Estimation of Ground State Energy of Molecules using a Variational Quantum Eigensolver Method on IBM's Quantum Computer

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Abstract

We investigate estimating the ground state energy, the lowest energy possible, for a molecule. To do this we use a estimation method known as a Variational Quantum Eigensolver (VQE), a method that finds a upper bound of the ground state energy given a parameter that we choose. Using this method we aim to recreate previously seen results on IBM's quantum computer, investigating the ground state energy of the H_2 molecule. We find a ground state energy of -1.1 Ha for a bond length of 0.75 Angstroms, which matches the predictions from numerical calculations. We then graph the ground state energy against a parameter θ and bond length r and find this too matches theory.

Introduction

The ground state energy of the hydrogen atom can be found analytically, but for more complicated systems numerical methods must be used. With this research we use one of many numerical methods to find the ground state energy of a molecule. We do this via the VQE method, a method that finds the upper bound on the ground state energy. This method implements the variational principle method on a quantum computer to find the upper bound on the ground state energy. We want to use this method to find a estimation of the ground state energy for a molecule.

Efficient simulation of physical systems, such as molecular energies, is one of the most desired applications of quantum computer. Finding such properties of a molecule has many uses and, in this case, finding a numerical estimations for molecular energies allows numerical predictions of chemical reaction rates [1]. Furthermore such investigations can allow for greater understanding of chemistry, allowing us to investigate classical intractable molecules, which can have commercial value [2].

There have been several investigations into this matter, with previous studies using these same techniques to find the ground state energy of H_2O [3] and a hydrogen molecule [4]. This work yielded the ground state energy of these molecules with extreme accuracy while using very few qubits. Furthermore research has demonstrated that useful uses of quantum computing is becoming more and more practical.

In this project we use this previous research as a guideline. We investigate how previous work was conducted on a quantum machine. We hope to replicate this analytically and see if we can replicate

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their results on the IBM's quantum computers using IBM's Q-experience machine. Once we know that this works we hope to extend these results on a separate molecule.

Theory

In order to find the ground state energy of a molecule we start with the Hamiltonian of the molecule. The exact form of this Hamiltonian depends on the molecule but can be described via this same method. For the H_2 molecule the Hamlitonian is

$$
\begin{aligned}
H = & -\sum_i \frac{\nabla^2_{R_i}}{2M_i} - \sum_i \frac{\nabla^2_{r_i}}{2} - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} \\
& + \sum_{i,j>i} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i,j>i} \frac{1}{|r_i - r_j|}
\end{aligned} \quad (1)
$$

where R_i, M_i, Z_i are the positions, masses, and number of protons of the nuclei respectfully and r_i are the positions of the electrons. This is a second order partial differential equation, and cannot be solved analytically due to its complexity; the interactions between all parts of the molecule mean that the process become intraceable. We must use numerical methods to find the ground state energy of this molecule.

We obtain an upper bound on the ground state energy with this Hamiltonian using the Variation Eigensolver method which states:

$$
\langle H \rangle = \frac{\langle \psi(\theta)|H|\psi(\theta)\rangle}{\langle \psi(\theta)|\psi(\theta)\rangle} \geq E_0, \quad (2)
$$

where E_0 is the ground state energy and $|\psi(\theta)\rangle$ is an ansatz with parameter θ. We seek to minimize this with respect to θ to get the tightest bound on our ansatz.

In order to implement this method on a quantum computer we must define both the ansatz, the Hamiltonian in terms of a series of quantum gates that can be implemented on a quantum computer, and a specific initial state. We first transform our Hamlitonian into the second quantized form [4]

$$
H = \sum_{pq} h_{pq} a^\dagger_p a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a^\dagger_p a^\dagger_q a_r a_s \quad (3)
$$

where $a^\dagger_i$ and a_j are the fermion creation and annihilation operators respectfully, with the anti-commutation relations of $\{a_i^\dagger, a_j\} = \delta_{ij}$ and $\{a_i^\dagger, a_j^\dagger\} = \{a_i, a_j\} = 0$, and the h terms come from integrals taken over the spatial part of the Hamiltonian. Then we employ the Bravyi-Kiatev transformation which writes the Hamiltonian in terms of qubit operators [5],

$$
H = g_0 + g_1 Z_0 + g_2 Z_1 + g_3 Z_0 Z_1 + g_4 Y_0 Y_1 + g_5 X_0 X_1 \quad (4)
$$

where g_n are real scalars that are functions of the hydrogen molecule bond length that can be computed classically, and (X_i, Z_i, Y_i) denote Pauli matrices acting on the ith qubit. We can then find the expectation values of the Hamiltonian by taking the expectation of all $(X_i Z_i Y_i)$ terms in the equation.

The ansatz has been defined previously as a quantum circuit [4] $U(\theta)$ acting on an initial state $|01\rangle$. Using the same definition, used in *O'Malley et. al.*, we define this state as

$$
|\psi\rangle = e^{-i\theta X_0 Y_1} |01\rangle, \quad (5)
$$

where X_0 is a Pauli X gate acting on the 0th qubit (the right most qubit) and Y_1 is a Pauli Y gate acting on the 1st qubit (the left most qubit), and $|01\rangle$ is the initial state.

Using this, we need to get the expectation values of (X_i, Z_i, Y_i) for Eq. 4. We can do this classically with little issue. However implementing this device on a quantum machine allows us to check the viability of such a method on more complicated molecules that perhaps cannot be calculated classically. With this in mind we seek to implement our state $|\psi\rangle$ on a quantum device to find our expectation values need for Eq. 4.

