

Variational quantum (and classical) algorithms for Hamiltonian Simulation

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Tonight's Menu

- Hamiltonian Simulation
- Variational Principle
- Variational Monte Carlo
- Quantum Computing Approach
- Variational Quantum Algorithm

Hamiltonian simulation: electronic structure

Molecular Orbital

Direct example: 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 (Transfer 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:

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

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

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

This yields two possible Energy Eigenvalues:

$$E = \epsilon \pm t$$

Molecular Energy Levels

Eigenvalue Solutions

Note that $t < 0$ is assumed)

Anti-Bonding State (E_-)

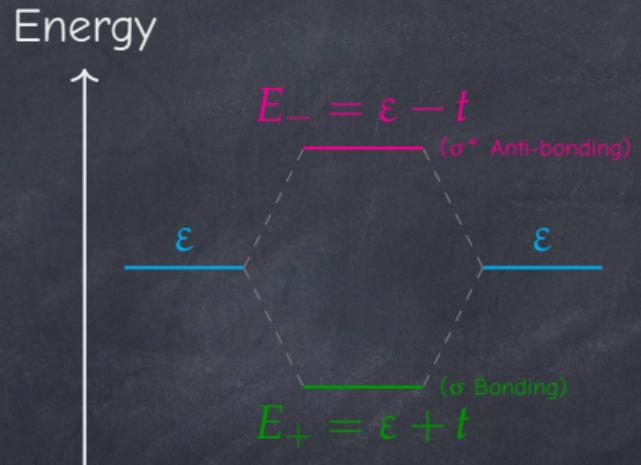
$$E_- = \varepsilon - t \approx -11.6\text{eV}$$

This state has a higher energy (unstable)

Bonding State (E_+)

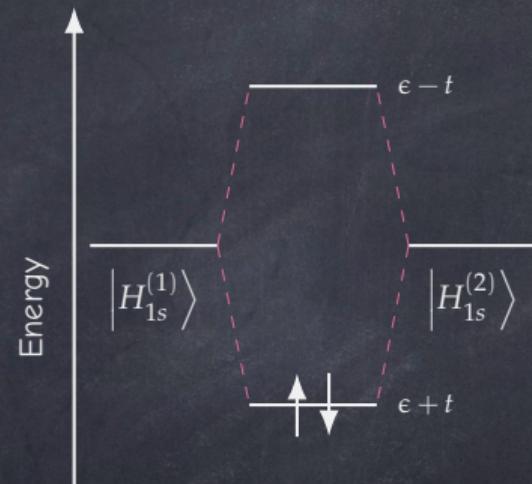
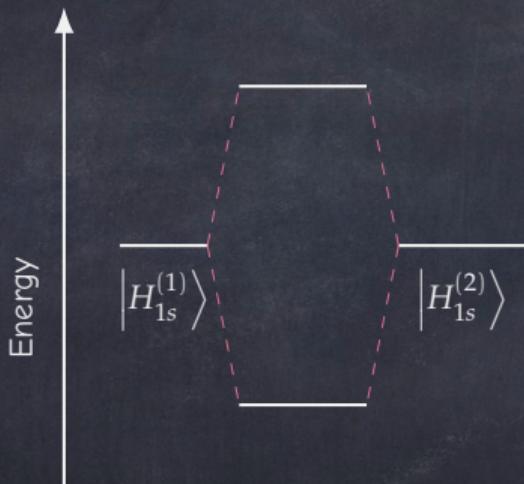
$$E_+ = \varepsilon + t \approx -15.6\text{eV}$$

This state has a lower energy (stable)



Electronic structure of hydrogen molecule

Molecular Orbital Diagram (H_2)



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

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

Caffeine ($C_8H_{10}N_4O_2$)

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
[assuming full configuration interaction (FCI)]

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

Fundamentals of Variational Principle

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 energy expectation value is always larger than the true ground state.

