

PH044

Modelling the Hydrogen Molecule (H_2) with
Quantum Circuits

1 Introduction

Quantum computers are a rather recent development, and refers to computational devices that use qubits (quantum bits) rather than classical bits. The distinguishing factor between a conventional bit and a qubit is its ability to exhibit quantum properties, such as superposition and entanglement. These properties offer them a remarkable edge when utilised in certain computational tasks such as prime factorisation and more recently, in quantum chemistry simulations.

Quantum chemistry is a branch of quantum computing which explores the electronic structures and interactions of molecules through properties such as bond distances, reaction rates, and potential energy curves. To understand how molecules behave in various physical and chemical settings, one can solve for its ground state energy as molecular characteristics can be derived from there. To find its ground state energy, it would be necessary to solve and minimise its Hamiltonian, which contains terms representing kinetic and potential energy for the electrons and nuclei involved.

Traditionally, methods of solving involve experimental measurements or classical computations. In the case of classical computation, its limitations become apparent when dealing with larger molecules as the resources required to simulate these systems grow exponentially. But that is not the case for quantum computers, as they are in fact able to exploit the shared quantum properties between an atom and a qubit to provide more effective and efficient solutions.

However, current quantum computers are also extremely susceptible to noise which can arise from a multitude of factors due to their high sensitivity. Some examples include qubit decoherence, gate imperfections, and environmental interference.

In this paper, we will calculate the ground state energy of the Hydrogen molecule (H₂) through the use of the Variational Quantum Eigensolver (VQE), a hybrid quantum-classical algorithm. The choice of VQE was due to its emergence as a promising approach to compute ground-state energies, and its balance of using both classical and quantum computational forms. After which, we will draw conclusions for the accuracy of our quantum circuit when the relaxation time of the quantum computer is varied.

2 Modelling the H₂ system

To formulate the Hamiltonian in a form suitable for quantum computation, we start with the classical Hamiltonian for an N -electron molecular system, incorporating kinetic energy and Coulomb interactions.

2.1 Potential Energy

The potential energy of a system of electrons and nuclei arises from the electrostatic interactions between the charged particles. There are 3 components, electron-electron repulsion, nuclear-nuclear repulsion, and electron-nuclear attraction. Coulomb's law $V = \frac{q_1 q_2}{4\pi\epsilon_0 r}$ can be used to calculate their potential energy:

$$\hat{V} = \underbrace{\sum_{i,j}^{\text{electrons}} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|}}_{\text{electron-electron repulsion}} + \underbrace{\sum_{i,j}^{\text{nuclei}} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |R_i - R_j|}}_{\text{nuclear-nuclear repulsion}} - \underbrace{\sum_i^{\text{electrons}} \sum_j^{\text{nuclei}} \frac{Z_j e^2}{4\pi\epsilon_0 |r_i - R_j|}}_{\text{electron-nuclear attraction}}$$

2.2 Kinetic Energy

The kinetic energy of the system is divided into kinetic energy of the nuclei and the electrons.

$$\hat{T} = - \sum_i^{\text{nuclei}} \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_i^{\text{electrons}} \frac{\hbar^2}{2m_e} \nabla_i^2$$

2.3 Molecular Hamiltonian

To make this less computationally intensive, we used the Born-Oppenheimer Approximation to assume that the the motion of the nuclei is negligible compared to that of the electrons, given that the nuclei have much greater mass compared to electrons. Thus, we can treat the nuclei as stationary points in space, removing the kinetic energy term for the nuclei. Furthermore, we can now approximate the nuclear-nuclear repulsion energy as a constant C'_n , since the positions of the nuclei are now considered fixed. We will also use atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$) to make calculations more convenient.

Now, only the kinetic energy term of the electrons, the electron-electron repulsion term, and the electron-nuclear attraction term remain.

$$\hat{H} \approx - \sum_i^{\text{electrons}} \frac{1}{2} \nabla_i^2 + \sum_{i,j}^{\text{electrons}} \frac{1}{|r_i - r_j|} - \sum_i^{\text{electrons}} \sum_j^{\text{nuclei}} \frac{Z_j}{|r_i - R_j|} + C'_n$$

This Hamiltonian, however, does not account for the quantum mechanical nature of fermions (electrons). Furthermore, directly solving it “as is” is very complicated because we would have to consider all electrons moving in continuous space and their pairwise interactions. To incorporate the Pauli exclusion principle and make the problem more tractable, we convert this Hamiltonian into its second quantised form.