Implementation

The implementation of the ansatz state is shown in Fig. 1 and the implementation of the same system in the IBM quantum computer is seen Fig. 2 for a $\theta = \frac{\pi}{3}$ rotation. To find the expectation values using a quantum machine we find the probabilities that certain

outcomes will be measured. The IBM machine returns the states $|0\rangle$ and $|1\rangle$ for a single qubit. For two qubits the states $|00\rangle, |01\rangle, |10\rangle$, and $|11\rangle$ are possible. For each state we assign them a value of either 1 or -1 to multiply there probabilities by and we add them together to find their expectation value. States $|0\rangle, |00\rangle$, and $|11\rangle$ have a +1 multiplier while states $|1\rangle, |01\rangle$, and $|10\rangle$ have a -1 multiplier. For example the expectation value of Z_0 is

$$\langle Z_0\rangle = prob(0) \times 1 + prob(1) \times -1, \quad (6)$$

where $prob(0)$ is the probability of measuring 0 and $prob(1)$ is the probability of measuring 1. The output of the IBM machine will give us the probabilities required to compute the expectation values required for the Hamiltonian, as shown in Eqs. (7)-(10)

$$\langle Z_1\rangle = prob(0) \times 1 + prob(1) \times -1, \quad (7)$$

$$\langle Z_0 Z_1\rangle = prob(00) \times 1 + prob(01) \times -1 \\ + prob(10) \times -1 + prob(11) \times 1, \quad (8)$$

$$\langle X_0 X_1\rangle = prob(00) \times 1 + prob(01) \times -1 \\ + prob(10) \times -1 + prob(11) \times 1, \quad (9)$$

$$\langle Y_0 Y_1\rangle = prob(00) \times 1 + prob(01) \times -1 \\ + prob(10) \times -1 + prob(11) \times 1. \quad (10)$$

We us the fact that Eq. 5 can be written as

$$e^{-i\theta X_0 Y_1} |01\rangle = \cos\theta |01\rangle - \sin\theta |10\rangle \quad (11)$$

to express these expectation values in terms of trigonometric functions,

$$\begin{aligned} \langle Z_0\rangle &= -\cos\theta \\ \langle Z_1\rangle &= \cos\theta \\ \langle Z_0 Z_1\rangle &= -1 \\ \langle X_0 X_1\rangle &= -\sin\theta \\ \langle Y_0 Y_1\rangle &= -\sin\theta \end{aligned} \quad (12)$$

Results

The output for the IBM machine (simulation) for the $\frac{\pi}{3}$ case is seen in Fig 3. The simulator is a virtual quantum machine that uses quantum theory to simulate how gates run on a physical quantum machine, this includes artificial noise to simulate the error found in these physical devices. It should be noted that the angle used in IBM's machine is $\frac{2\pi}{3}$. The reason it is different from the angle stated above is because the ansatz used in *O'Malley et. all* neglects the $\frac{\theta}{2}$ term in the rotation gate. Instead the $\frac{1}{2}$ term is absorbed into the θ. This simply means that the angle used in the IBM machine's rotation gates, must be twice the angle we use in our state. This is because the IBM rotation gates keep the $\frac{1}{2}$ term in their rotation, and we must account for this. Using these facts, we are able to calculate the expectation value of the Hamiltonian and therefore the upper bound on the ground state energy of the molecule. Using Eq. 4 with g_n values for bond length of 0.75 angstroms given by *O'Malley et. al*, i.e

$$\begin{aligned} g_0 &= 0.2252 \\ g_1 &= 0.3435 \\ g_2 &= -0.4347 \\ g_3 &= 0.5716 \\ g_4 &= g_5 = 0.091 \end{aligned} \quad (13)$$

we obtain

$$\begin{aligned} \langle Z_0\rangle &= -0.506 \\ \langle Z_1\rangle &= 0.506 \\ \langle Z_0 Z_1\rangle &= -1 \\ \langle X_0 X_1\rangle &= -0.8662 \\ \langle Y_0 Y_1\rangle &= -0.8695 \end{aligned} \quad (14)$$

With these results we calculate

$$\langle H\rangle = \langle\psi(\theta)|H|\psi(\theta)\rangle = -0.11\,Ha \geq E_0 \quad (15)$$

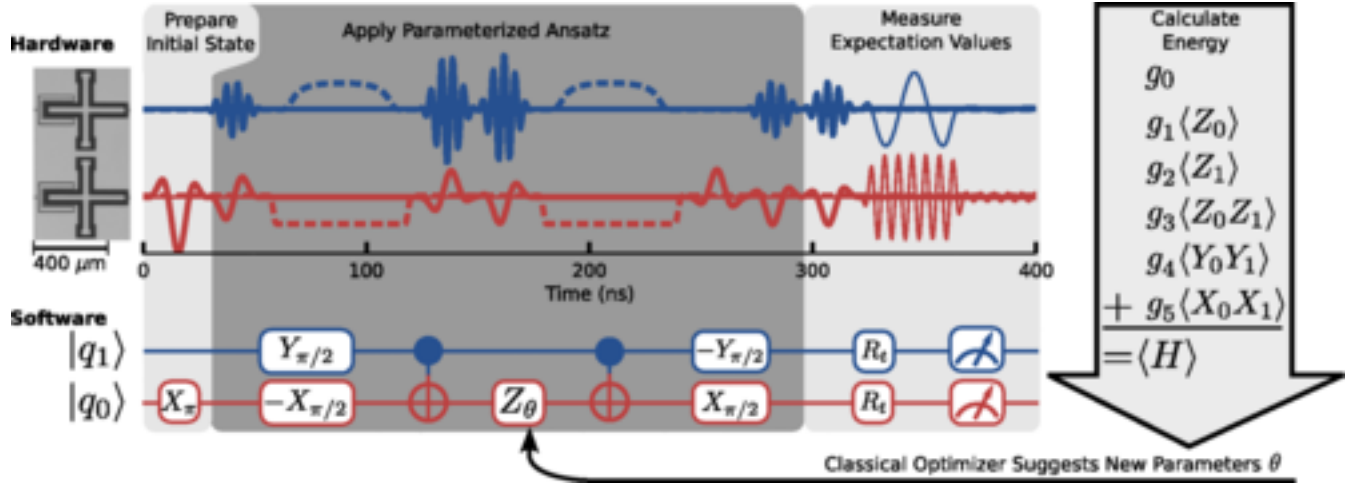which is comparable to theoretical value of $-0.125\,Ha$.

