

# **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
- Prospect : Winning Fujitsu Challenge

# 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** (Coulomb Integral).
- ▶  $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = t$ : **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 ( $\varepsilon$  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

### Bonding State( $E_+$ )

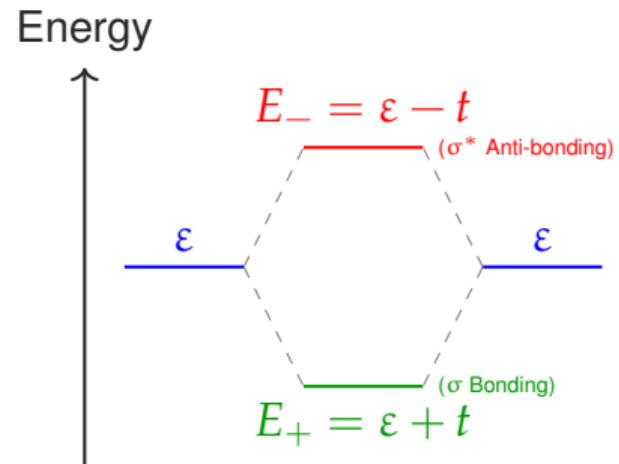
$$E_+ = \varepsilon + t \approx -15.6\text{eV}$$

This state has lower energy (stable)

### Anti-Bonding State ( $E_-$ )

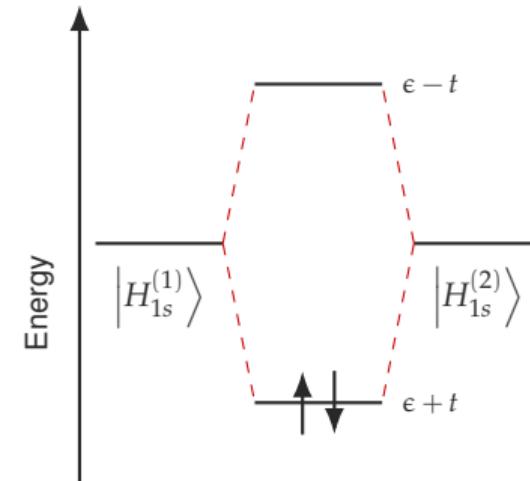
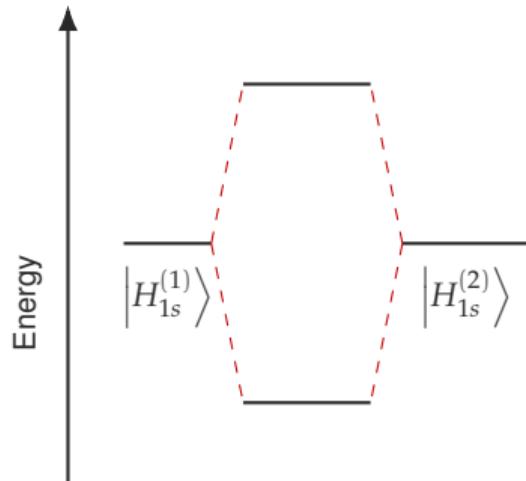
$$E_- = \varepsilon - t \approx -11.6\text{eV}$$

This state has a higher energy  
(unstable)



# Electronic structure of hydrogen molecule

Molecular Orbital Diagram ( $H_2$ )



Total Ground State Energy :  $2 \times E_+ = -31,2 eV \approx -1,14$  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):

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

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

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

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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

FYI :

Fastest CPU (i9-14900KF):  $9 \times 10^9$  ops/sec

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.