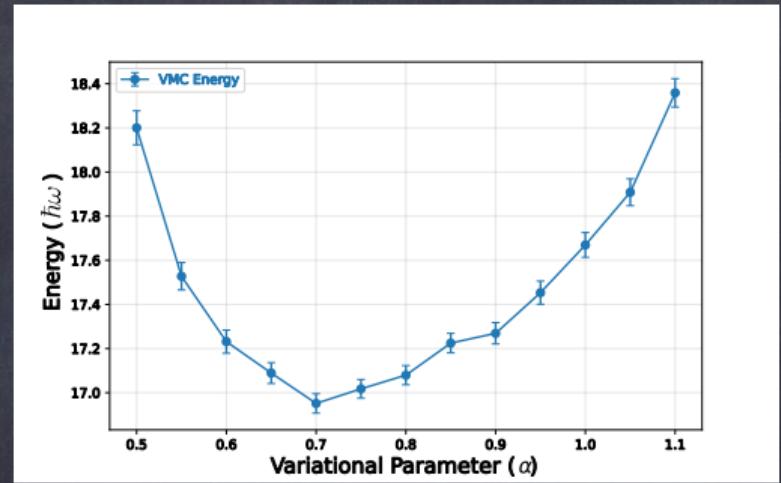
$$E(\theta) = \frac{\langle \Psi_T(\theta) | \hat{H} | \Psi_T(\theta) \rangle}{\langle \Psi_T(\theta) | \Psi_T(\theta) \rangle} \geq E_0$$

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

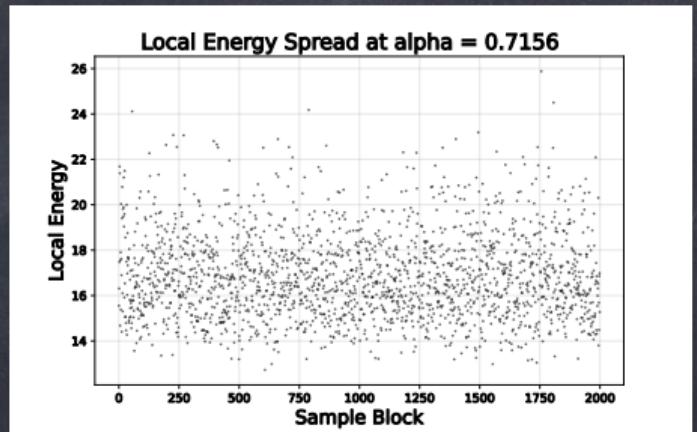
```
1: Input: Hamiltonian  $\hat{H}$  (Kinetic + Potential)
2: Input: Trial Wavefunction  $\Psi_T(\mathbb{R}; \alpha)$ 
3:                                         ▷ Define the analytic shape (e.g., Gaussian)

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

Algorithm: Run MC Sampling

Algorithm 2 Run Metropolis Sampling

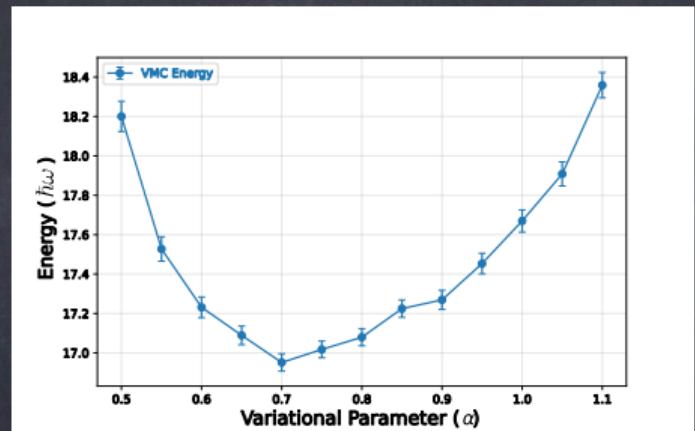
```
1: function GetEnergy( $\alpha$ )
2:   Init:  $E_{sum} \leftarrow 0$ ;  $\mathbb{R} \leftarrow \text{RandomPos}$ 
3:   for  $k = 1$  to  $N_{steps}$  do
4:      $\mathbb{R}_{new} \leftarrow \mathbb{R} + \Delta$ ;  $w \leftarrow |\Psi(\mathbb{R}_{new})/\Psi(\mathbb{R})|^2$ 
5:     if  $\text{rand}(0,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



