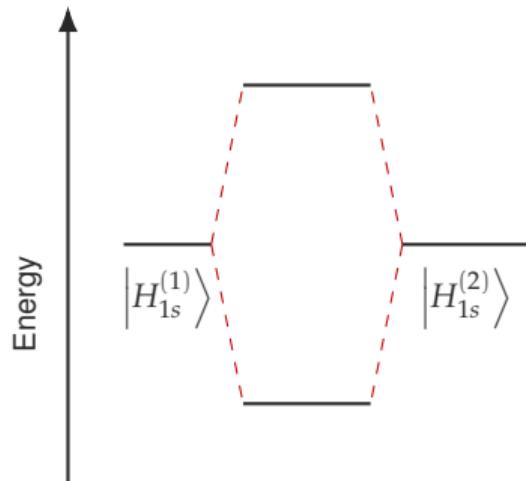
$$E_+ = \varepsilon + t \approx -15.6\text{eV}$$

This state has a lower energy (**stable**)



Electronic structure of hydrogen molecule

Molecular Orbital Diagram (H_2)



Total Ground State Energy : $2 \times E_+ = -31,2eV \approx -1,14 \text{ Ha}$

Computational Cost

The Matrix Representation for Problem Size

First, we calculate the number of possible electron configurations.

$$\hat{H} = \underbrace{\begin{pmatrix} H_{1,1} & H_{1,2} & \cdots & H_{1,D} \\ H_{2,1} & H_{2,2} & \cdots & H_{2,D} \\ \vdots & \vdots & \ddots & \vdots \\ H_{D,1} & H_{D,2} & \cdots & H_{D,D} \end{pmatrix}}_{\text{Dimension } D}$$

This $D \times D$ matrix captures the interactions between every possible way N electrons can occupy M spin-orbitals

Computational Cost

Hilbert Space Dimension (D)

Using **Stirling's Approximation** ($\ln n! \approx n \ln n - n$) and assumption $M = 2N$ for best case, we can derive the dimension of Hilbert Space (D):

$$D = \binom{M}{N} \approx \binom{2N}{N}$$
$$D \approx 4^N \quad (\text{Exponential Growth})$$

Since matrix diagonalization costs $O(D^3)$:

$$O(4^N)^3 = O(e^{4.158N}) = O(e^N)$$

Time Complexity for Molecule

Hydrogen (H_2)

Electrons (N) :	2
Spin Orbital (M) :	4
Hilbert Dim (D) :	${}_4C_2 = 6$
Complexity :	$O(D^3) = O(6^3)$

Total Ops : **216** operations

Caffein ($C_8H_{10}N_4O_2$)

Electrons (N) :	102
Spin Orbital (M) :	160
Hilbert Dim (D) :	${}_{160}C_{102} \approx 10^{46}$
Complexity :	$O(D^3) = O((10^{46})^3)$

Total Ops : **10^{138}** operations

FYI :

Fastest CPU (i9-14900KF): 9×10^9 ops/sec

Age of the Universe: 4×10^{17} seconds

Age of the Universe



13.8 Billion Years
($\sim 10^{17}$ Seconds)

Time to Calculate Caffeine with FCI



Some things are worth waiting for. This is not one of them.

Variational Principle Foundation

The Problem

Exact Diagonalization is too slow!

Time required: $\approx 10^{131}$ seconds.

Impossible.

The Strategy

Don't solve directly.

Propose a **Trial Wavefunction**

$|\Psi_T(\vec{\theta})\rangle$ with tunable parameters $\vec{\theta}$.

The Variational Theorem

"The expectation value is always larger than the true ground state."

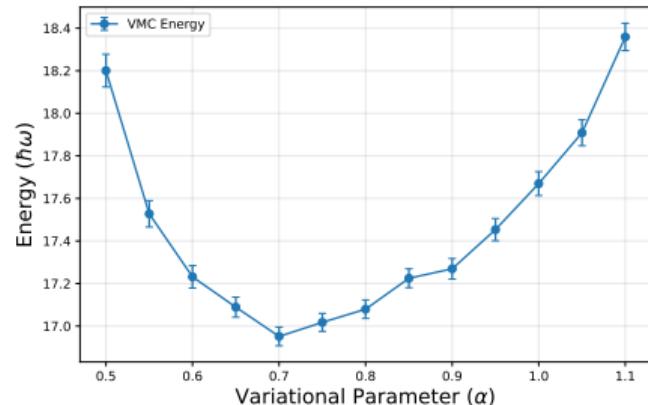
$$E(\theta) = \frac{\langle \Psi_T(\theta) | \hat{H} | \Psi_T(\theta) \rangle}{\langle \Psi_T(\theta) | \Psi_T(\theta) \rangle} \geq E_0$$