# 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 an **upper bound** to the true ground state."

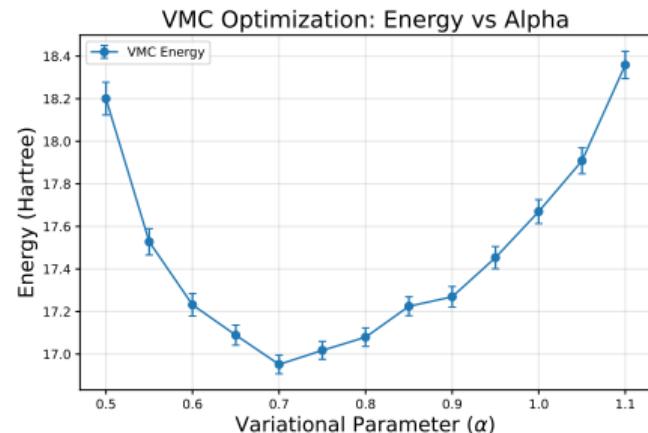
$$E(\theta) = \frac{\langle \Psi_T(\theta) | \hat{H} | \Psi_T(\theta) \rangle}{\langle \Psi_T(\theta) | \Psi_T(\theta) \rangle} \geq E_0$$

# 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

# VMC in Oscillator Harmonic

## 1D Harmonic Oscillator

Instead of solving conventionally, we "guess" the solution shape based on physical intuition

**Ansatz** : A Gaussian (Bell Curve)

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

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

Find the specific value of  $\alpha$  that minimizes the Total Energy?

# 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  $\Psi_T(\mathbf{R}; \alpha)$ 
3: ▷ Define the math 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
```

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# Algorithm : Run Sampling

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## Algorithm 2 Run Metropolis Sampling

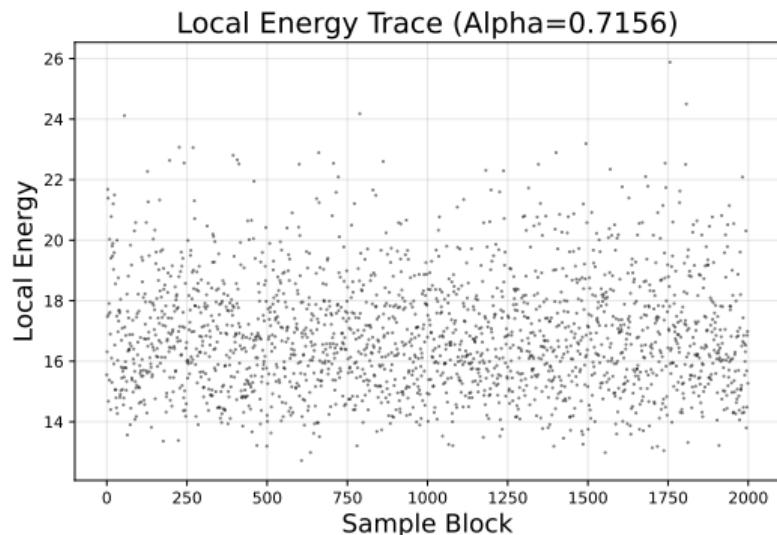
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```

1: function GETENERGY( $\alpha$ )
2:   Init:  $E_{sum} \leftarrow 0$ ;  $\mathbf{R} \leftarrow \text{RandomPos}$ 
3:   for  $k = 1$  to  $N_{steps}$  do
4:      $\mathbf{R}_{new} \leftarrow \mathbf{R} + \Delta$ ;  $w \leftarrow |\Psi(\mathbf{R}_{new})|/\Psi(\mathbf{I})$ 
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

```

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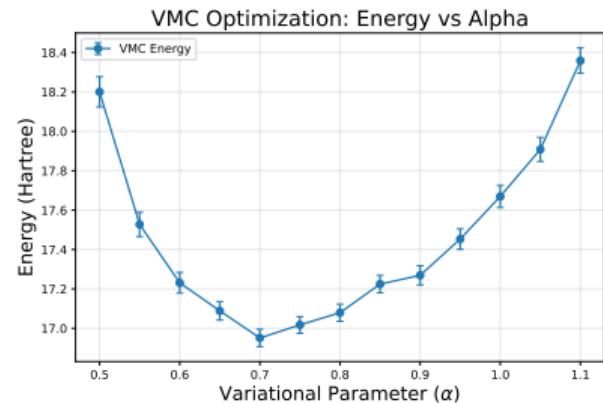