Algorithm: Optimization

Algorithm 3 Variational Optimization

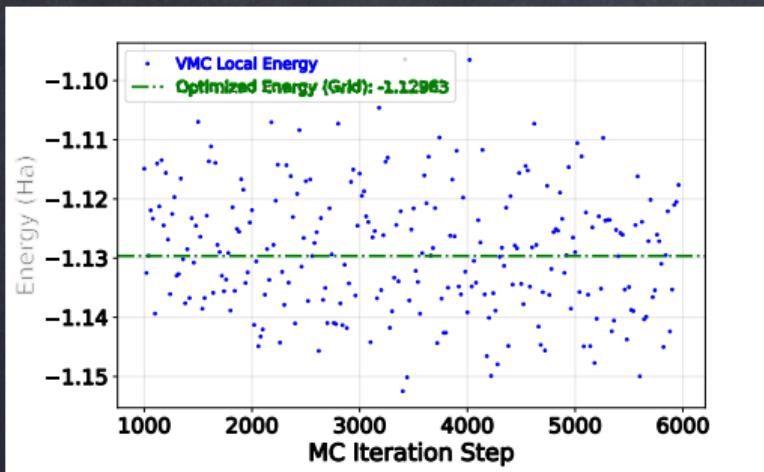
```
1:  $\alpha \leftarrow \text{InitialGuess}$ 
2:  $\eta \leftarrow 0.1$                                 ▷ Learning Rate
3: while not converged do
4:    $E_{avg} \leftarrow \text{GetEnergy}(\alpha)$ 
5:    $grad \leftarrow \text{CalculateGradient}(E_{avg}, \alpha)$ 
6:    $\alpha \leftarrow \alpha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



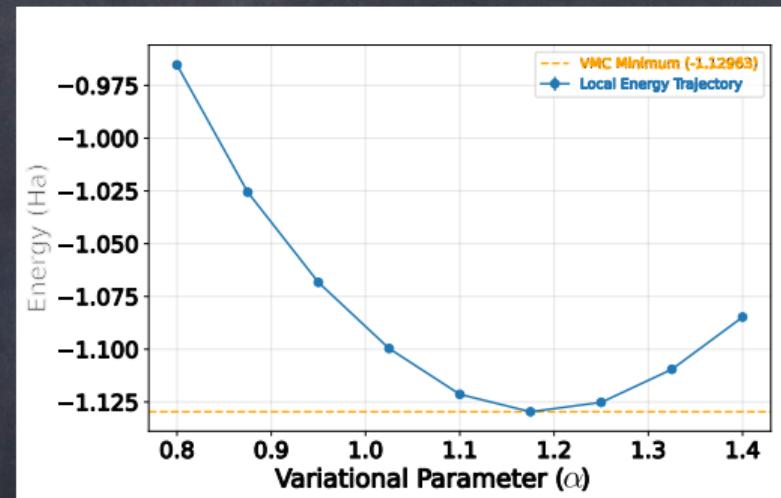
VMC for Hydrogen Molecule

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 with any optimizer you like (e.g. grad. descent)

Example VMC results for hydrogen molecule



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