Visualizing Optimization

Optimization Process

The ground state energy using Variational Monte Carlo (VMC) method

- ▶ **Parameter Sweep (α)**
- ▶ **Energy Minimization**
Showing a clear convex shape
- ▶ **Optimal Solution** $\alpha \approx 0.7$



Paradigm Shift

Exact Calculation (Intractable) → Variational Optimization (Scalable)
 High-Cost Diagonalization → Low-Cost Ansatz Optimization

Conventional VMC Workflow

[Reference: A. Gezerlis (2023), Numerical Methods in Physics]

Instead of solving exact diagonalizations, we “guess” the solution shape based on physical intuition

Ansatz (trial wavefunction): e.g. Gaussian

$$\Psi_T(x, \alpha) \sim e^{\alpha x^2}$$

α (Alpha): The tunable parameter that controls the width of the curve

Find the specific value of α that minimizes the Total Energy? The example in the following algorithm is first given for interacting harmonic oscillators

Algorithm: Initialize

Algorithm 1 Initialize System

```
1: Input: Hamiltonian  $\hat{H}$  (Kinetic + Potential)
2: Input: Trial Wavefunction  $\Psi_T(\mathbf{R}; \alpha)$ 
3:                                         ▷ Define the analytic shape (e.g., Gaussian)

4: function SETUP
5:     Set number of particles  $N$ , dimension  $D$ 
6:      $\mathbf{R} \leftarrow \text{RandomUniform}(-1, 1)$                                ▷ Random initial positions
7:      $\alpha \leftarrow \alpha_{\text{guess}}$                                          ▷ Initial variational parameter
8:     return  $\mathbf{R}, \alpha$ 
9: end function
```

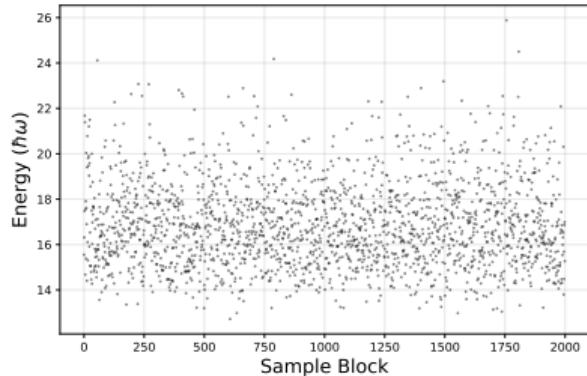
Algorithm: Run MC Sampling

Algorithm 2 Run Metropolis Sampling

```

1: function GETENERGY( $\alpha$ )
2:   Init:  $E_{sum} \leftarrow 0$ ;  $\mathbf{R} \leftarrow \text{RandomPos}$ 
3:   for  $k = 1$  to  $N_{steps}$  do
4:      $\mathbf{R}_{new} \leftarrow \mathbf{R} + \Delta$ ;  $w \leftarrow |\Psi(\mathbf{R}_{new})/\Psi(\mathbf{R})|^2$ 
5:     if  $\text{rand}(0, 1) < w$  then
6:        $\mathbf{R} \leftarrow \mathbf{R}_{new}$ 
7:     end if
8:      $E_{loc} \leftarrow \hat{H}\Psi(\mathbf{R})/\Psi(\mathbf{R})$ 
9:      $E_{sum} \leftarrow E_{sum} + E_{loc}$ 
10:   end for
11:   return  $E_{sum}/N_{steps}$ 
12: end function

```



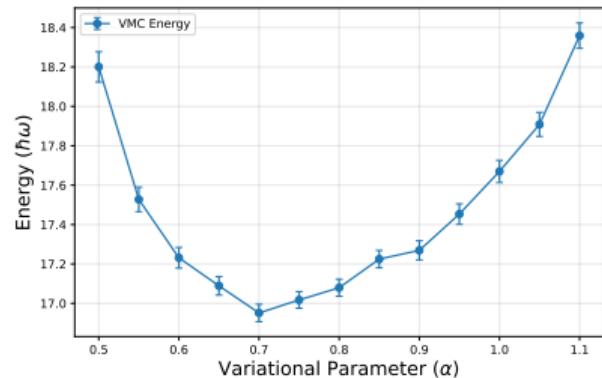
Local Energy Sampling at $\alpha : 0.7156$

