VQE – Molecular Energy Estimation

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1 Introduction

Quantum simulation is one of the most promising applications of near-term quantum computers. One of their biggest advantages is the ability to simulate molecular systems, a task that quickly becomes intractable for classical computers as system size increases. Accurately computing molecular energies is especially important because it helps us better understand chemical reactions, bonding, and material properties.

The Variational Quantum Eigensolver (VQE) is a hybrid quantum–classical algorithm designed to work within the limits of current noisy quantum hardware. [1, 2]. Rather than relying on deep circuits or full error correction, VQE uses a classical optimizer alongside a quantum circuit to evaluate energy expectation values, making it well-suited for near-term devices.

According to IBM, some of VQE's main strengths include its compatibility with modern hardware, its use of relatively shallow circuits [3]. (which reduces the impact of noise), and its versatility, since it can be applied to any problem that can be framed as an eigenvalue problem. However, VQE also has notable limitations: it is heuristic in nature, does not guarantee convergence to the true ground state, and often requires many parameters and measurements, which can make it expensive to run in practice.

2 Hamiltonian Formulation

In quantum mechanics, the Hamiltonian operator $\hat{H}$ describes the total energy of a system. This operator appears in Schrödinger's equation,

$$\hat{H}\Psi = E_n\Psi, \tag{1}$$

where E_n are the energy eigenvalues of the system. For molecular simulations, the primary goal is to determine the ground state energy, which corresponds to the lowest eigenvalue of the Hamiltonian.

Using the variational principle, the ground state energy can be written as

$$E_0 = \min_{|\psi\rangle} \langle\psi| \hat{H} |\psi\rangle . \tag{2}$$

This principle guarantees that the expectation value of the Hamiltonian with respect to any trial state provides an upper bound on the true ground state energy.

In practice, molecular Hamiltonians are mapped onto qubit operators using techniques such as the Jordan–Wigner transformations. After this mapping, the Hamiltonian can be expressed as a weighted sum of Pauli operators,

$$\hat{H} = \sum_i c_i P_i, \tag{3}$$

where c_i are real coefficients and P_i are tensor products of Pauli matrices. This form allows the Hamiltonian to be efficiently measured on quantum hardware. And with our simulation we were succeful in getting the Hamitonians for each of our 3 chosen molecules

3 Variational Quantum Eigensolver

The Variational Quantum Eigensolver is a hybrid algorithm that combines quantum state preparation with classical optimization. The algorithm consists of four main components:

- **Hamiltonian**: The operator whose ground state energy we aim to estimate.
- **Ansatz**: A parameterized quantum circuit that prepares a trial quantum state intended to approximate the ground state.
- **Estimator**: A procedure for computing expectation values of the Hamiltonian using measurements on the quantum circuit.
- **Classical Optimizer**: A classical routine that updates the circuit parameters to minimize the measured energy.

The VQE workflow is iterative. For a given set of parameters, the quantum computer prepares the ansatz state and measures the expectation value of the Hamiltonian. This value is then passed to a classical optimizer, which proposes new parameters. This loop continues until convergence is reached.

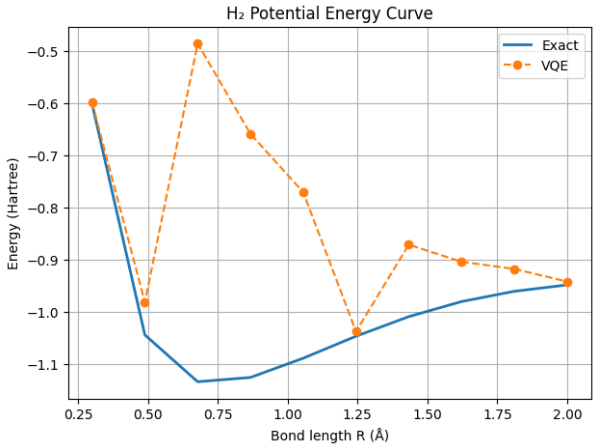

Figure 1: note that the large area at certain points far from equilbruim 0.75A

Below we also tested a comparison of depths and a compairson of optimizers (COBYLA and SPSA)