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

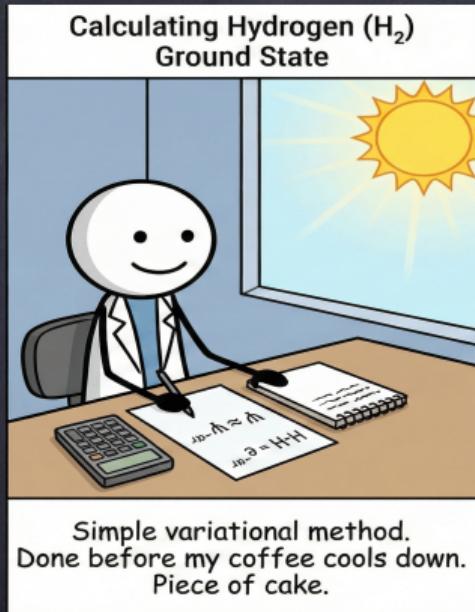
3. **Optimization**: Multiplies cost by steps (K) and samples (M).

Final Time Complexity

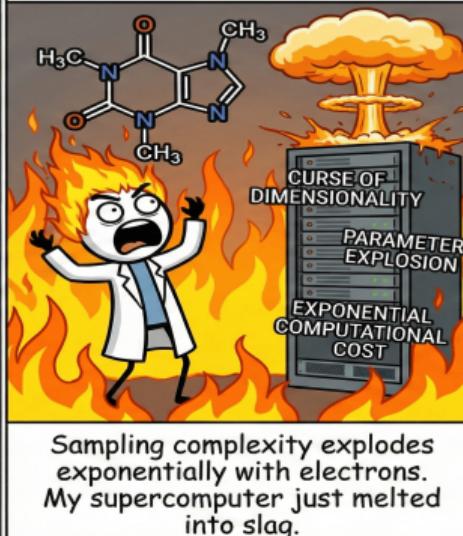
$$T_{VMC} \propto K \times M \times O(N^3)$$

Why Quantum?

The Limit of Classical VMC

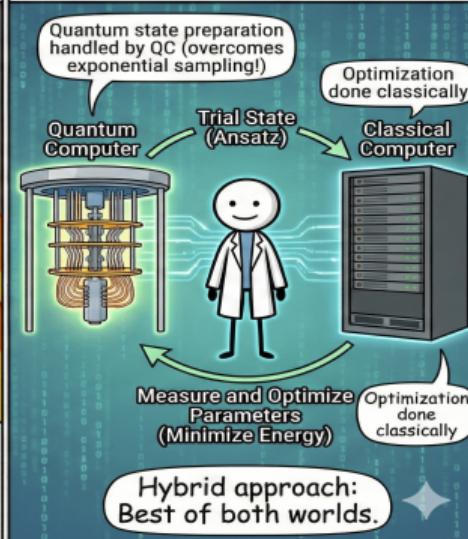


Calculating Caffeine ($C_8H_{10}N_4O_2$) Ground State with VMC



When "Good Enough" is not Enough

Enter VQE (Variational Quantum Eigensolver) - The Hybrid Solution



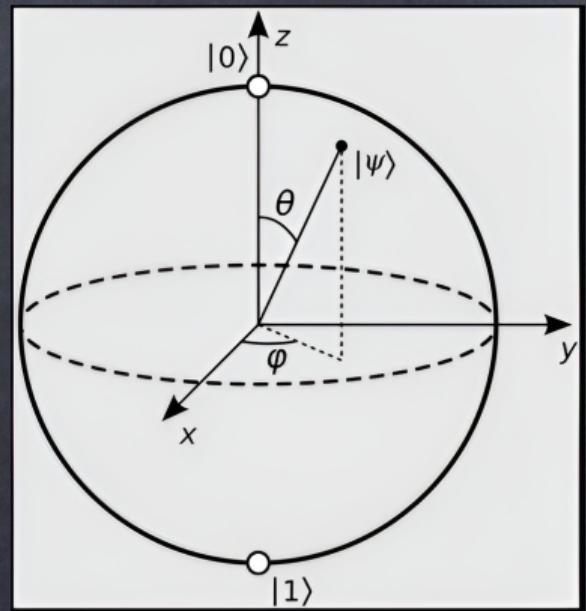
Qubit & Superposition

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.

Hamiltonian Mapping

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.

What we want: Qubit Hamiltonian