Figure 1: Quantum circuit that implements the ansatz parameter for molecular hydrogen. The R_t gates change if the measurements are in the X,Y or Z basis. O'Malley, P.J.J. et al. "Scalable Quantum Simulation of Molecular Energies." Physical Review X 6.3 (2016)

We can now use this same procedure on a physical quantum device. Using IBM's Vigo 5 qubit machine we investigate the expectation values as discussed above, and see if how they change as θ changes. If the graph we produce matches the theoretical values seen in Eq. 12 then we can say with confidence that this method can be implemented on IBM's machine and we can create a full landscape of how $\langle H \rangle$ changes with r and θ.

To do this we write a Python code using the qiskit python package, allowing us to scan θ and obtain expectation value for each. The results of this code being ran on IBM's Vigo machine can be seen in Fig. 4.

We obtain $\langle H \rangle$ as a function of θ using Eq. 13 and 4. The results match with the theoretical values seen in Eq. 12, allowing us to use these results to obtain further results, by using the same constants of $g_i s$ for a bond length of 0.75 angstroms we are able to obtain a graph of how $\langle H \rangle$ changes with θ. The results of this are seen in Fig. 5.

In this case our ground state energy is bounded between a maximum of 0.4 and a minimum of -1.1, this minimum is what our best estimate of the ground state energy for a bond length of 0.75 angstroms, cor-

responding to a $\theta = 0.5$. This lies within range of the results of [4] and theory. It should be noted however that looking at angle $\theta = \frac{\pi}{3}$, the value we ran the simulator at to get the result in Eq. 15, the expectation value of H is much smaller than the simulation indicating larger error in the results from the physical machine than the simulator.

We extend $\langle H \rangle$ to be a function of θ and bond length r, this is seen in Fig. 6. as a heat map, and is zoomed in on a region of the minimum as seen in Fig 7. We can compare this to a similar figure from [4] in Fig 8. and it is apparent that the two are similar to one another, indicating that the IBM machine is able to replicate previous results.

Our final goal is to minimize error in our results, to do this we redefine our parameter state in terms of different gates then before. Our new circuit is seen in Fig. 9, the results for the expectation value are seen in Fig. 10 as ran on a simulator to show that the two circuits are equivalent. The results of running it one the Vigo machine are seen in Fig. 11 and 12, where Fig. 11 shows the expectation values as a function of θ and Fig. 12 shows the ground state energy as a function of θ both are at a bond length of 0.75 angstroms. In both figures we can see that

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the error has increased from the previous circuit. We expected the error to be smaller since the new circuit has few gates, this contradiction is the subject to future research.

Conclusion

Results from the IBM machine matches previous results from [4] and matches theoretical results. This indicates that this process can be implemented successfully on IBM's quantum devices. Trying the same method with a new circuit resulted in greater error than previously. The reason for this is the subject of future research, in order to minimize error and use this method with other molecules.

References

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[2] L. Mueck, Quantum Reform, Nat. Chem. 7, 361 (2015).

[3] Nam, Y., Chen, J., Pisenti, N.C. et al. Ground-state energy estimation of the water molecule on a trapped-ion quantum computer. npj Quantum Inf 6, 33 (2020). https://doi.org/10.1038/s41534-020-0259-3

[4] O'Malley, P.J.J. et al. "Scalable Quantum Simulation of Molecular Energies." Physical Review X 6.3 (2016):

[5] Seeley, Jacob T., Martin J. Richard, and Peter J. Love. "The Bravyi-Kitaev Transformation for Quantum Computation of Electronic Structure." The Journal of Chemical Physics 137.22 (2012): 224109.
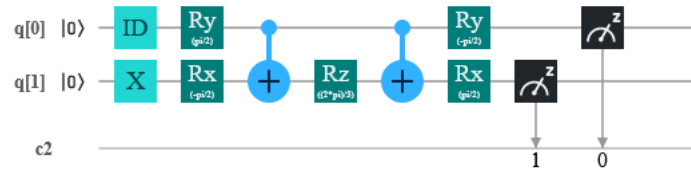
(a) Circuit on IBM machine for the Z basis measurement
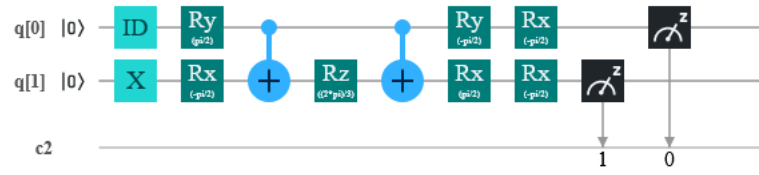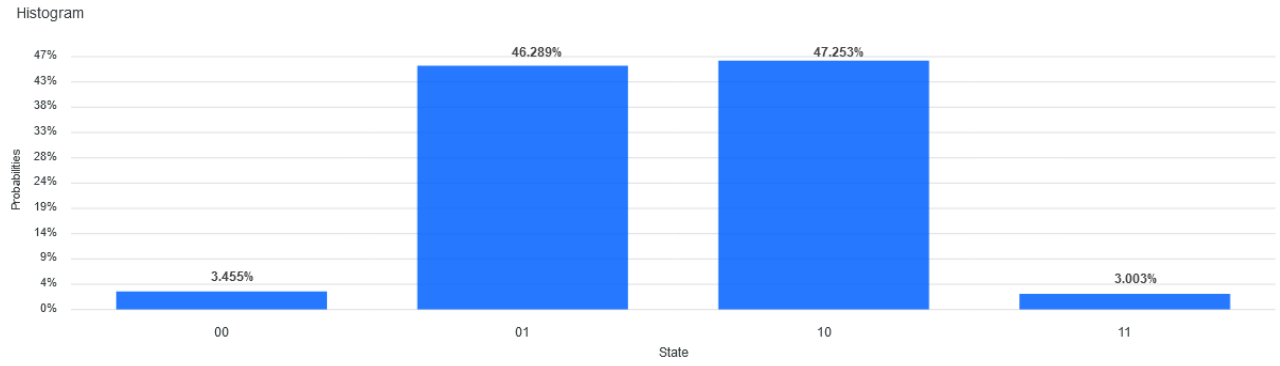

