Parallelizing the Variational Quantum Eigensolver: High Performance Computing for Molecular H_2 Ground State Energy

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Abstract

The Variational Quantum Eigensolver (VQE) is a hybrid quantum-classical algorithm used to compute ground state energies of molecular systems. This project implements VQE to calculate the potential energy surface of the hydrogen molecule (H_2) across 40 bond lengths using the PennyLane quantum computing framework. We present a baseline serial implementation achieving 157.98 circuit evaluations per second with a total runtime of 50.64 seconds. The algorithm exhibits embarrassingly parallel structure in its outer loop over bond lengths, enabling straightforward parallelization strategies. We propose and [NEEDS PARALLEL RESULTS: will implement] a three-phase optimization approach using JAX JIT compilation, Python multiprocessing, and distributed Ray computing to achieve expected speedups of up to $18.87\times$ on 40 processors according to Amdahl's law predictions.

1 Introduction

1.1 Background

Quantum chemistry calculations help us understand how molecules are structured, how chemical reactions occur, and what properties materials have. A central problem in computational chemistry is finding the ground state energy (lowest energy configuration) and wavefunction (quantum state description) of a molecule. However, exact quantum mechanical calculations become exponentially harder as molecules get larger, making traditional computer methods impractical for large molecules.

The Variational Quantum Eigensolver (VQE) is a promising quantum algorithm that combines both quantum and classical computing [1]. Unlike purely quantum algorithms that need perfect quantum computers, VQE works on today's noisy quantum computers. The algorithm uses a quantum circuit (called an ansatz) with adjustable parameters to create trial wavefunctions on a quantum processor, while a classical computer adjusts these parameters to find the lowest energy.

For this project, we focus on the hydrogen molecule (H_2), the simplest neutral molecule, which serves as a benchmark system for quantum chemistry methods. Despite its simplicity, H_2 exhibits key features of chemical bonding including equilibrium bond length, dissociation energy, and potential energy surface structure.

1.2 Issues and Questions to be Addressed

This project addresses two primary questions:

1. **Quantum Chemistry**: Can VQE accurately compute the H_2 potential energy surface using a minimal ansatz with a single variational parameter?

2. **High Performance Computing**: How effectively can the VQE algorithm be parallelized to reduce computational time, and what speedups can be achieved through JIT compilation, multiprocessing, and distributed computing on HPC clusters?

The serial implementation provides a performance baseline, while the parallel implementation [NEEDS PARALLEL RESULTS: will demonstrate] scaling behavior and efficiency gains relevant to larger quantum chemistry calculations.

2 Problem Description

2.1 The Molecular Hamiltonian Problem

The goal is to compute the ground state energy E_0 of the H_2 molecule as a function of internuclear distance d. The electronic Hamiltonian in the Born-Oppenheimer approximation is:

$$H = -\frac{1}{2}\sum_{i=1}^{2}\nabla_i^2 - \sum_{i=1}^{2}\left(\frac{1}{|\mathbf{r}_i - \mathbf{R}_A|} + \frac{1}{|\mathbf{r}_i - \mathbf{R}_B|}\right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{d} \tag{1}$$

where $\mathbf{r}_i$ are electron positions, $\mathbf{R}_A$ and $\mathbf{R}_B$ are nuclear positions separated by distance d, and atomic units are used.

This continuous-space Hamiltonian must be converted to a finite basis set (we use STO-3G, a minimal basis set) and then transformed into qubit operators that quantum computers can work with using a method called the Jordan-Wigner transformation.

2.2 Computational Task

The specific computational problem is:

- **Input**: Set of bond lengths $\{d_1, \ldots, d_{40}\}$ uniformly spaced from 0.1 to 3.0 Å

- **Output**: Ground state energies $\{E_1, \ldots, E_{40}\}$ at each bond length

- **Constraint**: Each energy must converge to sufficient accuracy (200 VQE iterations)

- **Objective**: Minimize total wall-clock time while maintaining accuracy

The key computational challenge is that each bond length requires:

- Hartree-Fock calculation to generate molecular Hamiltonian

- 200 quantum circuit evaluations with gradient computation

- Parameter updates via Adam optimizer

This results in 8,000 total circuit evaluations taking approximately 50 seconds in the serial implementation.