2.4 Second Quantisation

We use a set of known, simpler functions called orbitals. Each orbital $\phi_p(\mathbf{r})$ is like a “shape” in space that an electron can occupy. By choosing a finite set of these orbitals (for example a standard set known as STO-3G), we create a discrete basis that can be combined to approximate the full wave function of all electrons. Instead of allowing electrons to roam freely in 3D space, each electron is described as a combination of these chosen orbitals. Note that the orbitals are not just some arbitrary function, they are solutions to the Schrodinger equation.

By rewriting the original Hamiltonian in terms of these orbitals, we obtain integrals that describe how each pair of orbitals interact. For instance, the one-electron integral h_{pq} which represents how orbital p and orbital q interact through kinetic energy and the attraction to the nuclei is:

$$h_{pq} = \int \phi_p^*(r) \left(-\frac{1}{2} \nabla^2 - \sum_j^{\text{nuclei}} \frac{Z_j}{|r_i - R_j|} \right) \phi_q(r) d^3r$$

Similarly, the two-electron integral which represents how pairs of electrons in orbitals (p, q) interact with pairs in orbitals (r, s) is as follows:

$$h_{pqrs} = \int \int \phi_p^*(r_1) \phi_q^*(r_2) \frac{1}{|r_1 - r_2|} \phi_r(r_2) \phi_s(r_1) d^3r_1 d^3r_2$$

By computing these integrals once, we obtain the information needed to build a discrete, matrix-like representation of the molecular Hamiltonian. Using these integrals, we rewrite the Hamiltonian in second-quantized form, in terms of creation and annihilation operators, a_p^\dagger and a_q , which add or remove an electron from an orbital p or q which is easier to handle on quantum computers:

$$H = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

3 Ansatz Preparation

3.1 Fermionic Mapping

Fermionic systems, such as electrons in molecular orbitals, are inherently different from qubit systems due to their anti-commutative behavior. To simulate molecular systems on quantum computers, fermionic creation and annihilation operators must be mapped to qubit operators while preserving these relations.

3.2 Jordan-Wigner Transformation

A tool commonly used in fermionic simulations is the Jordan-Wigner Transformation (JWT). The JWT is able to “translate” a Fermionic Hamiltonian to a Spin Hamiltonian (which is equivalent to a system of qubits) while preserving the anticommutative laws through exploiting the properties of the creation and annihilation operators. This is crucial as quantum systems run on qubits, which were not designed with anticommutative constraints whereas fermions naturally follow anticommutative rules. In essence, this transformation ensures the accuracy of Quantum-Chemistry simulations through “forcing” anticommutative laws to hold true for the qubit system.

Before we start, let’s first briefly go through the use of the two aforementioned operators.

The creation operator (a_p^\dagger) adds a fermion to site p if it is unoccupied ($0 \rightarrow 1$) and returns 0 otherwise ($1 \rightarrow 0$):

$$\begin{aligned} \tilde{a}_p |z_0 \dots, z_{p-1}, 1, z_{p+1}, \dots, z_{N-1}\rangle \\ = (-1)^{\sum_{q=0}^{p-1} z_q} |z_0 \dots, z_{p-1}, 0, z_{p+1}, \dots, z_{N-1}\rangle \\ \tilde{a}_p |z_0 \dots, z_{p-1}, 0, z_{p+1}, \dots, z_{N-1}\rangle = 0. \end{aligned}$$

Conversely, the annihilation operator (a_p) removes a fermion from site p if it is occupied ($1 \rightarrow 0$) but also returns 0 otherwise ($0 \rightarrow 0$):

$$\begin{aligned} \tilde{a}_p^\dagger |z_0, \dots, z_{p-1}, 0, z_{p+1}, \dots, z_{N-1}\rangle \\ = (-1)^{\sum_{q=0}^{p-1} z_q} |z_0, \dots, z_{p-1}, 1, z_{p+1}, \dots, z_{N-1}\rangle \\ \tilde{a}_p^\dagger |z_0, \dots, z_{p-1}, 1, z_{p+1}, \dots, z_{N-1}\rangle = 0 \end{aligned}$$

The above are also equivalent to the following equations, which is the form that we will be using in

the JWT due to its use of Pauli Z operators which allows for sign flips otherwise unachievable. These equations are also known as Pauli strings.

