

# 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 ( $\epsilon$  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 ( $E_-$ )**

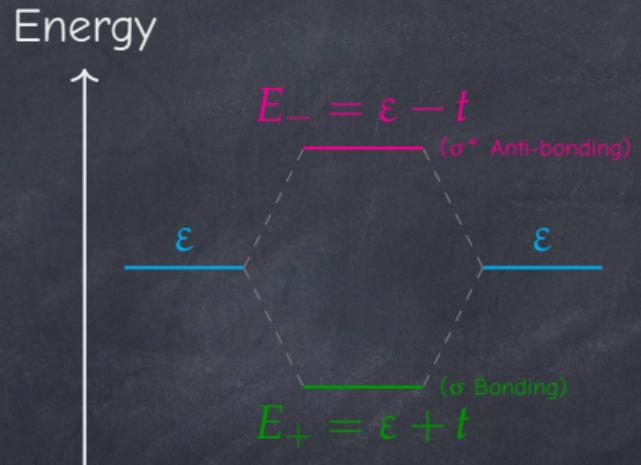
$$E_- = \varepsilon - t \approx -11.6\text{eV}$$

This state has a higher energy (unstable)

**Bonding State ( $E_+$ )**

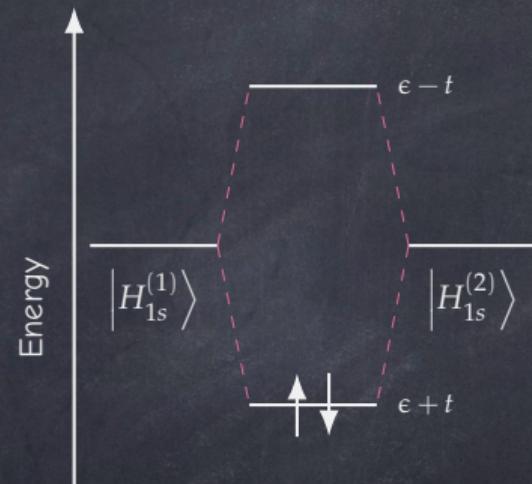
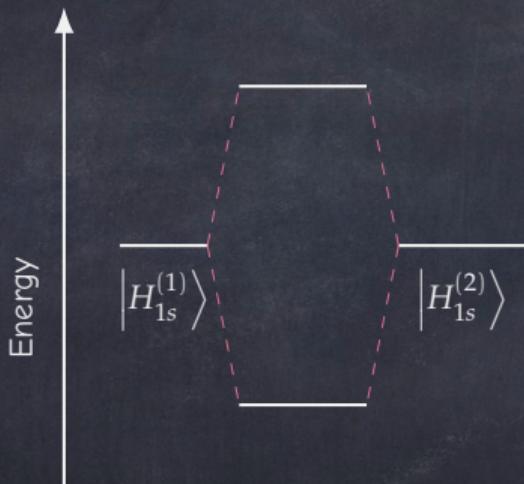
$$E_+ = \varepsilon + t \approx -15.6\text{eV}$$

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 ( $H_2$ )

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

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Total Ops : **216** operations

## Caffeine ( $C_8H_{10}N_4O_2$ )

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

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Total Ops :  **$10^{138}$**  operations  
[assuming full configuration interaction (FCI)]

FYI, Fastest CPU (i9-14900KF):  $9 \times 10^9$  ops/sec, while Age of the Universe:  $4 \times 10^{17}$  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.

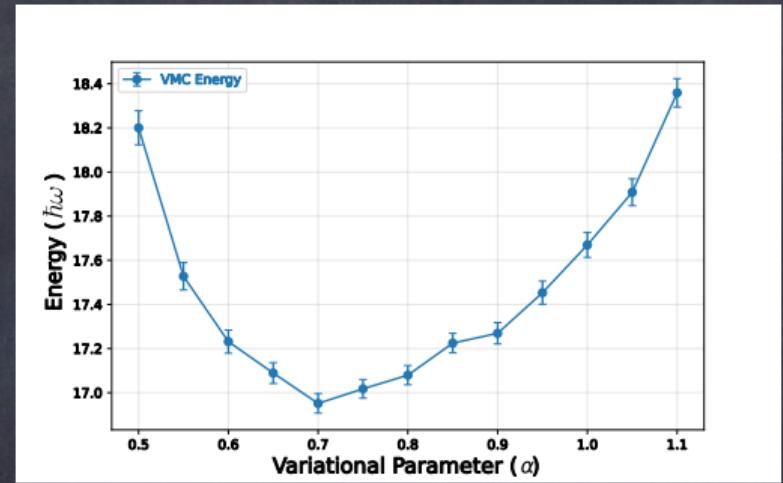
$$E(\theta) = \frac{\langle \Psi_T(\theta) | \hat{H} | \Psi_T(\theta) \rangle}{\langle \Psi_T(\theta) | \Psi_T(\theta) \rangle} \geq E_0$$