(b) Circuit on IBM machine for the Y basis measurement
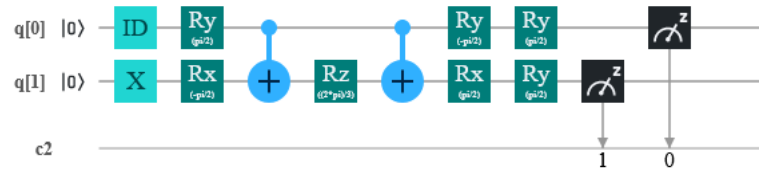
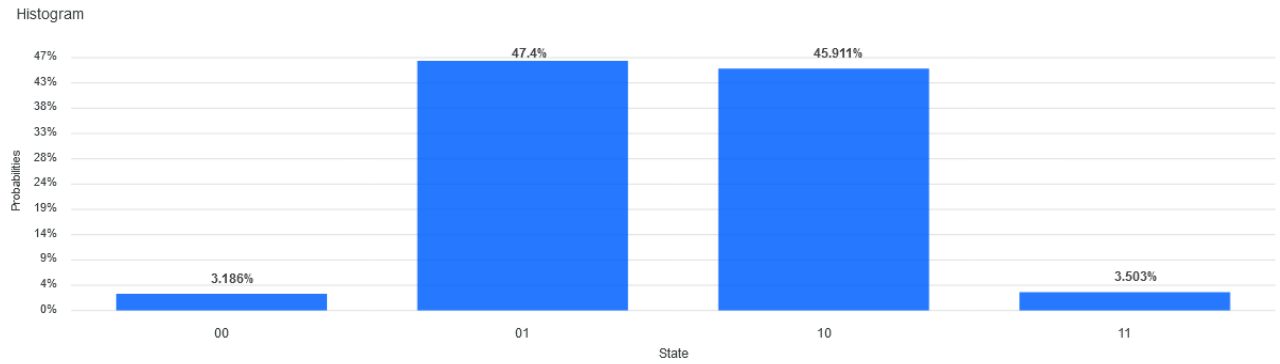(c) Circuit on IBM machine for the X basis measurement

Figure 2: Circuits implemented on the IBM machine for molecular hydrogen

Histogram
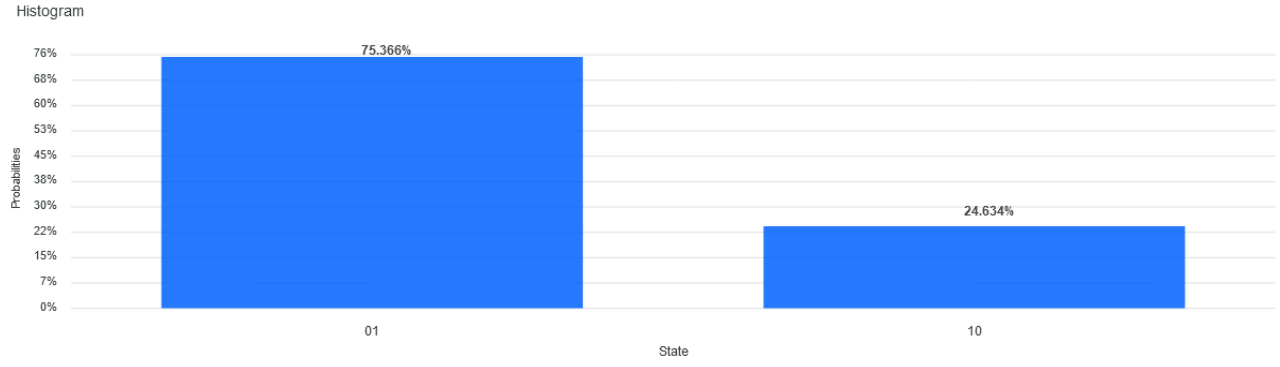
(a) Probability of measurements in the Z basis