# Algorithm : Optimization

## Algorithm 3 Variational Optimization

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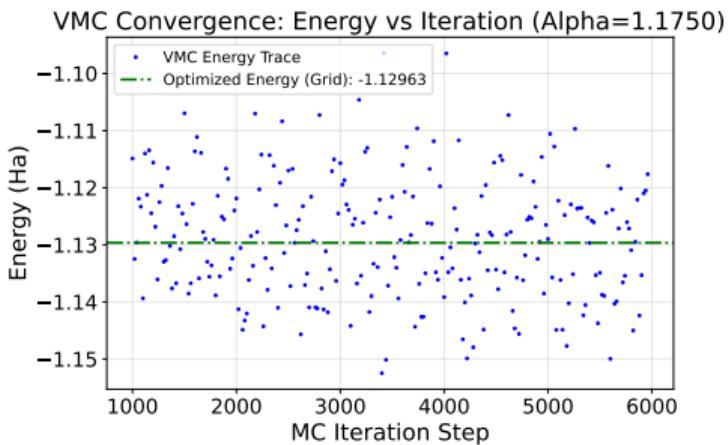
1:  $\alpha \leftarrow \text{InitialGuess}$ 
2:  $\eta \leftarrow 0.1$                                 ▷ Learning Rate
3: while not converged do
4:    $E_{avg} \leftarrow \text{GETENERGY}(\alpha)$       ▷ Call Phase 2
5:    $grad \leftarrow \text{CalculateGradient}(E_{avg}, \alpha)$ 
6:    $\alpha \leftarrow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



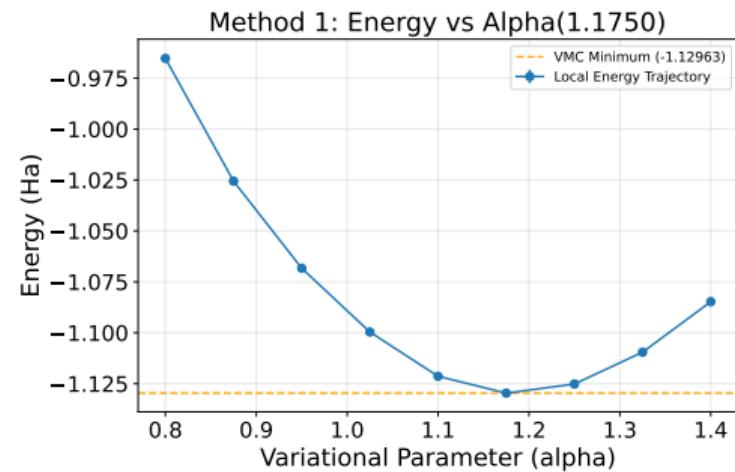
# VMC in Hydrogen Molecule

- 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



Energy in Iteration graph in optimal alpha



Energy in Alpha Trajectory Graph

# Computational Cost

- 1 **Wavefunction ( $\Psi_T$ ):** 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 ( $M$ ).