# Visualizing Optimization

## Optimization Process

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

- ▶ Parameter Sweep ( $\alpha$ )
- ▶ 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

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

$\alpha$  (Alpha): The tunable parameter that controls the width of the curve

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

# Algorithm: Initialize

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## Algorithm 1 Initialize System

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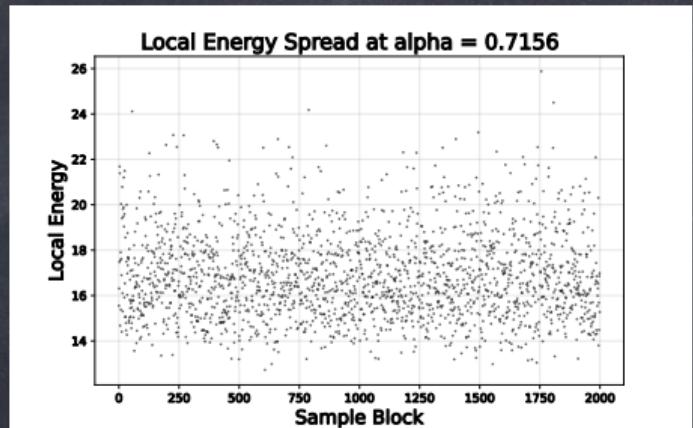
```
1: Input: Hamiltonian  $\hat{H}$  (Kinetic + Potential)
2: Input: Trial Wavefunction  $\Psi_T(\mathbb{R}; \alpha)$ 
3: ▷ Define the analytic shape (e.g., Gaussian)
4: function Setup
5:   Set number of particles  $N$ , dimension  $D$ 
6:    $\mathbb{R} \leftarrow \text{RandomUniform}(-1, 1)$  ▷ Random initial positions
7:    $\alpha \leftarrow \alpha_{\text{guess}}$  ▷ Initial variational parameter
8:   return  $\mathbb{R}, \alpha$ 
9: end function
```

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# Algorithm: Run MC Sampling

## Algorithm 2 Run Metropolis Sampling

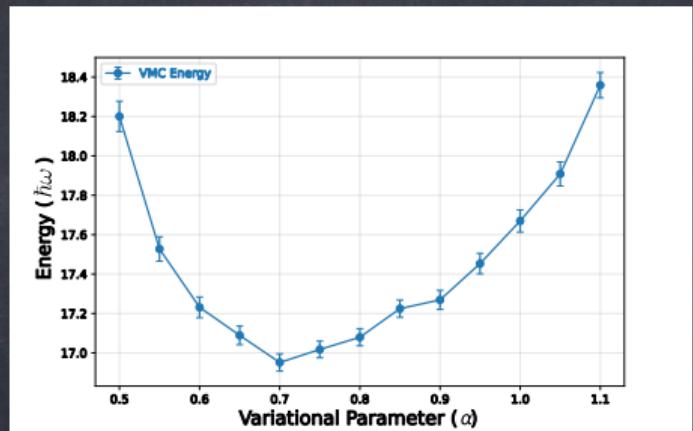
```
1: function GetEnergy( $\alpha$ )
2:   Init:  $E_{sum} \leftarrow 0$ ;  $\mathbb{R} \leftarrow \text{RandomPos}$ 
3:   for  $k = 1$  to  $N_{steps}$  do
4:      $\mathbb{R}_{new} \leftarrow \mathbb{R} + \Delta$ ;  $w \leftarrow |\Psi(\mathbb{R}_{new})/\Psi(\mathbb{R})|^2$ 
5:     if  $\text{rand}(0, 1) < w$  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

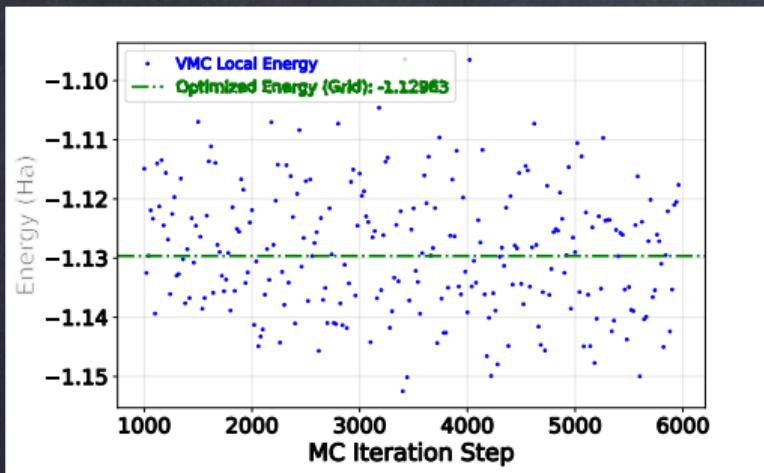
```
1:  $\alpha \leftarrow \text{InitialGuess}$ 
2:  $\eta \leftarrow 0.1$                                 ▷ Learning Rate
3: while not converged do
4:    $E_{avg} \leftarrow \text{GetEnergy}(\alpha)$ 
5:    $grad \leftarrow \text{CalculateGradient}(E_{avg}, \alpha)$ 
6:    $\alpha \leftarrow \alpha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