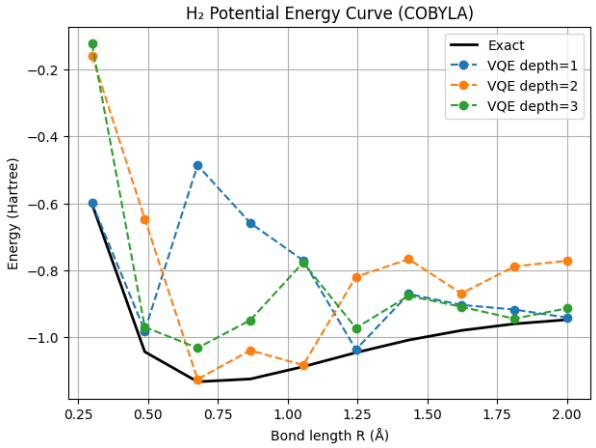

Figure 2: Note the increase in accuracy at higher depths

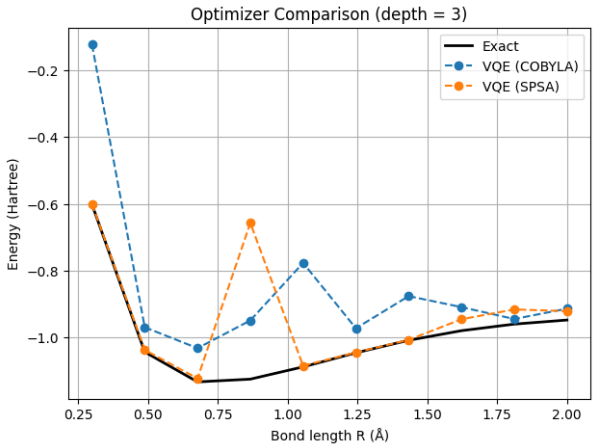

Figure 3: In this run we see that SPSA performed better

We also wanted to see how are own custom Ansatz to IBM's TwoLocal ansatz

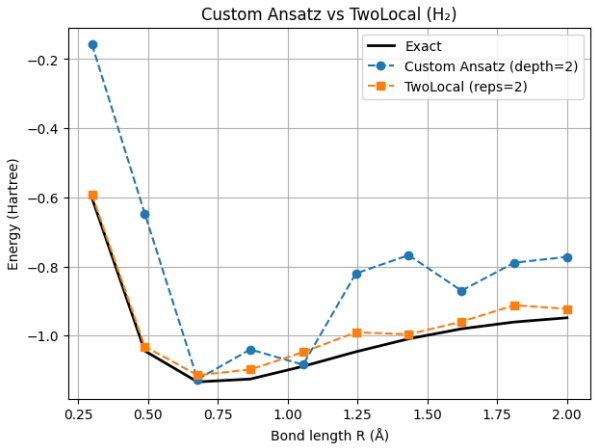

Figure 4: We see that the TwoLocal from IBM performed much better

4 Implementation Details

In this work, VQE was applied to several small molecular systems to study its performance and behavior. [4]. The implementation consists of three main aspects:

- **Hamiltonian construction**: Molecular Hamiltonians were built for three simple systems: H_2, LiH, and HeH^+. These molecules were chosen because they are small enough to be simulated exactly, allowing direct comparison with VQE results.
- **Ansatz and optimizer choice**: Two different ansätze were explored. A custom-built ansatz was implemented and compared against IBM's Two-Local ansatz. For optimization, the COBYLA and SPSA optimizers were used, as they are commonly employed in VQE and are well-suited for noisy environments.
- **Measurement strategy**: Expectation values were computed by measuring the individual Pauli terms of the Hamiltonian and summing the results weighted by their coefficients.

All simulations were performed using quantum circuit simulators, which allowed benchmarking against exact diagonalization results. This made it possible to evaluate both accuracy and convergence behavior.

5 Noise Analysis

One of the main challenges facing current quantum hardware is noise. Errors can arise from imperfect gate operations, decoherence, and readout inaccuracies. To understand how these effects influence VQE, noise models were introduced into the simulations.

The results show that noise generally degrades the accuracy of the estimated ground state energy and can slow convergence. In some cases, the optimizer may even converge to an incorrect minimum. These observations highlight the need for error mitigation techniques, such as measurement error correction and noise-aware optimization strategies, in practical VQE applications.