Histogram

(b) Probability of measurements in the Y basis

Histogram

(c) Probability of measurements in the X basis

Figure 3: Probabilities for measurements for the X,Y and Z basis for the respective circuits on IBM simulator.
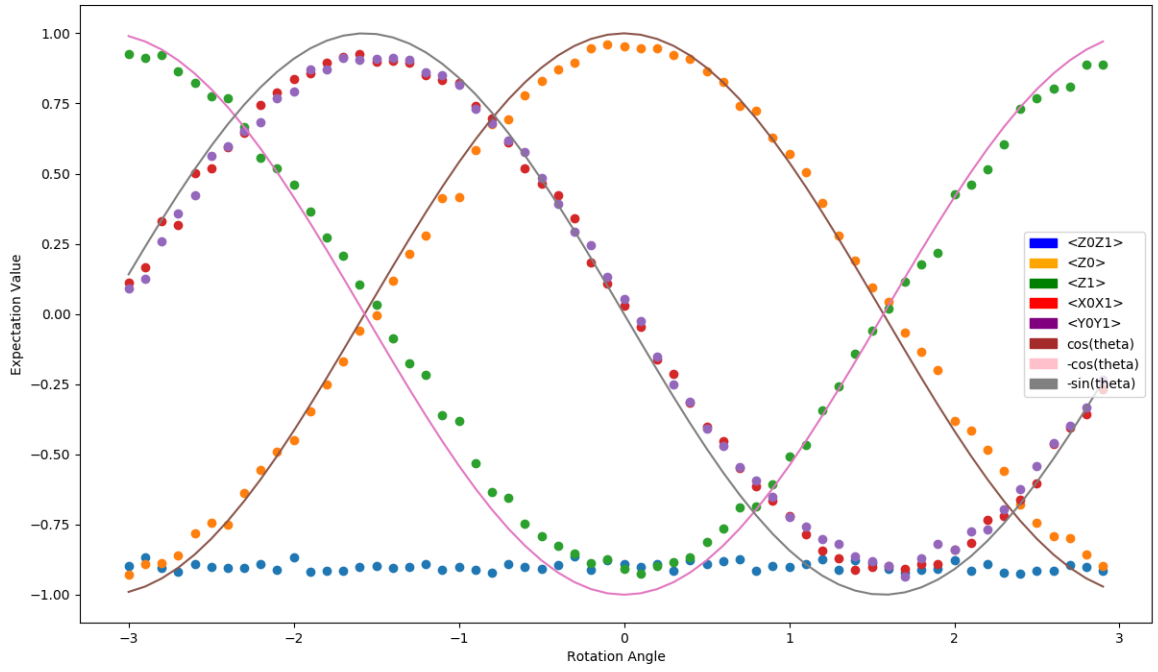
Figure 4: Our graph of expectation values graphed against θ, results from IBM's Vigo quantum computer
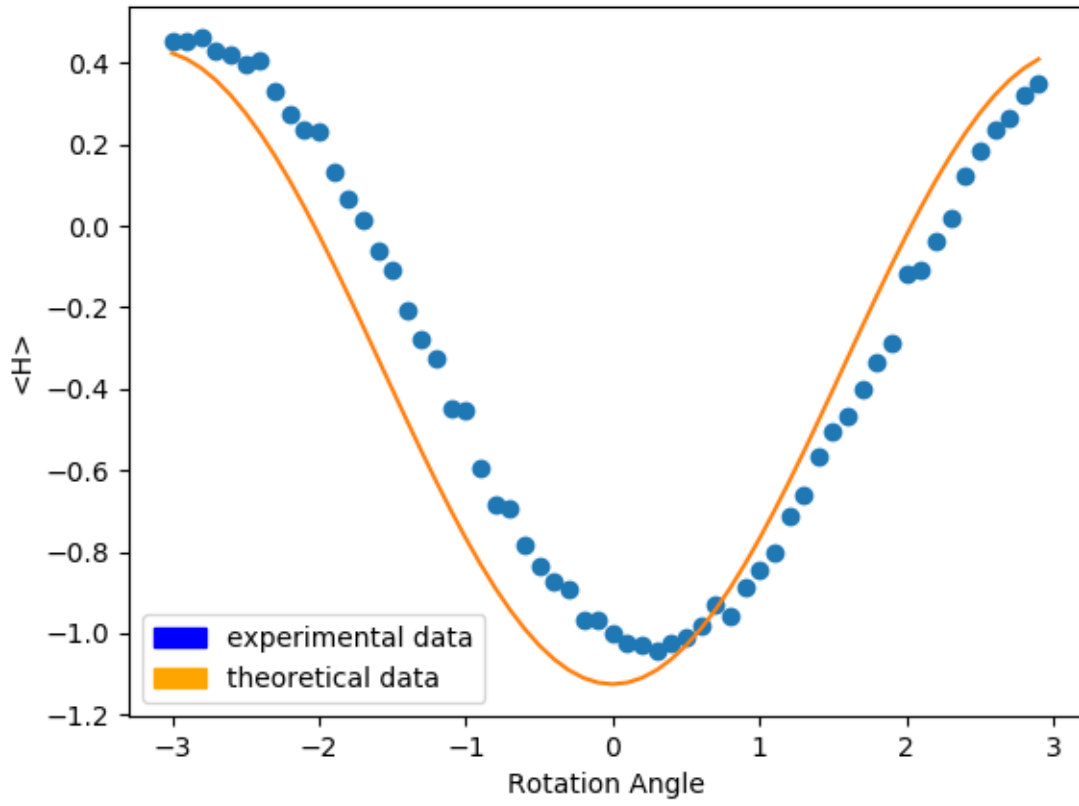
Figure 5: Expectation value of H graphed against θ, results from IBM's Vigo quantum