Algorithm: Optimization

Algorithm 3 Variational Optimization

```

1:  $\alpha \leftarrow \text{InitialGuess}$ 
2:  $\eta \leftarrow 0.1$                                 ▷ Learning Rate
3: while not converged do
4:    $E_{avg} \leftarrow \text{GETENERGY}(\alpha)$ 
5:    $grad \leftarrow \text{CalculateGradient}(E_{avg}, \alpha)$ 
6:    $\alpha \leftarrow \alpha - \eta \cdot grad$       ▷ Update Parameter
7:   Print "Energy: ",  $E_{avg}$ 
8: end while
9: return  $\alpha_{opt}, E_{min}$ 
  
```

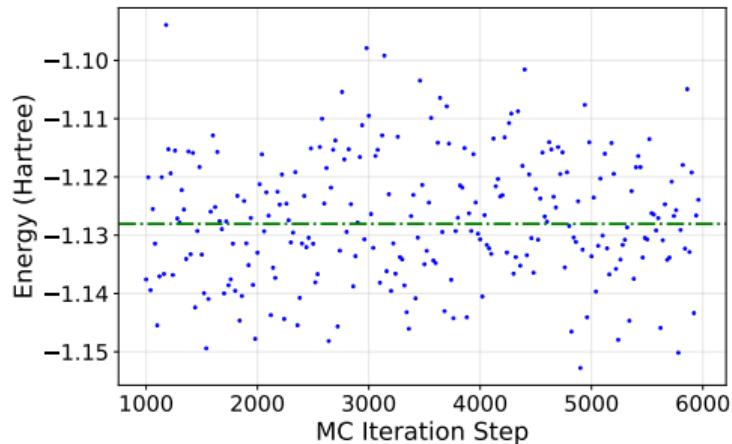


Energy Optimization

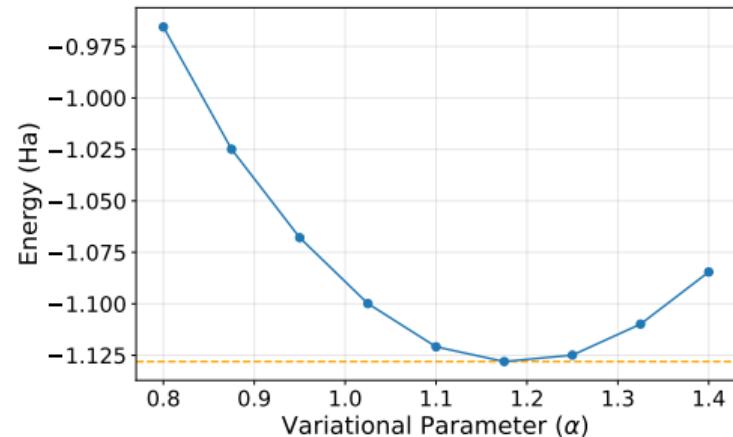
VMC in Hydrogen Molecule

- 1 **Trial Wavefunction ($|\Psi_T\rangle$)** : $\Psi_T = \Phi_{MO}(\mathbf{r}) \times e^{J(\mathbf{r})}$
Combines LCAO orbitals with Jastrow correlation.
- 2 **Run Metropolis Sampling** : Accept if $|\Psi_{new}|^2 > \text{rand}[0,1]$
Randomly move electrons to calculate Local Energy (E_L).
- 3 **Optimization** : $\alpha_{new} \leftarrow \alpha_{old} - \eta \frac{\partial \langle E \rangle}{\partial \alpha}$
Minimize average energy using Gradient Descent.

Graph Result



MC sampling at $\alpha = 1.175$



Optimizing the variational parameter

Computational Cost

- 1 **Wavefunction (Ψ_T):** Single update costs
- 2 **Sampling Loop:** Updates all N electrons per sweep

$$N \times O(N^2) = \mathbf{O}(N^3)$$

- 3 **Optimization:** Multiplies cost by steps (K) and samples (M).