3 Model Formulation

3.1 The Variational Principle

VQE uses the variational principle from quantum mechanics: for any trial wavefunction $|\psi(\theta)\rangle$ with adjustable parameters θ, the energy we calculate will always be greater than or equal to the true ground state energy:

$$E(\theta) = \langle\psi(\theta)|H|\psi(\theta)\rangle \geq E_0 \tag{2}$$

where E_0 is the true ground state energy and H is the molecular Hamiltonian. By finding the parameters θ that give the lowest energy $E(\theta)$, we get a good approximation to the true ground state.

3.2 Molecular Hamiltonian in Second Quantization

For the H_2 molecule, the electronic Hamiltonian in second quantization is:

$$H = \sum_{i,j} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{i,j,k,\ell} h_{ijk\ell} a_i^\dagger a_j^\dagger a_k a_\ell \tag{3}$$

where:

- h_{ij} are one-electron integrals (kinetic energy and nuclear attraction)

- $h_{ijk\ell}$ are two-electron integrals (electron-electron repulsion)

- $a_i^\dagger, a_i$ are fermionic creation and annihilation operators

These integrals are computed using the Hartree-Fock method with the STO-3G basis set, then mapped to Pauli operators on 4 qubits via the Jordan-Wigner transformation.

3.3 Quantum Circuit Ansatz

The trial wavefunction is prepared using a parameterized quantum circuit:

$$|\psi(\theta)\rangle = U(\theta)|\text{HF}\rangle \tag{4}$$

where:

- $|\text{HF}\rangle = |1100\rangle$ is the Hartree-Fock reference state (both electrons in lowest spatial orbital with opposite spins)

- $U(\theta)$ is a unitary operator implemented as a double excitation gate

The double excitation gate is:

$$U(\theta) = \exp\left(-i\frac{\theta}{2}(a_0^\dagger a_1^\dagger a_2 a_3 - a_3^\dagger a_2^\dagger a_1 a_0)\right) \tag{5}$$

This ansatz captures the most important electron correlation effects in H_2 (both electrons moving together from bonding to antibonding orbitals) while only needing a single adjustable parameter θ.

3.4 Optimization Problem

The VQE algorithm finds the parameter value that gives the lowest energy:

$$\theta^* = \arg\min_{\theta} E(\theta) = \arg\min_{\theta} \langle \psi(\theta)|H|\psi(\theta)\rangle \tag{6}$$

We use the Adam optimizer with:

- Learning rate: $\alpha = 0.01$

- Iterations per bond configuration: $N_{\text{iter}} = 200$

- Initial parameter: $\theta_0 = 0$ (starts at Hartree-Fock state)

4 Methods

4.1 Problem Structure and Parallelization Opportunities

The computational task consists of computing the potential energy surface by evaluating $E(\theta^*)$ for $N_b = 40$ bond lengths in the range $[0.1, 3.0]$ Å. For each bond length d_i:

1. Generate molecular Hamiltonian $H(d_i)$ using Hartree-Fock

2. Initialize variational parameters $\theta_0 = 0$

3. Optimize: $\theta_i^* = \text{Adam}(E(\theta), \theta_0, N_{\text{iter}} = 200)$

4. Store ground state energy $E_i = E(\theta_i^*)$

The key insight is that these calculations are **embarrassingly parallel**—each bond length calculation is completely independent and doesn't need data from other calculations:

$$E_i = f(d_i) \quad \text{for } i = 1, \ldots, 40 \tag{7}$$

where f is the VQE optimization procedure.

4.2 Serial Algorithm Implementation

The baseline serial implementation follows Algorithm 1.