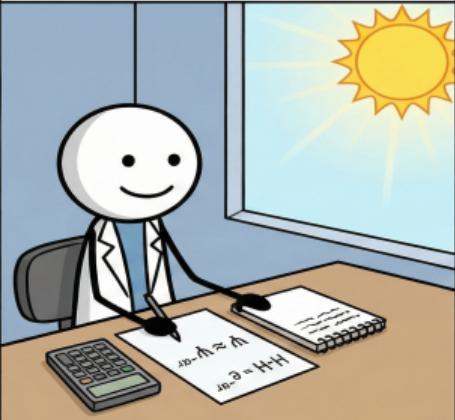
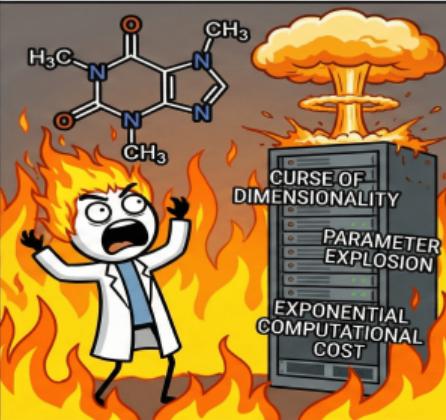
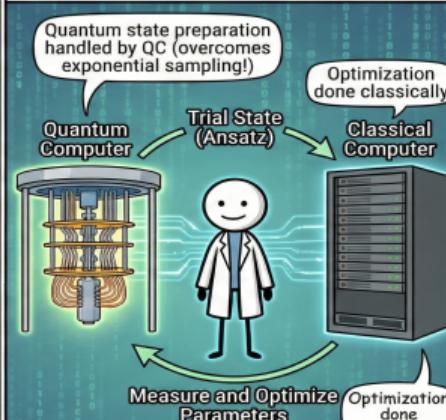
## Final Time Complexity

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

# 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 <math>V \approx V_{\text{HF}}</math> and <math>H = e^{-V_{\text{HF}}}</math>. 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 monitor has text overlays: "CURSE OF DIMENSIONALITY", "PARAMETER EXPLOSION", and "EXPONENTIAL COMPUTATIONAL COST". The scientist is surrounded by flames and looking shocked.</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 person in a lab coat stands between them. Speech bubbles explain the process: "Quantum state preparation handled by QC (overcomes exponential sampling!)" from the Quantum Computer, "Optimization done classically" from the Classical Computer, "Trial State (Ansatz)" from the Quantum Computer, "Measure and Optimize Parameters (Minimize Energy)" from the Classical Computer, and "Optimization done classically" from the Classical Computer again. A final bubble at the bottom right says "Hybrid approach: Best of both worlds."</p>