Creation operator applied at spin-orbital j :

$$a_j^\dagger = \frac{1}{2}(X_j - iY_j) \prod_{k=0}^{j-1} Z_k$$

Annihilation operator applied at spin-orbital j :

$$a_j = \frac{1}{2}(X_j + iY_j) \prod_{k=0}^{j-1} Z_k$$

Where X_j and Y_j are the Pauli X and Y operators acting on qubit j , representing the bit-flip needed to change the state. $\prod_{k=0}^{j-1} Z_k$ is the parity operator for all qubits preceding j that changes the wavefunction's sign if the number of electrons in preceding modes is odd.

3.3 Parity Mapping

While the Jordan-Wigner Transformation uses parity in the form of Pauli Z operators, it can be resource intensive for larger systems due to the long Z -operator strings, as each value in the string corresponds to one qubit. To reduce the qubit requirements, we can employ parity mapping. Instead of JWT's fermion-qubit mapping, parity mapping encodes the electron parity of the orbital groups.

For the H₂ molecule in the STO-3G basis, which initially requires four spin-orbitals, parity mapping reduces the qubit requirement from four to two since 1) spin must be conserved and 2) the total number of electrons in this molecule is fixed at two. Both electrons are also located in the same orbital lobe (since H₂'s lowest molecular orbital where the electrons are located in only has one lobe), making them spatially symmetric. Meanwhile, Pauli's Exclusion Principle forces them to have opposite spins which gives an antisymmetry. As parity is given by both the spatial and the spin components, with symmetry being even and antisymmetry being odd, this gives an odd parity for the whole system.

This also has the added benefit of eliminating unrealistic electronic configurations as without this mapping, the quantum computer will simulate all available configurations (such as by allowing a state where all four orbitals are occupied). This reduces the computational time greatly as a significant portion of configurations are now removed.

3.4 Unitary Coupled Cluster Ansatz

The Unitary Coupled Cluster (UCC) ansatz is one of the most widely used approaches for simulating molecular systems in VQE. It is based on Coupled Cluster Theory, which approximates the wavefunction of a molecule by applying an exponential operator to a reference state.

The cluster operator T encodes electronic excitations. For single (T_1) and double (T_2) excitations, it is written as:

$$T = T_1 + T_2 = \sum_{i,a} \theta_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{i,j,a,b} \theta_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

where i, j are occupied spin-orbitals in the reference state, a, b : virtual (unoccupied) spin-orbitals, and θ_i^a , θ_{ij}^{ab} are variational parameters determining the weight of excitations.

For the specific case of H₂, the Hartree-Fock (HF) reference state is $|\Phi_{\text{HF}}\rangle = |1100\rangle$, where the two electrons occupy the lowest-energy spin-orbitals.

Since the original equation is not unitary, which means that it cannot be ran on a quantum computer, the equation is modified to become

$$|\Psi_{\text{UCC}}\rangle = e^{T-T^\dagger} |\Phi_{\text{HF}}\rangle$$

which is unitary. The operator $T - T^\dagger$ includes both excitations (T) and de-excitations (T^\dagger), ensuring that the operation preserves the norm of the wavefunction.

3.5 Energy Measurement

After preparing the trial state $|\Psi(\vec{\theta})\rangle$, the next step is to measure the energy expectation value of the Hamiltonian H :

$$E(\vec{\theta}) = \langle \Psi(\vec{\theta}) | H | \Psi(\vec{\theta}) \rangle$$

This is done by measuring the quantum circuit in different computational bases and averaging the results. Specifically, each qubit would have an expected value in the Pauli X and Z bases. These values are plugged into the Hamiltonian that was expressed in Pauli operators to obtain its energy expectation value.

4 Methodology

Originally, we expected to run and collect data from both classical and quantum devices. This would enable us to have a holistic assessment of the differences between the two devices when running a quantum circuit. Unfortunately, our plan to run the circuit on the quantum computer in our mentor's lab fell short due

to logistical complications. Publicly available quantum computers on the cloud such as IBM Quantum have a time limit which our circuit exceeds.