computer. Plotted against the theoretical values from eq. 12 and 13, and using them with eq 4.
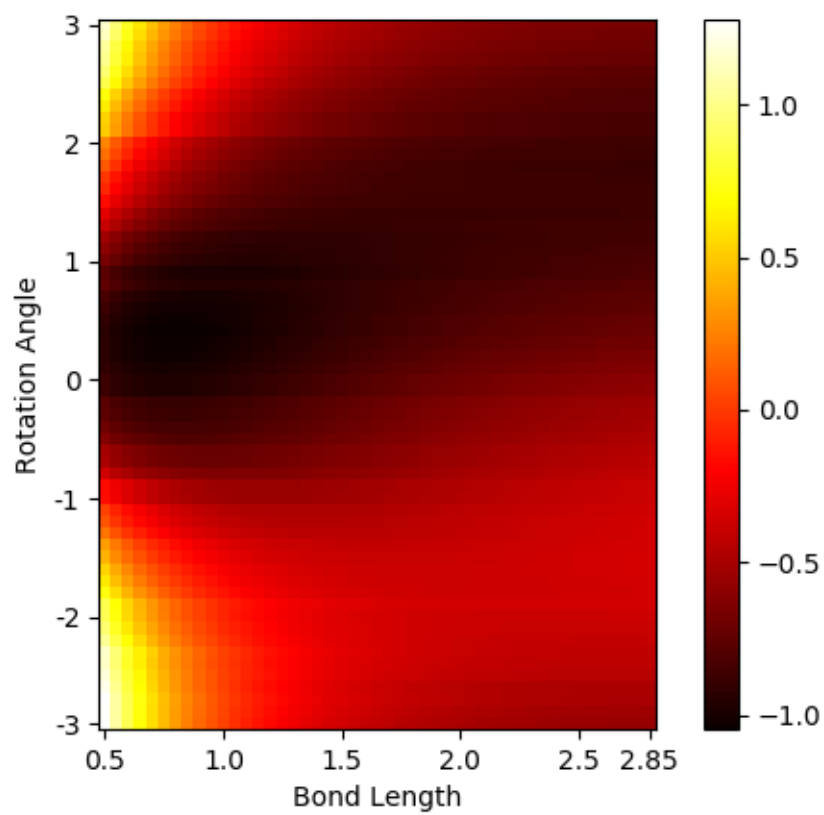
Figure 6: Heat map of the ground state energy as a function of our rotation angle θ and bond length r (angstroms).
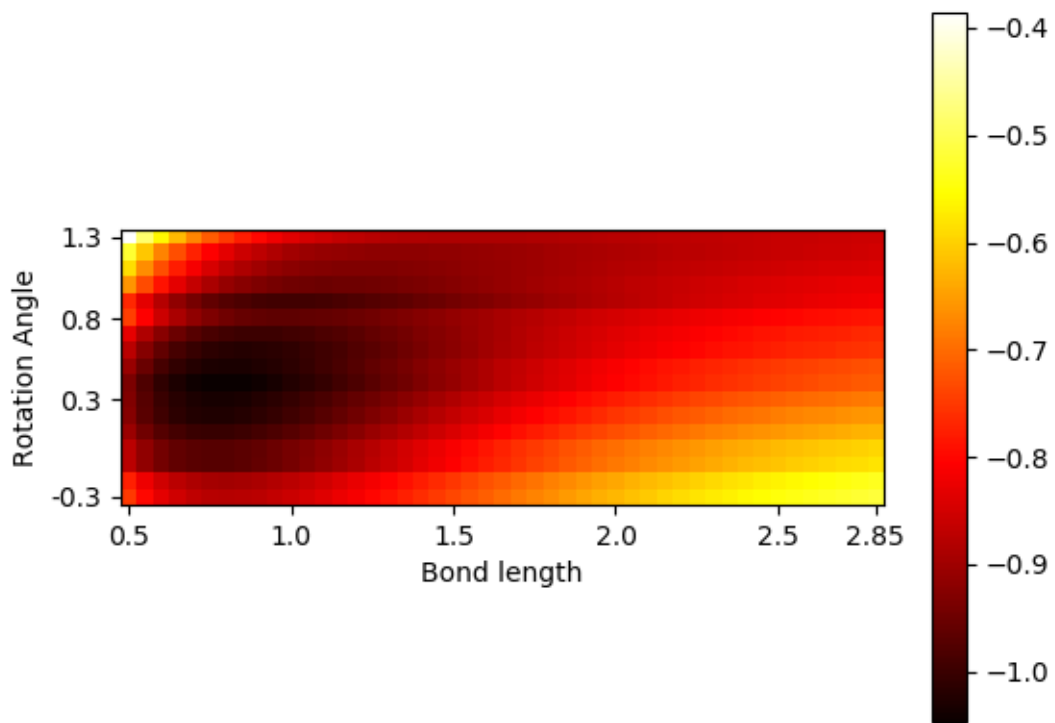
Figure 7: Heat map of the ground state energy as a function of our rotation angle θ and bond length r (angstroms), zoomed in around the minimum.
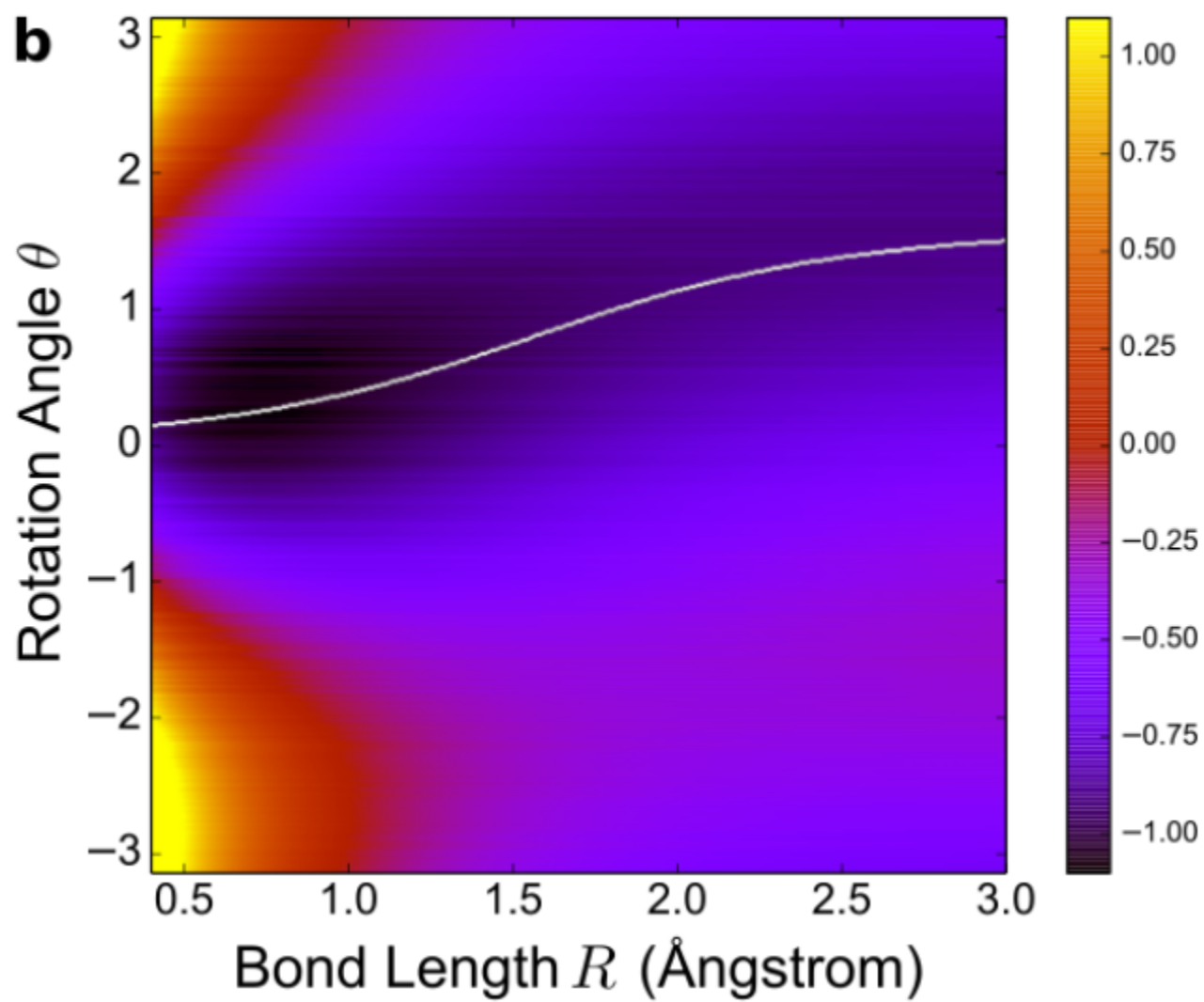