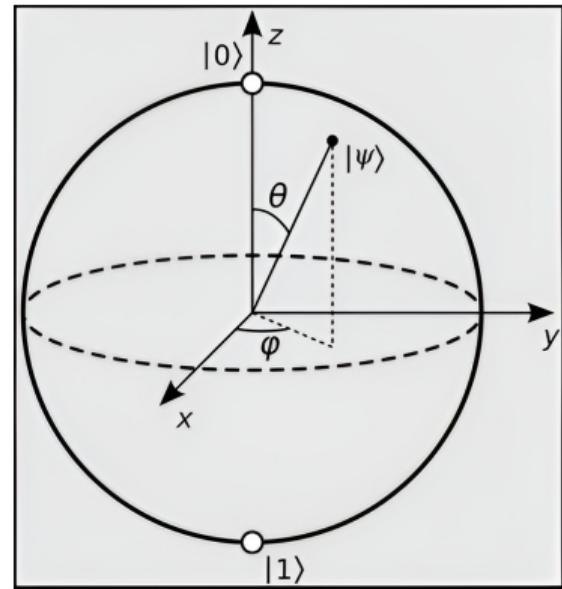
# The Qubit & Superposition

## 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**

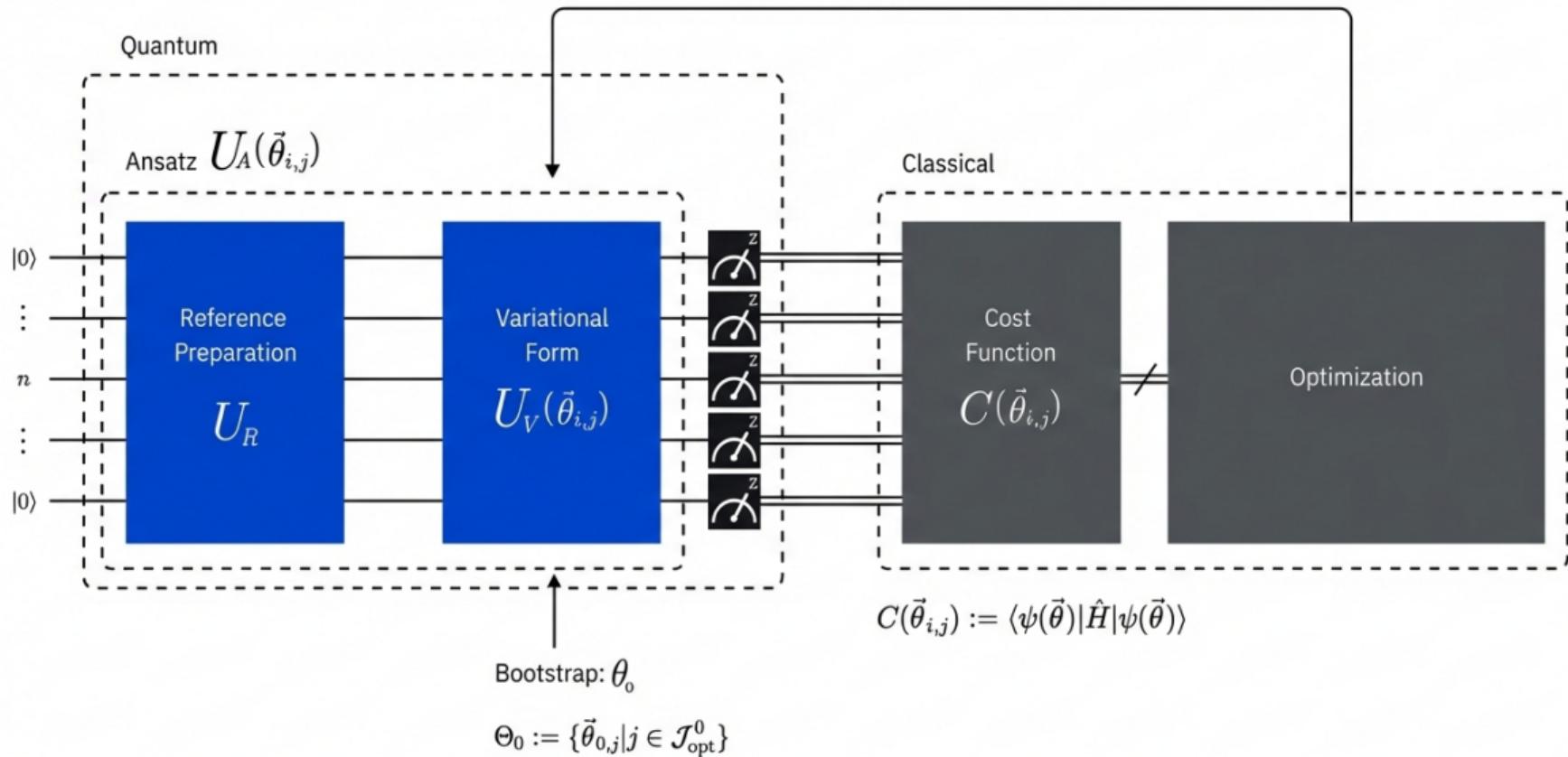
## Input

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

## Loop

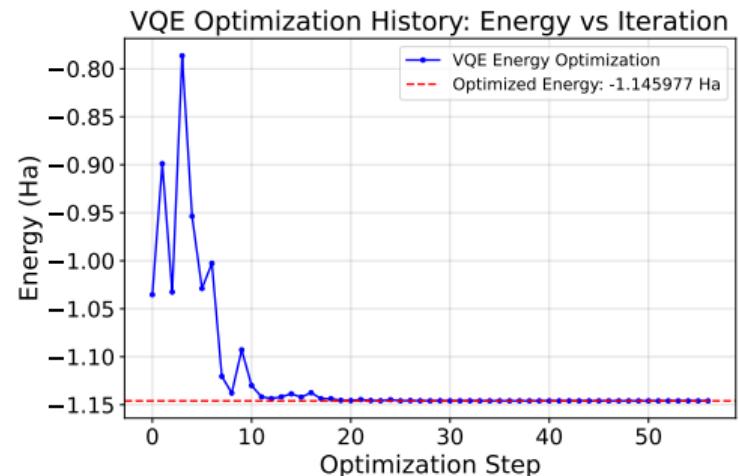
**QPU (Measure):** Run circuit  $U(\vec{\theta})$  and sample expectation values. **CPU (Optimize):** Aggregate Energy ( $E_{tot}$ ) and update  $\vec{\theta}$  to minimize cost. **Repeat:** Iterate until convergence to Ground State.

Adjust parameters with results, and re-run  $\Theta_{i+1}$



# 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)
<b>Ansatz Approach</b>	<b>Heuristic Guessing</b> (Based on Physical Intuition)	<b>Scalable Approximation</b> (Systematic Circuit Expansion)
<b>Computational Cost</b>	<b><math>O(N^3)</math></b> (Polynomial)	<b><math>O(N)</math></b> (Hamiltonian Terms)*
<b>Bottleneck</b>	<b>Sampling Loop</b> (Moving Electrons via CPU)	<b>Measurement Loop</b> (Shot Noise via QPU)
<b>Limit</b>	Fixed-Node Approximation	Hardware Noise (NISQ)

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

# Fujitsu Challenge



## Fujitsu Quantum Application Research Package (Fujitsu QARP)

The Quantum Applications Research Package (QARP) is a comprehensive Python package for research and development of quantum computing applications. It enables quantum circuit simulation across physics, chemistry, mathematical optimisation, data science, and other research domains—combining problem modelling with circuit compilation for real quantum hardware and circuit cutting techniques.