Therefore, we only simulated the quantum circuit on a classical machine. This can be achieved as wavefunctions can be expressed as sum of vector states, quantum gates are equivalent to matrix operations, and measurements can be taken by sampling the wavefunction distribution. For the Hydrogen molecule, the computational resources required is achievable on our devices, and so that was how we obtained our data. Thus, for the results section, all data collected were from our classical simulation of the quantum circuit that models the Hydrogen molecule.

5 Results

5.1 Energy Landscape

Using the VQE, we varied the internuclear distance between the two hydrogen atoms to determine the minimum energy at each point, generating the energy landscape of the H_2 molecule. The plot compares the Self-Consistent Field (SCF) energy and the VQE energy against reference energies: the Hartree-Fock (HF) energy and the Full Configuration Interaction (FCI) energy.

The SCF energy lies consistently above the VQE energy because the SCF energy neglects electron correlation effects in the mean-field approximation. In contrast, the VQE energy, which accounts for electron correlation, closely approximates the exact FCI energy. The FCI energy represents the exact ground state energy within the chosen basis set. Notably, the VQE energy achieves a minimum value of -1.1371 Hartree, deviating from the FCI energy by only 0.01346%, demonstrating the effectiveness of the VQE approach.

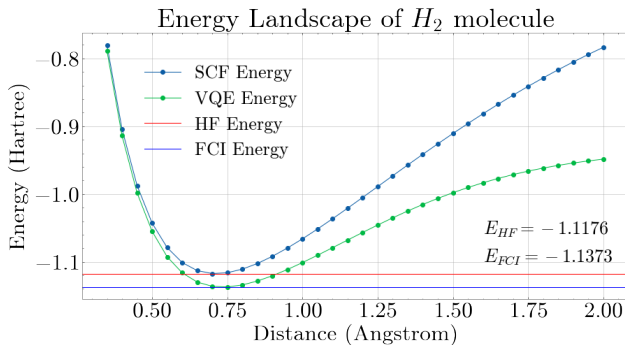


Figure 1: Self-Consistent Field (SCF) approximated energy and the energy obtained from the Variational Quantum Eigensolver (VQE)

We aimed to determine the true ground state energy of the molecule, which also allows us to identify the molecule's optimal geometry by locating the minimum of the VQE energy curve. In real-world applications, quantum computers are subject to the probabilistic nature of measurement (also known as shot noise), which can introduce irregularities in the energy curve and complicate the process of accurately identifying the minimum. To mitigate this, we chose to simultaneously optimize the excitation parameters and the internuclear distance, a feature not readily available in existing libraries. Furthermore, the Simultaneous perturbation stochastic approximation (SPSA) optimization algorithm was used due to its effectiveness in optimizing noisy systems.

The simulation converged to an energy of -1.1360 Hartree, corresponding to an error of 0.1101% compared to the exact result. The optimized bond length was found to be 0.7558 Å, with a 1.947% error relative to the true ground state bond length of 0.7414 Å. These results demonstrate the feasibility and accuracy of our approach despite the presence of simulated shot noise.

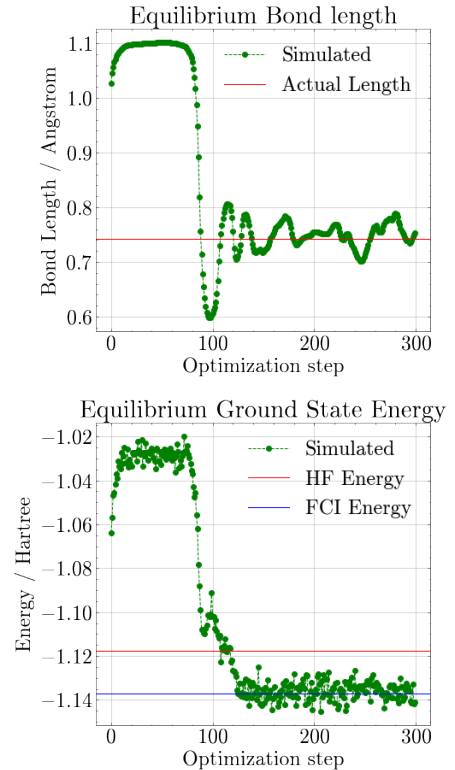


Figure 2: Optimization of bond length and ansatz parameters to converge to the true ground state energy for one run

Another major source of noise is decoherence. T1 and T2 relaxation times are critical parameters in characterizing this type of noise.