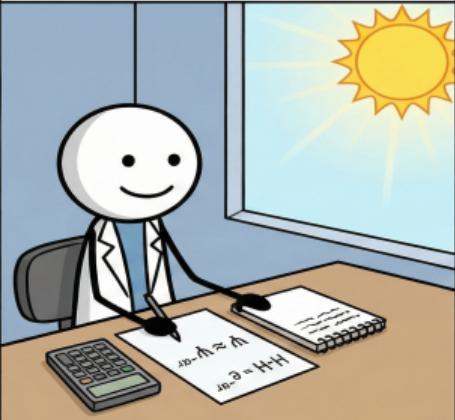
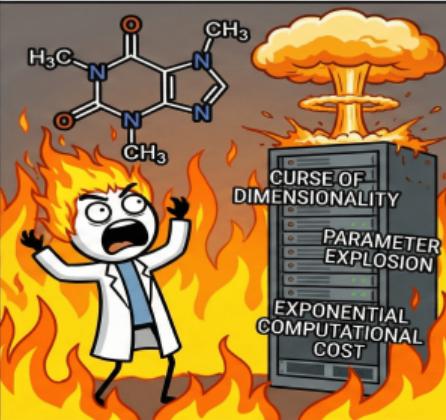
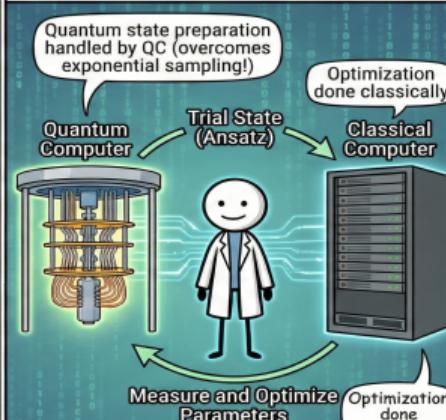
Final Time Complexity

$$T_{VMC} \propto K \times M \times O(N^3)$$

Why Quantum?

The Limit of Classical VMC

When "Good Enough" is not Enough

Calculating Hydrogen (H_2) Ground State	Calculating Caffeine ($C_8H_{10}N_4O_2$) Ground State with VMC	Enter VQE (Variational Quantum Eigensolver) - The Hybrid Solution
 <p>A cartoon scientist in a lab coat sits at a desk with a calculator and a piece of paper showing the equation $V \approx V_{\text{eff}}$. A sun is visible through the window.</p> <p>Simple variational method. Done before my coffee cools down. Piece of cake.</p>	 <p>A cartoon scientist in a lab coat stands in front of a computer monitor displaying a large molecular structure of caffeine. The scientist is surrounded by fire and flames. The monitor shows the text "CURSE OF DIMENSIONALITY", "PARAMETER EXPLOSION", and "EXPONENTIAL COMPUTATIONAL COST".</p> <p>Sampling complexity explodes exponentially with electrons. My supercomputer just melted into slag.</p>	 <p>A diagram illustrating the VQE hybrid solution. It shows a Quantum Computer (represented by a coil) connected to a Classical Computer (represented by a server tower). A scientist stands between them. The process involves:</p> <ul style="list-style-type: none"> Quantum state preparation handled by QC (overcomes exponential sampling!) Trial State (Ansatz) Measure and Optimize Parameters (Minimize Energy) Optimization done classically Optimization done classically <p>Hybrid approach: Best of both worlds.</p>

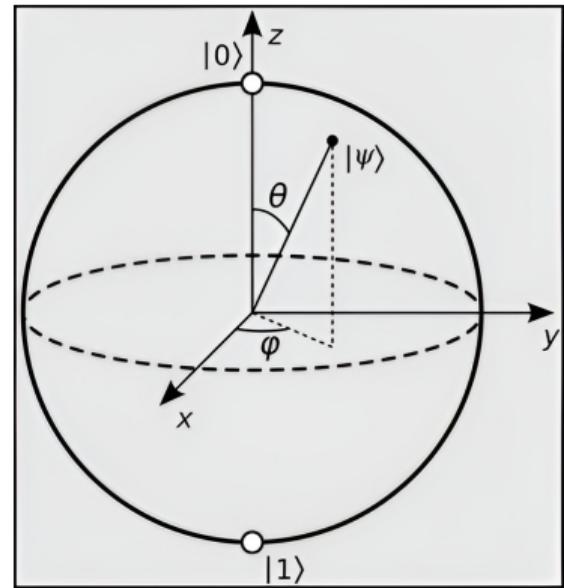
The Qubit & Superposition

Classical Bit vs Quantum Bit:

- ▶ Classical: State is either 0 OR 1.
- ▶ Quantum: State can be a linear combination:

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

where $|\alpha|^2 + |\beta|^2 = 1$.