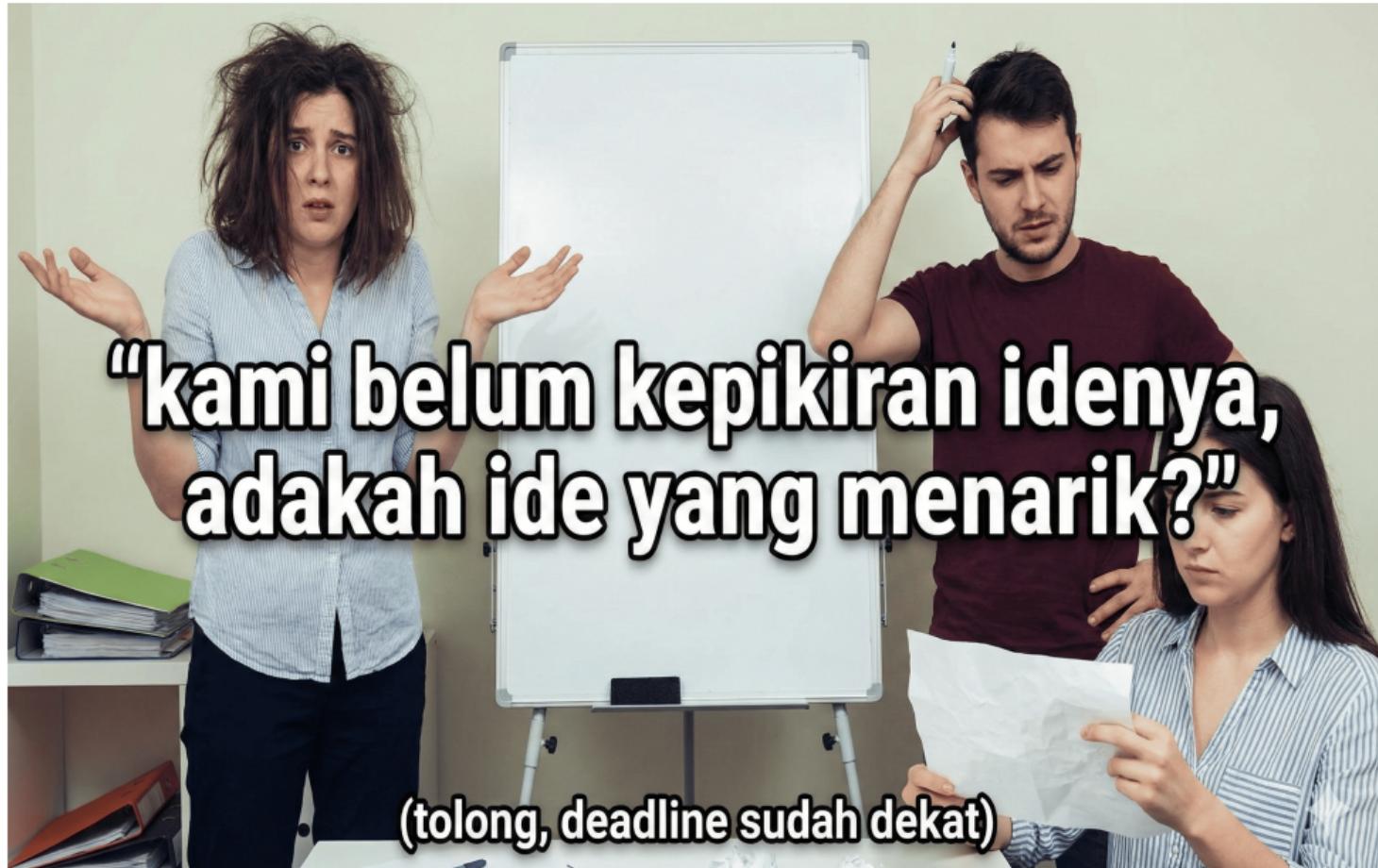
### Evaluation Criteria

Every project will be scored using the following evaluation criteria. The team which scores the highest will be awarded the prize.

- Project Uniqueness
  - Uniqueness of a project theme, use case scenario
- Business Applicability
  - How a project impacts actual business with an emphasis on solutions for real-world applications
- Algorithms Quality
  - How well the quantum algorithms were developed
- Solving complex problems
  - The number of qubits used for simulation with preference given to higher qubit utilization and solutions to complex problems
- Utilization of Fujitsu Quantum Application Research Package (Fujitsu QARP)
  - Use of Fujitsu QARP, with valuable feedback on usability.

### Key Features

- Quantum Algorithms
  - ✓ VQE — Variational Quantum Eigensolver
  - ✓ VQD — Variational Quantum Deflation
  - ✓ ADAPT-VQE/ADAPT-VQD — Adaptive derivative-assembled pseudo-Trotter ansatz
  - ✓ QAOA — Quantum Approximate Optimisation Algorithm
  - ✓ QPE — Quantum Phase Estimation
  - ✓ DOS-QPE — Density-of-States QPE
  - ✓ SSVQE — Subspace-Search Variational Quantum Eigensolver
  - ✓ PCE — Pauli Correlation Encoding
- Modular Circuit Construction
  - ✓ Block-based architecture — Build circuits using composable, reusable blocks
  - ✓ Predefined blocks — QAOA ansatzes, hardware-efficient ansatzes, Trotterised circuits
  - ✓ Custom blocks — Easily define your own circuit components
- Fermionic Systems
  - ✓ Create and manipulate fermionic systems for electronic structure calculations
  - ✓ Built on PySCF and OpenFermion
  - ✓ Support for various fermion-to-qubit mappings



**“kami belum kepikiran idenya,  
adakah ide yang menarik?”**

**(tolong, deadline sudah dekat)**