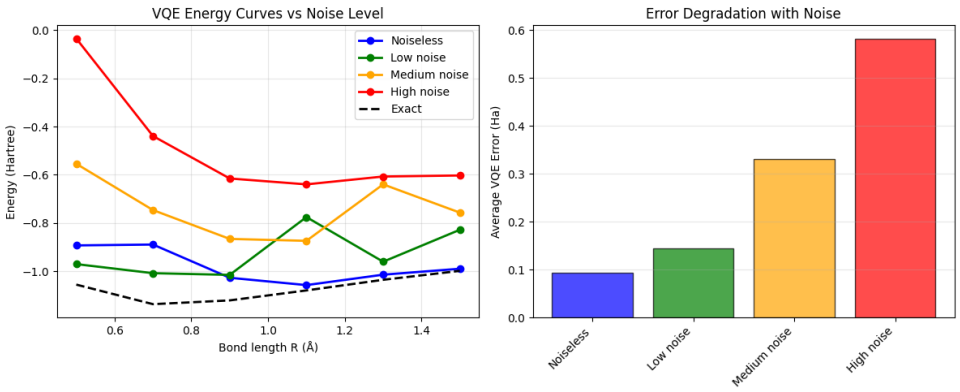

Figure 5: Can see how the less noise the better

6 Results

This section summarizes the results obtained from applying the Variational Quantum Eigensolver to the H_2 molecule under varying noise conditions. The algorithm was evaluated across multiple bond lengths, ansatz depths, and optimizers to assess both accuracy and robustness.

Table 1: VQE calculation summary for the H_2 molecule.

Quantity	**Value**
Estimated equilibrium bond length R_e (Å)	0.734878
Estimated energy $E(R_e)$ (Ha)	-1.137306
Number of bond lengths sampled	10
Number of ansatz depths tested	3
Number of optimizers tested	2
Total VQE calculations	60
Average error (depth = 2, COBYLA) (Ha)	0.186697

Equilibrium Geometry

The estimated equilibrium geometry for the H_2 molecule was found to be

$$R_e = 0.734878 \text{ Å}, \quad E(R_e) = -1.137306 \text{ Ha}.$$

For reference, the experimental equilibrium bond length of H_2 is approximately 0.741 Å, indicating good agreement with the VQE result.

Table 2: VQE energies and absolute errors for different noise levels.

Noise Level	R **(Å)**	$E_{\mathbf{VQE}}$ **(Ha)**	**Error (Ha)**
Low	0.50	-0.970148	0.085012
Low	0.70	-1.007773	0.128416
Low	0.90	-1.014751	0.105809
Low	1.10	-0.775265	0.303928
Low	1.30	-0.960267	0.074919
Low	1.50	-0.827785	0.170364
Medium	0.50	-0.554267	0.500893
Medium	0.70	-0.746214	0.389975
Medium	0.90	-0.865684	0.254877
Medium	1.10	-0.873694	0.205499
Medium	1.30	-0.639602	0.395585
Medium	1.50	-0.756753	0.241397
High	0.50	-0.035136	1.020023
High	0.70	-0.439310	0.696880
High	0.90	-0.615164	0.505397
High	1.10	-0.639587	0.439606
High	1.30	-0.607083	0.428103
High	1.50	-0.602740	0.395409

Table 3: Performance degradation as a function of noise level.

Noise Level	**Average Error (Ha)**	**Increase (%)**
Noiseless	0.092592	0.0
Low noise	0.144741	56.3
Medium noise	0.331371	257.9
High noise	0.580903	527.4

Observations

- Noise introduces significant error into the VQE optimization process, particularly due to depolarizing and readout errors.
- The impact of noise is non-linear, with higher noise levels leading to disproportionately larger errors.
- As noise increases, more optimizer iterations are required to achieve convergence.
- At high noise levels, the optimizer may converge to incorrect local minima.
- These results motivate the use of error mitigation techniques in practical VQE implementations.

7 Conclusion

In this report, the Variational Quantum Eigensolver was applied to molecular energy estimation problems. The formulation of molecular Hamiltonians, the structure of the VQE algorithm, and the impact of noise were discussed. While noise remains a major obstacle for near-term quantum devices, VQE continues to be a promising approach for quantum chemistry simulations. With improvements in hardware and error mitigation, VQE may play a significant role in future quantum applications.

References

[1] Alberto Peruzzo, Jarrod McClean, Peter Shadbolt, et al. A variational eigenvalue solver on a photonic quantum processor. *Nature Communications*, 5:4213, 2014.

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[3] IBM Quantum. Quantum diagonalization algorithms: Variational quantum eigensolver. `https://quantum.cloud.ibm.com/learning/en/courses/quantum-diagonalization-algorithms/vqe`, 2023. Accessed: 2024.

[4] Qiskit Community. Qiskit nature documentation. `https://qiskit-community.github.io/qiskit-nature/`, 2023. Accessed: 2024.