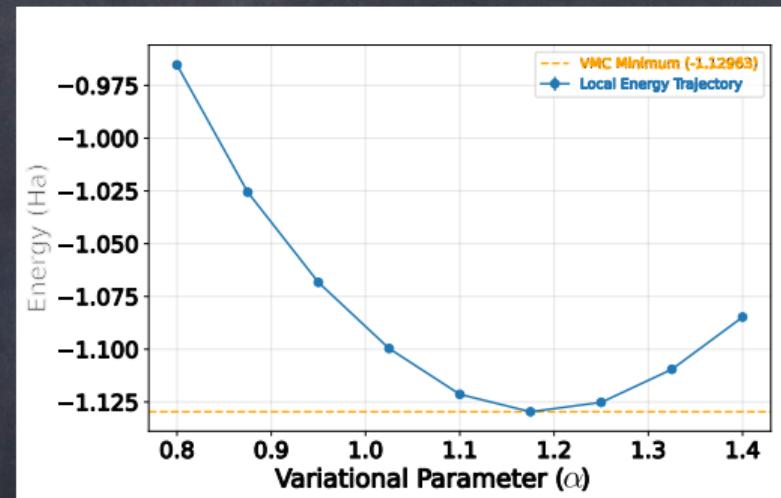
# VMC for Hydrogen Molecule

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 ( $\Psi_T$ )**: Single update costs
2. **Sampling Loop**: Updates all  $N$  electrons per sweep

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

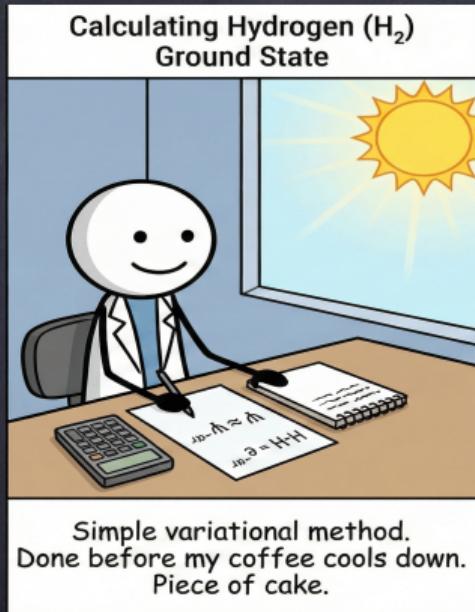
3. **Optimization**: Multiplies cost by steps ( $K$ ) and samples ( $M$ ).