Figure 8: Heat map from *O'Malley et. all*, note the white line marking the theoretical minimum.
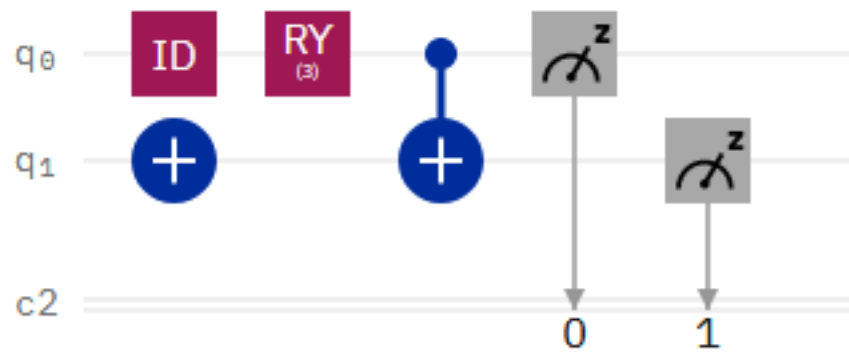
Figure 9: New quantum circuit that is equivalent to the grey box in Fig. 1, implementing the ansatz state.
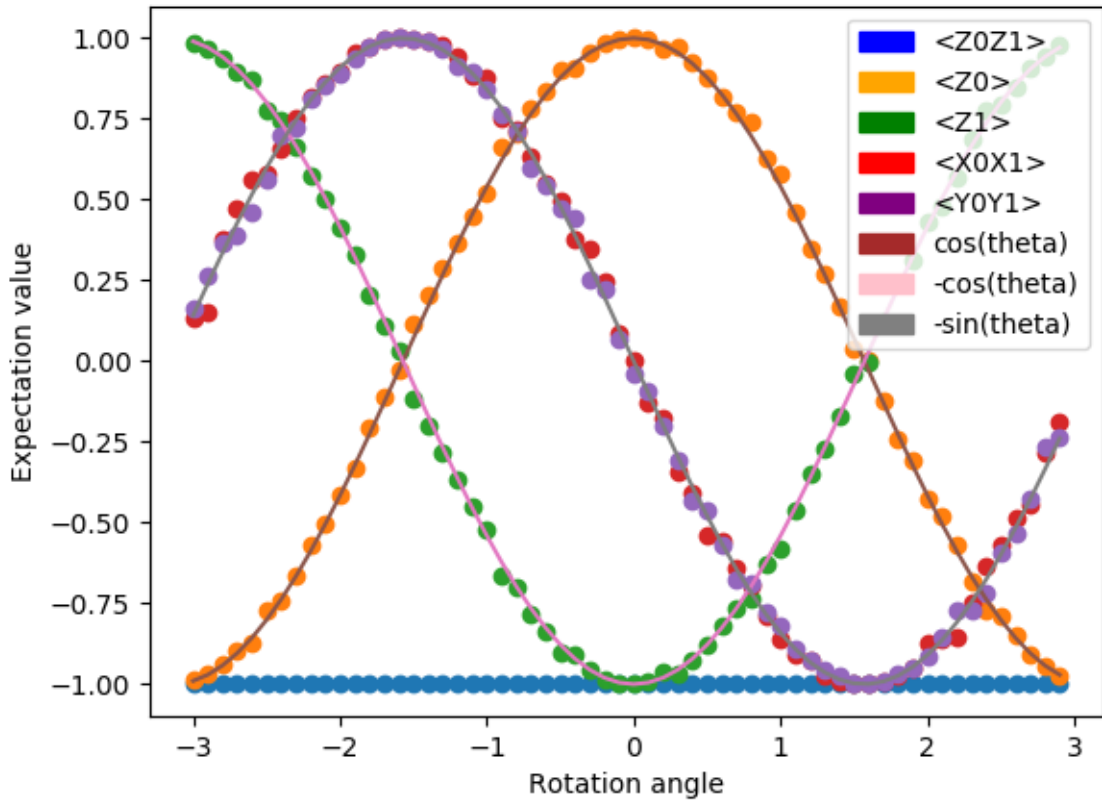
Figure 10: Our graph of expectation values graphed against θ, results from IBM's simulator, using the new circuit in Fig. 9
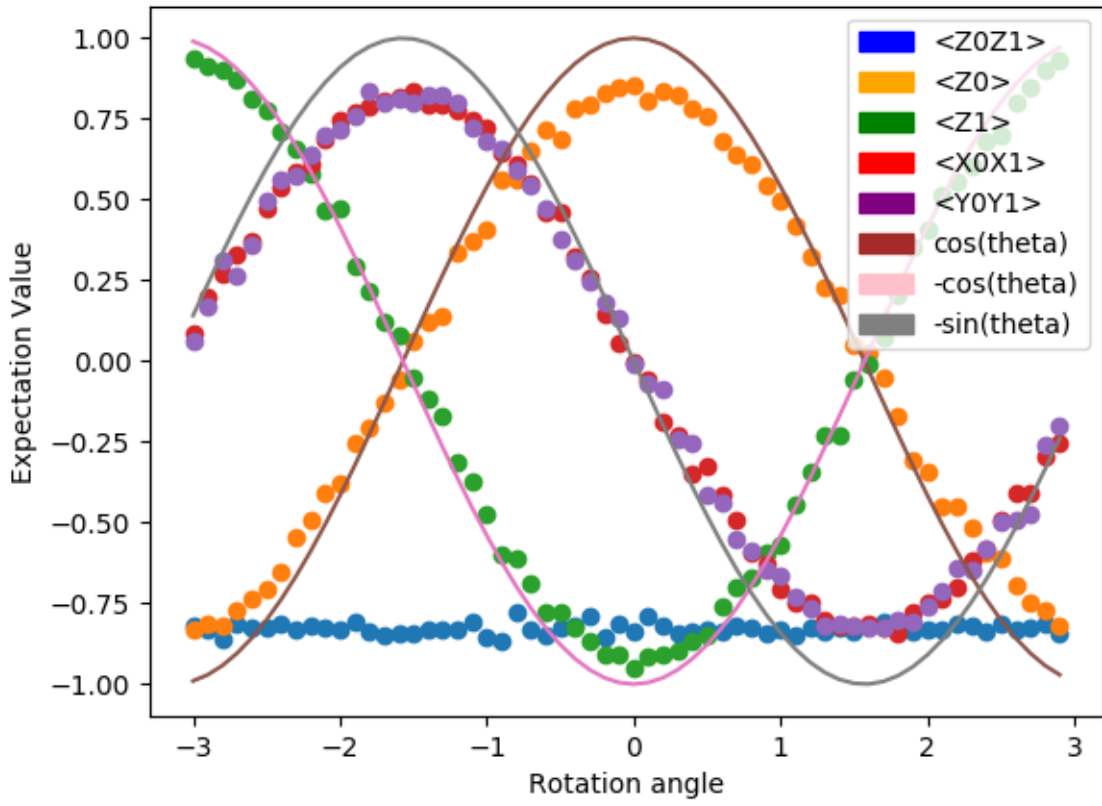
Figure 11: Our graph of expectation values graphed against θ, results from IBM's Vigo quantum computer, using the new circuit in Fig. 9