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

Components 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)

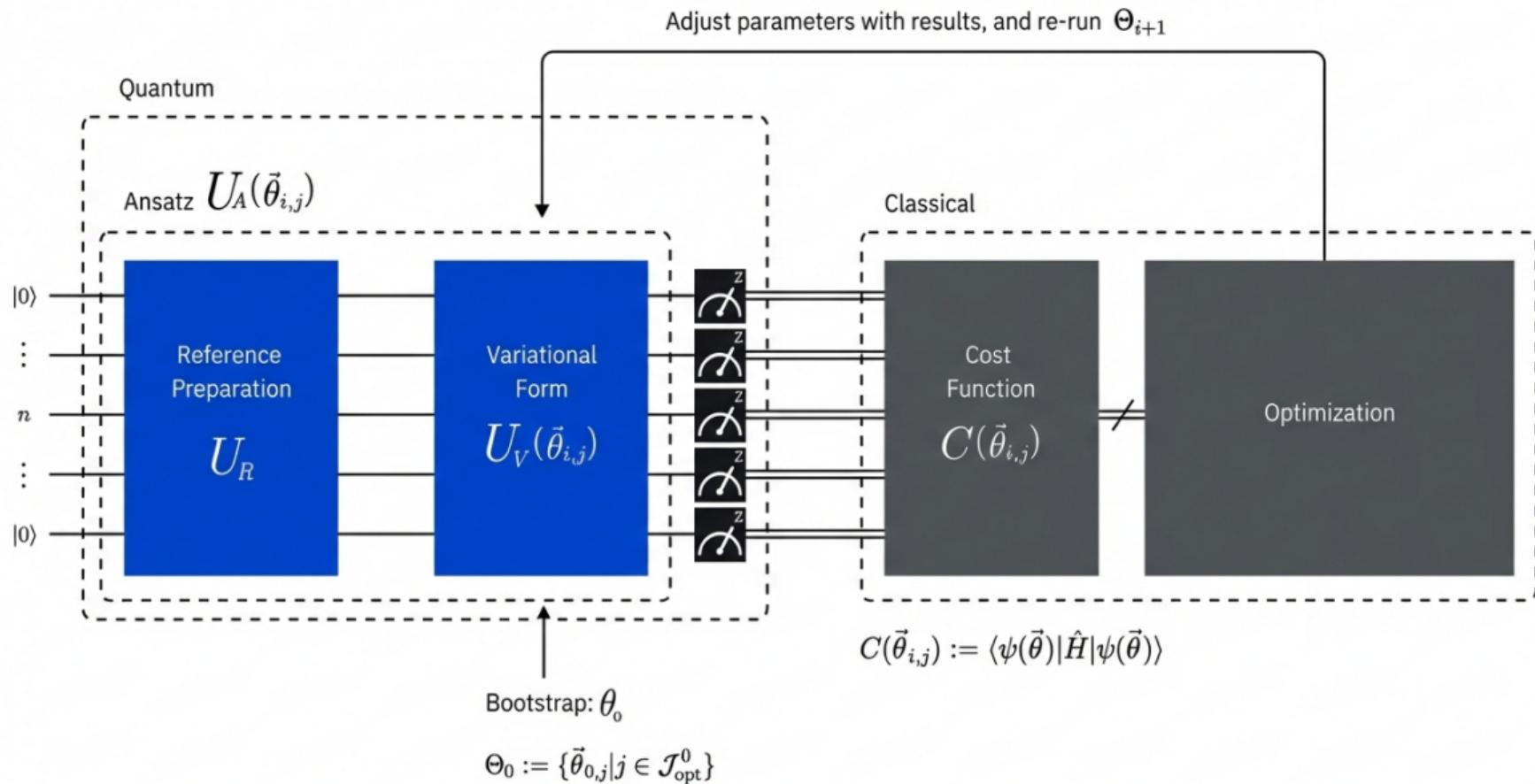
VQE is a **hybrid algorithm** (Quantum + Classical) designed to find the ground state energy (E_0) (e.g. of a molecule) using **Variational Principle**

Input

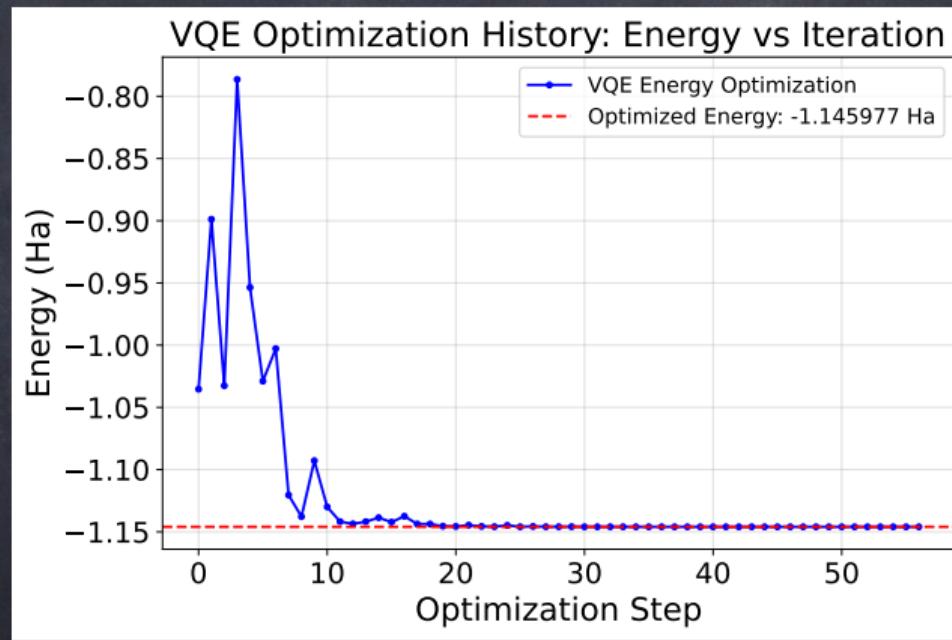
Hamiltonian (\hat{H}_{qubit}): Decomposed into Pauli Strings $\sum c_i P_i$. **Parameters** ($\vec{\theta}$): Rotation angles controlling the Ansatz.

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.



“Path” to optimized energy for H_2



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	$\mathbb{O}(N^3)$ (Polynomial)	$\mathbb{O}(N)$ (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.