## Final Time Complexity

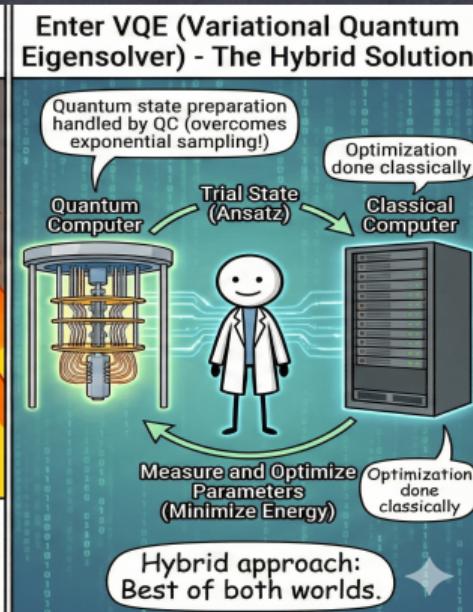
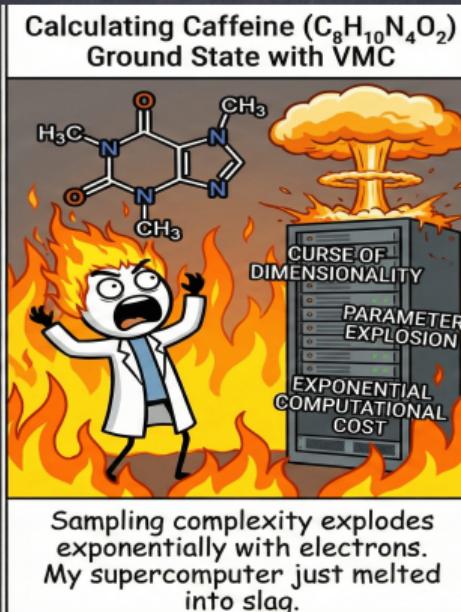
$$T_{VMC} \propto K \times M \times O(N^3)$$