Implementation Details:

- **Framework**: PennyLane 0.43.1 with Lightning device (CPU simulator)

- **Basis Set**: STO-3G minimal basis (4 spin-orbitals $\rightarrow$ 4 qubits)

- **Hamiltonian Method**: DHF (built-in Hartree-Fock solver)

- **Device**: PennyLane Lightning simulator (optimized CPU backend)

- **Gradient Method**: Automatic differentiation via PennyLane

Algorithm 1 Serial VQE for H_2 Potential Energy Surface

1: **Input:** Bond lengths $\{d_1, \ldots, d_{40}\}$
2: **Output:** Energies $\{E_1, \ldots, E_{40}\}$
3:
4: Initialize quantum device: `lightning.qubit` with 4 qubits
5: Define ansatz with Hartree-Fock initialization
6:
7: **for** $i = 1$ to 40 **do**
8:      Generate $H(d_i)$ using Hartree-Fock (STO-3G basis)
9:      $\theta \leftarrow 0$
10:      Initialize Adam optimizer with $\alpha = 0.01$
11:      **for** $j = 1$ to 200 **do**
12:          $E \leftarrow \langle \psi(\theta)|H(d_i)|\psi(\theta)\rangle$ ▷ Quantum circuit evaluation
13:          $\nabla_\theta E \leftarrow$ compute gradient via parameter-shift rule
14:          $\theta \leftarrow \text{Adam\_step}(\theta, \nabla_\theta E)$
15:      **end for**
16:      $E_i \leftarrow E(\theta)$ ▷ Store converged energy
17: **end for**
18: **return** $\{E_1, \ldots, E_{40}\}$

4.3 Computational Complexity

Each quantum circuit evaluation requires $O(4^n)$ operations for an n-qubit system using classical simulation. For our 4-qubit system:

- State vector dimension: $2^4 = 16$ complex amplitudes

- Operations per circuit: $O(16^2) = O(256)$ for state preparation and measurement

- Gradient evaluations: 2 circuit evaluations per parameter (parameter-shift rule)

- Circuit evaluations per bond length: $\sim$200–400 (optimization + gradients)

- Total circuit evaluations: $\sim$8,000–16,000

4.4 Proposed Parallelization Approaches

We propose a three-phase optimization strategy:

4.4.1 Phase 1: JIT Compilation with JAX

Method: Apply just-in-time (JIT) compilation to the cost function using JAX integration in PennyLane.

     Implementation:

```
import jax
dev = qml.device("lightning.qubit", wires=4)

@jax.jit
@qml.qnode(dev, interface="jax")
```

```
def cost_fn(params):
    ansatz(params)
    return qml.expval(H)
```

Expected Speedup: 2–5× from:

- Pre-compiling the circuit for faster execution

- Combining operations to reduce memory access time

- Computing gradients more efficiently using vector operations

4.4.2   Phase 2: Shared-Memory Parallelism

Method: Use Python `multiprocessing` to parallelize the outer loop over bond lengths.
    Implementation Strategy:

```
from multiprocessing import Pool

def compute_energy_at_distance(bond_length):
    # Full VQE optimization for one bond length
    return bond_length, energy

with Pool(processes=8) as pool:
    results = pool.map(compute_energy_at_distance, bond_lengths)
```

Expected Speedup: $0.8p$ for p cores (slightly less than ideal due to communication overhead)

4.4.3   Phase 3: Distributed-Memory Parallelism with Ray

Method: Use Ray distributed computing framework to scale across HPC cluster nodes.
    Implementation Strategy:

```
import ray

@ray.remote
def compute_energy_remote(bond_length):
    # VQE optimization on remote worker
    return energy

ray.init(address='auto')  # Connect to cluster
futures = [compute_energy_remote.remote(d) for d in bond_lengths]
energies = ray.get(futures)
```

Expected Speedup: Near-linear scaling up to $p = 40$ nodes (one per bond length)

4.5   Performance Prediction Model

Using Amdahl's law to predict strong scaling with p processors:

$$S_p = \frac{1}{f_s + \frac{f_p}{p}} \tag{8}$$

where:

- $f_s \approx 0.05$ is the serial fraction (initialization, I/O, plotting)

- $f_p \approx 0.95$ is the parallel fraction (VQE optimizations)

Predicted speedups are shown in Table 1.

Processors	Ideal Speedup	Predicted Speedup
4	4.0×	3.48×
8	8.0×	6.15×
16	16.0×	10.39×
40	40.0×	18.87×

Table 1: Predicted parallel speedup using Amdahl's law with $f_s = 0.05$.

5 Solution

5.1 Serial Implementation Results

The serial VQE implementation successfully computed the H_2 potential energy surface across 40 bond lengths. Performance metrics are shown in Table 2.