T1 time is the time constant associated with energy relaxation, where a qubit in an excited state $|1\rangle$ decays to the ground state $|0\rangle$. It represents the lifetime of the excited state of the qubit and affects the qubit's ability to retain information.

T2 time is the time constant associated with dephasing, where the relative phase between the qubit's superposition states is lost. It affects the coherence of quantum superpositions and gate fidelity. Varying the relaxation times, keeping $T1 = 2T2$, and finding the true ground state energy, we obtain the following graph with an interesting correlation.

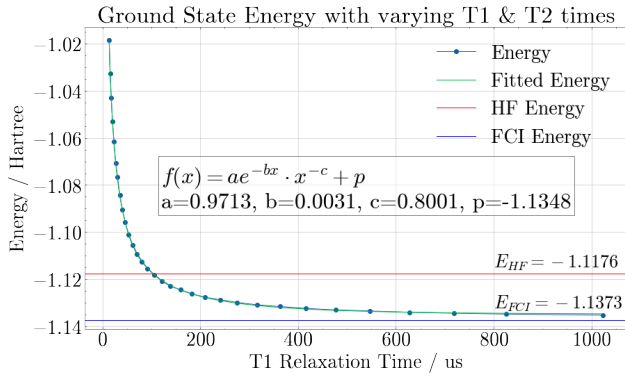


Figure 3: Noise graph with our fitted equation

Considering the lack of data from a true quantum computer, we are unsure of the relevance of Figure 3

7 Appendices

7.1 Derivation of Kinetic Energy Operator

Since classically, kinetic energy in the x -direction $T_x = \frac{P_x^2}{2m}$, and the quantum momentum operator $\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$, so

$$\hat{T}_x = \frac{\hat{P}_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

If the particle is moving in 3 dimensions, then $P = \vec{x}P_x + \vec{y}P_y + \vec{z}P_z$ and the total momentum and kinetic energy operator would respectively be

$$\hat{P} = -i\hbar(\vec{x}\frac{\partial}{\partial x} + \vec{y}\frac{\partial}{\partial y} + \vec{z}\frac{\partial}{\partial z}) = -i\hbar\nabla$$

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$$

when it is actually put into application. This is an aspect that we would like to investigate further into if possible, so that we can deduce whether this correlation applies to a real quantum device.

But if we were to assume that what we have observed here does apply to true quantum computers, this would be quite significant. T1 time can be decreased by introducing randomness or noise, so one can obtain multiple (albeit low) values from the same quantum computer and use these values to graph out what a more accurate result would look like. The exponential nature of the graph also means that it is largely dependent on the results from the lower T1 times, which is beneficial to quantum computers with low T1 times. In fact, most quantum computers do suffer from low T1 relaxation timings, hence this new method of graphical analysis can be used to acquire more accurate results. In other words, this means that low T1 time (and by extension hardware) would be less of a constraint towards accuracy for further computations involving low T1 quantum computers.

6 Conclusion

Given the aforementioned significance, we hope that more research can be done in this area to validate the findings presented in this report. If instead they indicate that this graph only applies for classical devices simulating quantum circuits, further investigation into current methods of classical to quantum simulations might be necessary since this discrepancy would imply that there are still areas of improvement to ensure that the quantum properties are being modelled correctly in a classical environment.

7.2 Circuit Representation

To model the H_2 molecule, we used this circuit:

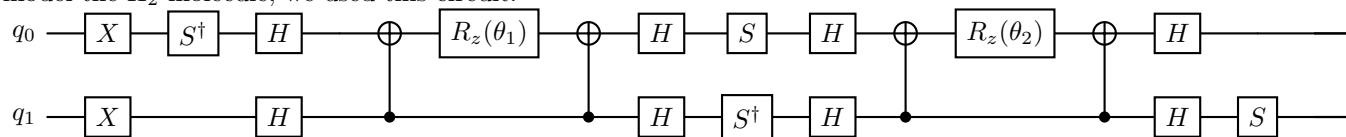


Figure 1. The circuit representation of our Hamiltonian

7.3 Code Used

All the code that we have used to obtain our data is located in this repository attached here:

<https://github.com/TheTrustyPwo/Hydrogen>

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[1] [2] [3] [4] [5] [6]