# Why Quantum?

## The Limit of Classical VMC



## When "Good Enough" is not Enough



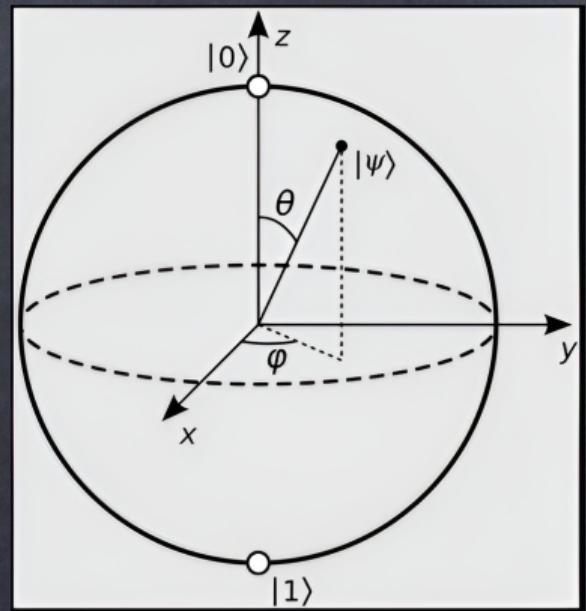
# Qubit & Superposition

## 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)

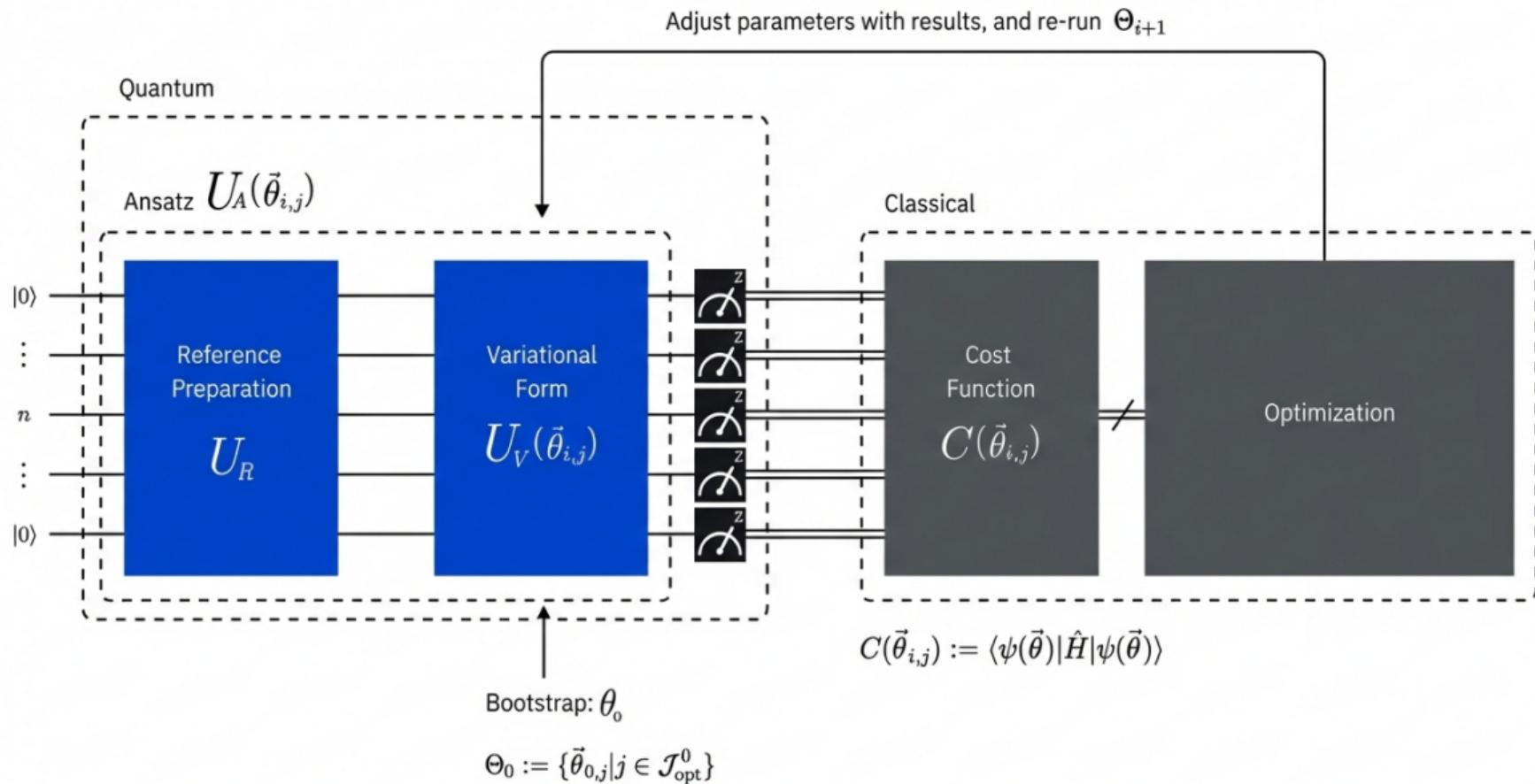
VQE is a **hybrid algorithm** (Quantum + Classical) designed to find the ground state energy ( $E_0$ ) (e.g. of a molecule) using **Variational Principle**

## Input

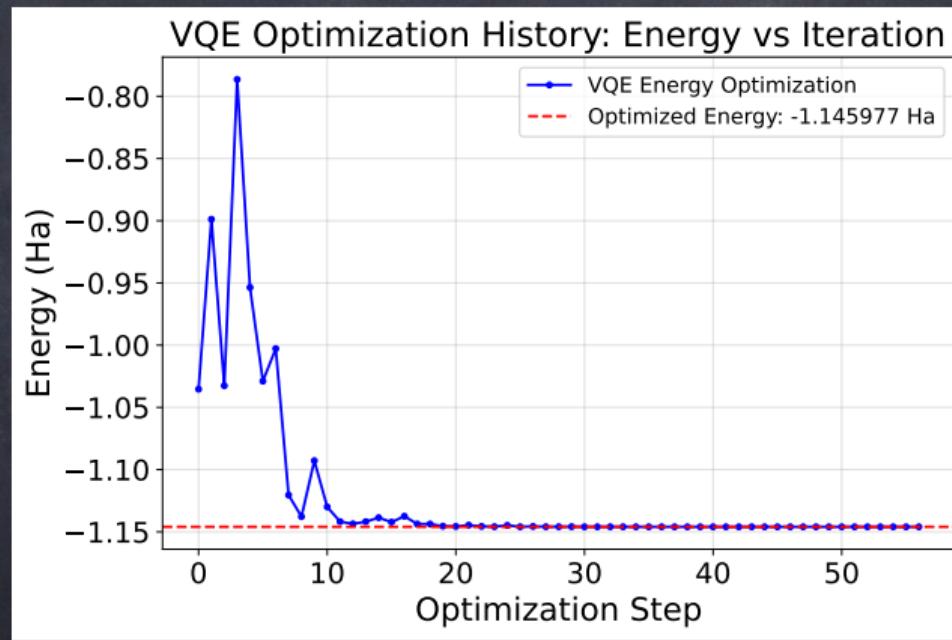
**Hamiltonian** ( $\hat{H}_{qubit}$ ): Decomposed into Pauli Strings  $\sum c_i P_i$ . **Parameters** ( $\vec{\theta}$ ): Rotation angles controlling the Ansatz.

## 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	$\mathbb{O}(N)$ (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.