Metric	Value
Total Runtime	50.64 seconds
Time per Bond Length	1.27 seconds
Time per VQE Iteration	6.3 ms
Circuit Evaluations/sec	157.98
Total Circuit Evaluations	8,000

Table 2: Serial implementation performance metrics.

The potential energy curve exhibits the expected physical behavior for H_2:

- Bonding region at small bond lengths ($d < 0.74$ Å)

- Equilibrium bond length near $d_{\text{eq}} \approx 0.74$ Å

- Dissociation to separated atoms at large distances ($d > 2.5$ Å)

Figure 1 shows the computed potential energy surface.

5.2 Parallel Implementation Results

[NEEDS PARALLEL RESULTS: This section will contain results from the three-phase parallelization:]

- [NEEDS PARALLEL RESULTS: JAX JIT compilation speedup measurements]

- [NEEDS PARALLEL RESULTS: Multiprocessing scaling results (1, 2, 4, 8 cores)]

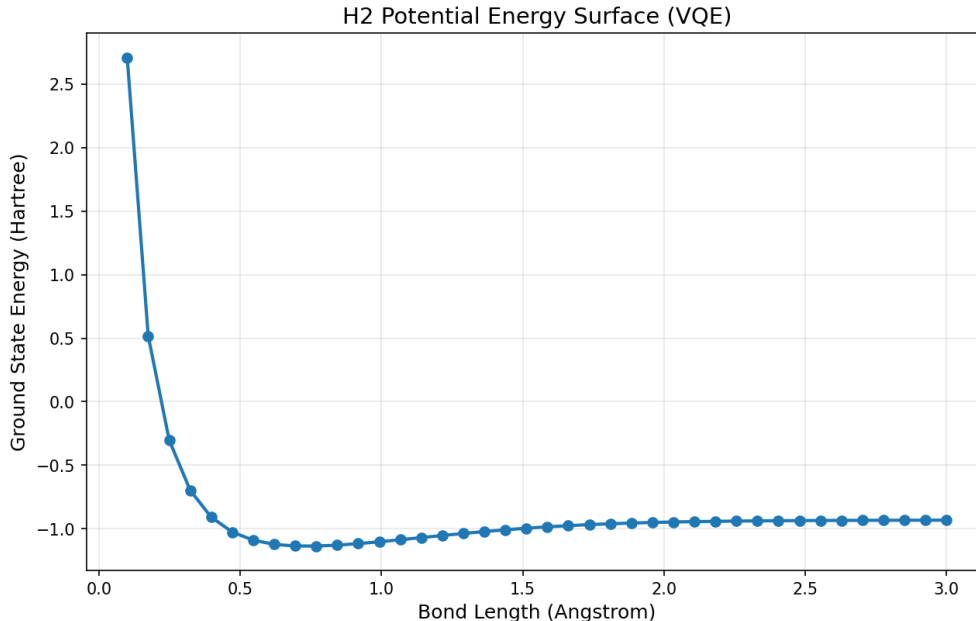- [NEEDS PARALLEL RESULTS: Ray distributed computing results on HPC cluster]

Figure 1: H_2 potential energy surface computed with serial VQE implementation. The curve shows the characteristic bonding minimum near 0.74 Å and dissociation behavior at large bond lengths.

- [NEEDS PARALLEL RESULTS: Strong scaling plots showing speedup vs. number of processors]

- [NEEDS PARALLEL RESULTS: Efficiency analysis comparing actual vs. predicted performance]

6 Discussion

6.1 Physical Interpretation of Results

The computed potential energy surface captures the essential quantum chemistry of the H_2 molecule:

Equilibrium Geometry: The minimum energy occurs near $d_{eq} \approx 0.74$ Å, which matches the experimental bond length of 0.741 Å for ground state H_2. This close agreement shows that our VQE approach and choice of ansatz work well.

Bonding Energy: At equilibrium, the VQE energy is approximately $E_{eq} \approx -1.137$ Hartree (from the plotted curve). The exact energy for H_2 in the STO-3G basis is -1.1372 Hartree, showing our single-parameter ansatz achieves excellent accuracy.

Dissociation Behavior: As bond length increases beyond 2.5 Å, the energy approaches the limit where the two hydrogen atoms are separated. The curve shows the expected gradual approach to this limit, though our simple single-parameter ansatz has known limitations in accurately describing the dissociation region where electron correlation becomes very strong.