Qubit Representation in Bloch Sphere

Observables & Pauli Operators

The Language of Qubits: To calculate energy, we must translate the Molecular Hamiltonian (\hat{H}) into Qubit Operators.

The Pauli Matrices (The Alphabet):

$$X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Hamiltonian Mapping

The Hamiltonian becomes a weighted sum of Pauli strings:

$$\hat{H}_{mol} \longrightarrow \sum_i c_i (P_i \otimes P_j \otimes \dots)$$

Measurement & Expectation Value

- **Expectation Value ($\langle H \rangle$):** The average outcome of many measurements.

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

The Process (Shots)

- 1 Prepare the state $|\psi(\theta)\rangle$.
- 2 Measure the qubits (Collapse to 0 or 1).
- 3 Repeat N times (e.g., 1024 shots).
- 4 Calculate the statistical average.

The Mapping Flow

Stage A: First Quantization

Process: Calculate electronic integrals (h_{pq}, h_{pqrs}) on CPU.

Stage B: Second Quantization (Fermions)

Model: Hamiltonian with operators a^\dagger (create) & a (annihilate). $\hat{H} = \sum h_{pq}a_p^\dagger a_q + \dots$

Stage C: Jordan-Wigner Transform (The Bridge)

Mapping: Translate Fermions to Qubits ($a^\dagger \rightarrow X, Y, Z$). **Mechanism:** Uses Parity Strings to mimic anti-symmetry.

Output: Qubit Hamiltonian

Target: Weighted sum of Pauli Strings to be measured. $\hat{H}_{qubit} = \sum c_i(P_0 \otimes P_1 \dots)$

Component of VQE

- ▶ **The Objective (Hamiltonian)**

The Qubit Hamiltonian derived from the mapping, represented as a sum of Pauli Strings:

- ▶ **The Ansatz (Quantum Circuit)**

A parameterized circuit $U(\vec{\theta})$ that prepares the trial wavefunction. It utilizes *Superposition* (Rotations) and *Entanglement* (CNOTs).

- ▶ **The Estimator (QPU)**

Measures the expectation value via statistical sampling (shots):

- ▶ **The Optimizer (Classical CPU)**

Updates the parameters $\vec{\theta}$ using classical methods (e.g., Gradient Descent, SPSA) to minimize $\langle E \rangle$.

Variational Quantum Eigensolver

VQE is a **hybrid algorithm (Quantum + Classical)** designed to find the ground state energy (E_0) of a molecule using **Variational Principle**