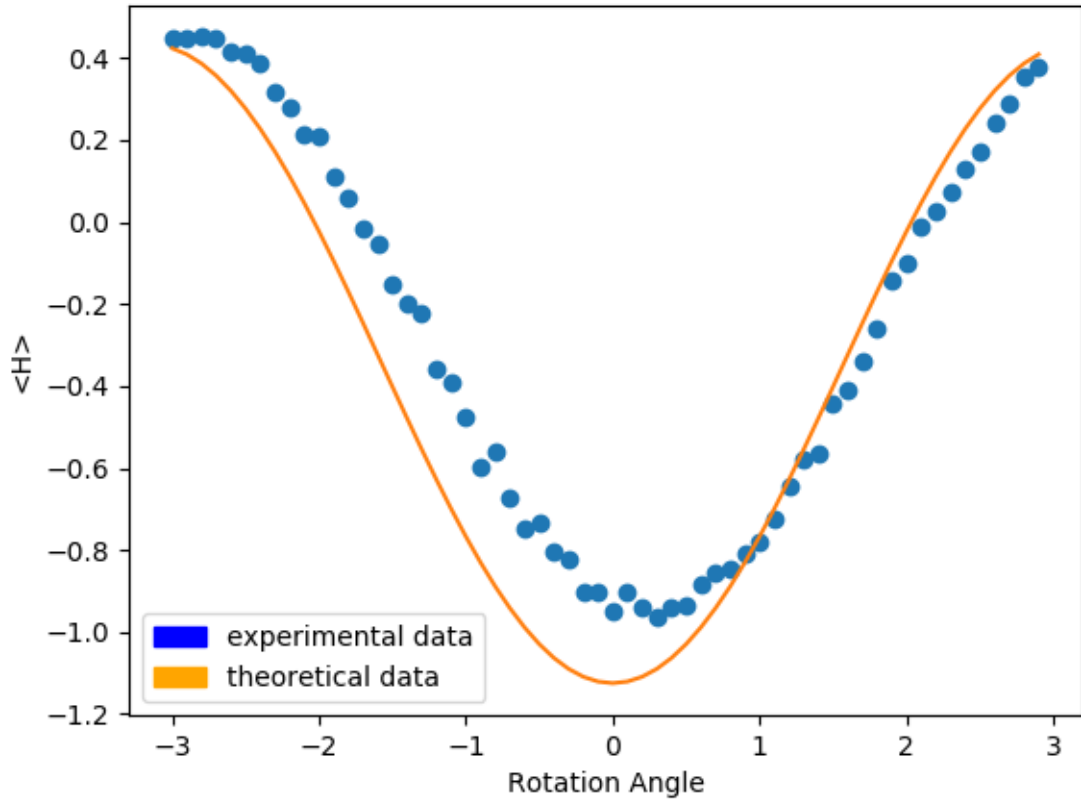
Figure 12: Expectation value of H graphed against θ, results from IBM's Vigo quantum computer, using the new circuit in Fig. 9. Plotted against the theoretical values from eq. 12 and 13, and using them with eq 4.
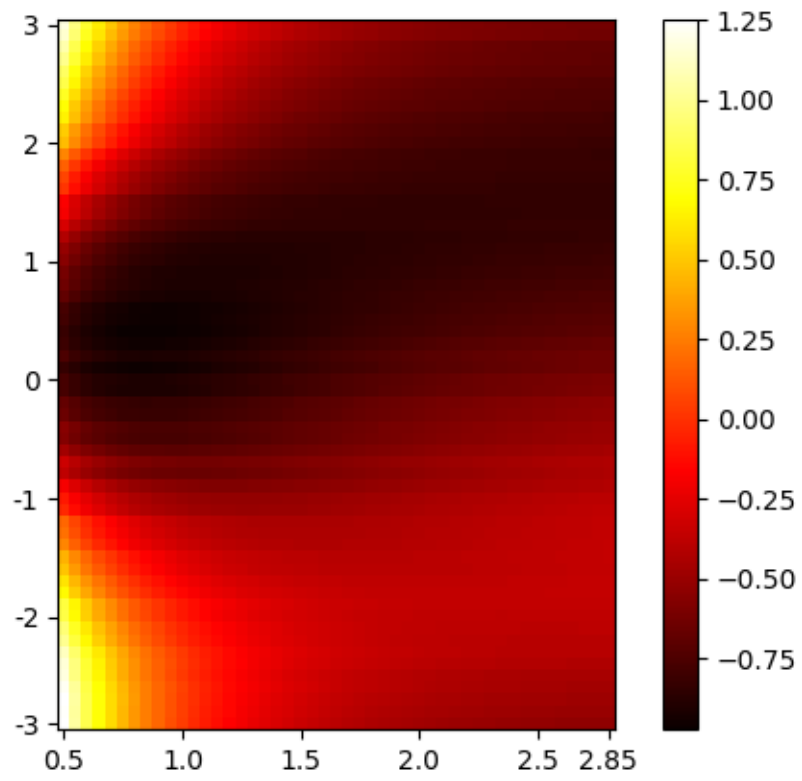
Figure 13: Heat map of the ground state energy as a function of our rotation angle θ and bond length r (angstroms), for the new circuit in Fig. 9.