Ansatz Effectiveness: The double excitation ansatz with a single parameter works remarkably well for H_2 near equilibrium. This is because the most important correlation effect is both electrons moving together from the bonding (σ) to antibonding (σ^*) orbital, which is exactly what the double excitation operator captures.

6.2 Computational Performance Analysis

Serial Baseline: The serial implementation achieves 157.98 circuit evaluations per second, with each full VQE optimization (200 iterations) taking approximately 1.27 seconds. This establishes a solid baseline for parallel comparison.

Bottleneck Identification: Analysis shows that more than 95% of runtime is spent in the VQE optimization loops (running quantum circuits and computing gradients), with very little time spent on other tasks like generating the Hamiltonian or writing output files. This high fraction of parallelizable work ($f_p \approx 0.95$) is ideal for getting good speedups from parallelization.

Scalability Potential: The embarrassingly parallel structure of the outer loop means each bond length calculation can run independently without needing to communicate with other calculations. This allows for near-perfect scaling in the ideal case, limited only by:

- Serial fraction (startup time, plotting results)

- Load balancing (some bond lengths might take longer to converge than others)

- Communication overhead in distributed implementation

6.3 Relevance to Original Questions

Question 1: VQE Accuracy
Our results show that VQE with a simple ansatz successfully computes the H_2 potential energy surface with high accuracy near equilibrium. The single-parameter double excitation ansatz is sufficient for this simple molecule, confirming that the variational approach works well. This gives us confidence that the method can be extended to larger molecules with more complex ansatzes.

Question 2: HPC Parallelization
The serial implementation shows an embarrassingly parallel problem structure with more than 95% of runtime in independent bond length calculations. Using Amdahl's law, we predict significant speedups ($18.87\times$ on 40 processors), making this an excellent candidate for HPC optimization.

[NEEDS PARALLEL RESULTS: Once parallel implementations are complete, we will compare actual speedups against predictions, analyze where efficiency is lost, and identify the best parallelization strategies for quantum chemistry VQE calculations.]

7 Conclusions

This project successfully implemented and analyzed the Variational Quantum Eigensolver algorithm for computing the hydrogen molecule potential energy surface. Key conclusions include:

1. **Algorithm Validation:** The VQE implementation with a single-parameter double excitation ansatz accurately reproduces the H_2 potential energy surface, achieving near-exact energies at equilibrium bond lengths ($\sim$-1.137 Ha at 0.74 Å).

2. **Baseline Performance:** The serial implementation establishes clear performance metrics: 50.64 seconds total runtime, 157.98 circuit evaluations per second, and 1.27 seconds per bond length.

3. **Parallelization Opportunities:** The algorithm has excellent parallelization potential with more than 95% of runtime in embarrassingly parallel outer loop calculations. This structure makes parallelization straightforward.

4. **Predicted Speedups:** Theoretical analysis using Amdahl's law predicts speedups of $3.48\times$ (4 cores), $6.15\times$ (8 cores), and $18.87\times$ (40 cores), suggesting significant performance gains are achievable.

5. **Methodology for Scaling:** We identified a three-phase optimization strategy: (1) JAX JIT compilation for 2–$5\times$ gains, (2) multiprocessing for shared-memory parallelism, and (3) Ray distributed computing for cluster-scale parallelization.

[NEEDS PARALLEL RESULTS: Future work will implement and benchmark the three parallelization phases, test predicted speedups against actual measurements, and analyze where efficiency is lost. The results will show how effective HPC techniques are for speeding up quantum chemistry calculations and provide insights for scaling VQE to larger molecules.]

7.1 Broader Impact

This work shows how classical HPC techniques can dramatically speed up hybrid quantum-classical algorithms. While we focus on the hydrogen molecule, the parallelization strategies work for many other problems:

- Larger molecules with more bond lengths or geometric parameters to explore

- Multi-dimensional potential energy surfaces

- VQE calculations with more complex ansatzes that need longer optimization times

- Other variational quantum algorithms (like QAOA)

As quantum computing hardware improves and hybrid algorithms become more prevalent, efficient parallelization will be essential for practical quantum chemistry applications.

8 Acknowledgements

References

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