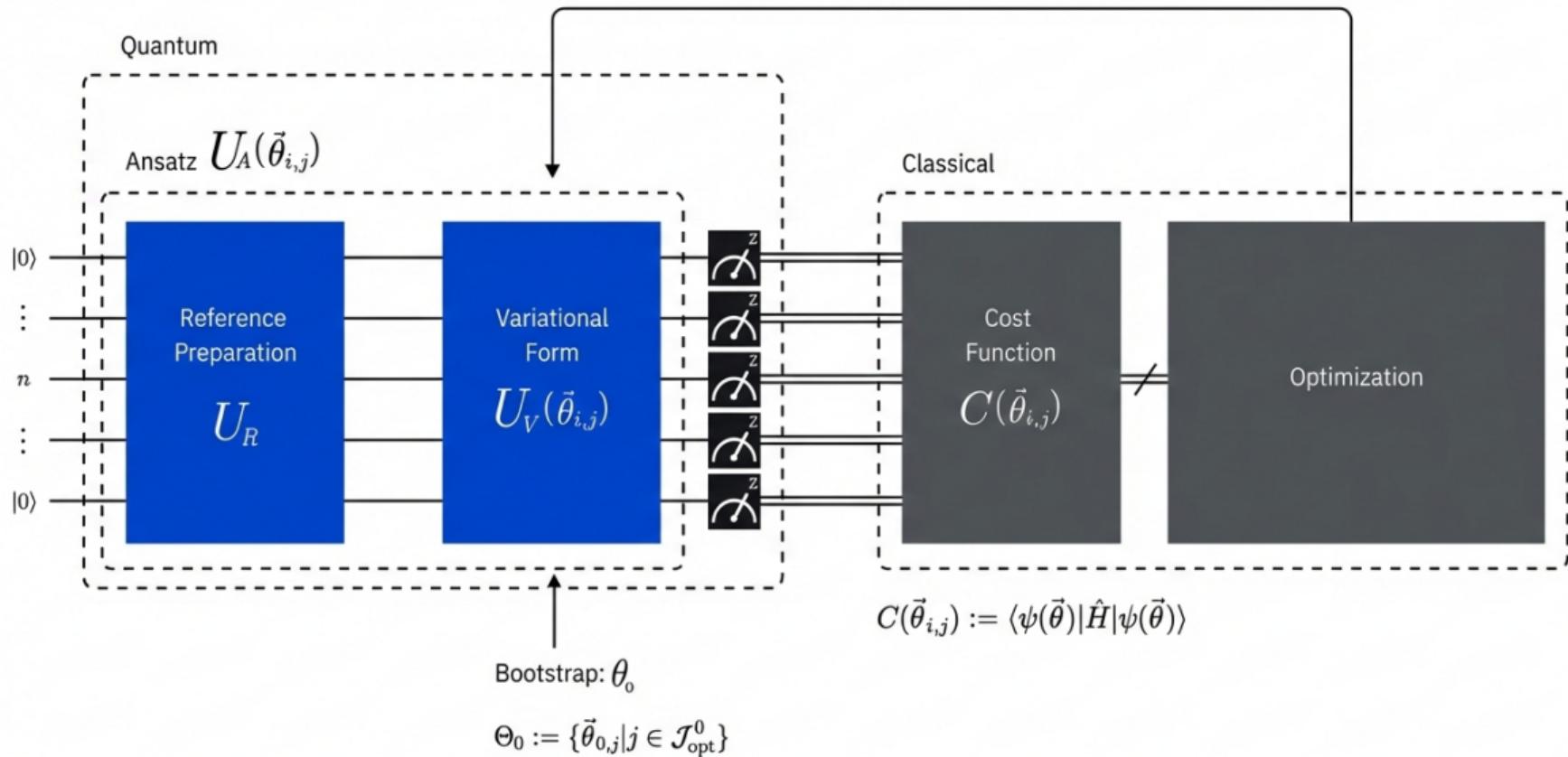
Input

Hamiltonian (\hat{H}_{qubit}): Decomposed into Pauli Strings $\sum c_i P_i$. **Parameters** ($\vec{\theta}$): Rotation angles controlling the Ansatz.

Loop

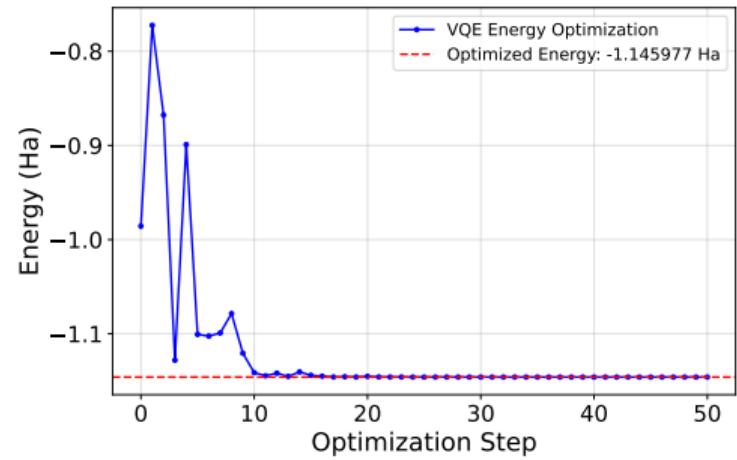
QPU (Measure): Run circuit $U(\vec{\theta})$ and sample expectation values. **CPU (Optimize):** Aggregate Energy (E_{tot}) and update $\vec{\theta}$ to minimize cost. **Repeat:** Iterate until convergence to Ground State.

Adjust parameters with results, and re-run Θ_{i+1}



Results

This Graph shows the trajectory of energy optimization based on iteration steps



Optimization Graph Trajectory to Ground State

Clash of Algorithms: VMC vs. VQE

Feature	Classical VMC (The Specialist)	Quantum VQE (The Generalist)
Ansatz Approach	Heuristic Guessing (Based on Physical Intuition)	Scalable Approximation (Systematic Circuit Expansion)
Computational Cost	$O(N^3)$ (Polynomial)	$O(N)$ (Hamiltonian Terms)*
Bottleneck	Sampling Loop (Moving Electrons via CPU)	Measurement Loop (Shot Noise via QPU)
Limit	Fixed-Node Approximation	Hardware Noise (NISQ)

*Note: VQE scaling can be improved with advanced measurement grouping techniques.