Finding Ground State Energy of Molecules with Variational Quantum Eigensolver

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1 Overview

Due to recent advance in quantum computing technologies with superconducting quantum chips, we expect to solve classically intractable problems with a quantum computer in the near future. A fully quantum algorithm might not be implemented with sufficiently high performance in the near future, as the number, connectivity, and coherence time of qubits should be dramatically improved from the state-of-art in order to perform quantum error correction. However, quantum-classical hybrid algorithms, such as Variational Quantum Eigensolver (VQE) [4], can be performed with noisy qubits with the help of classical routines. In 2016, Google used 2-qubit quantum chip to calculate the ground state energy of H2 molecule [3]. In 2017, IBM used 6-qubit chip to solve the ground state energy of H2, LiH, and BeH2 molecules [1].

In this project we use VQE to find the ground state energies of the simplest molecules, such as H2, LiH, and BeH2, with various interactomic distances. We study the theory behind how to implement the molecular Hamiltonian into quantum circuit. We use quantum programming language pyQuil's WavefunctionSimulator and Quantum Virtual Machine (QVM) [7] to simulate VQE in classical computer and study how the performance of VQE depends on its methods and number of parameters. Finally, we introduce our attempts to implement VQE on an actual Quantum Processing Unit (QPU) and address future prospects.

2 Methodology

In this research we primarily use OpenFermion [2], an open source electronic structure package. The VQE algorithm is built and performed on the WaveFunctionSimulator, supported by quantum programming language pyQuil [7]. Our code can be accessed at https://github.com/horraywwkd/cs269q_openfermion.

Molecular Hamiltonian in second quantization form is caclulated by quantum chemistry package Psi4, and the result is retrieved in HDF5 container. OpenFermion reads the container and saves it in the form of `InteractionOperator` object by `load_molecular_hamiltonian` function. The `InteractionOperator` object is then easily converted into `FermionOperator` object. Then, OpenFermion's `bravyi_kitaev` function converts the `FermionOperator` object into `QubitOperator`, which is linear combination of Pauli operators. Finally, by using the ForestOpenFermion's `qubitop_to_pyquilpauli` function, we obtain the `PauliSum` object representation of the molecular Hamiltonian, which can be immediately implemented as Forest QVM's quantum circuit.

We implement both hardware ansatz and Unitary Coupled Cluster (UCC) as ansatz states that depend on the set of parameters $\boldsymbol{\theta}$. Hardware ansatz is easily constructed by using pyQuil's quantum gate objects, such as `CNOT` and parametrized gates `RZ` and `RX`. To implement UCC state $|\psi_{UCC}\rangle = e^{\hat{T}-\hat{T}^\dagger}|G\rangle$, we use OpenFermion's `uccsd_generator` function and forestOpenFermion's `exponentiate` function.

The molecular Hamiltonian and the ansatz state implemented above compose the entire quantum circuit used in the VQE algorithm. The circuit is run by `expectation` function of pyQuil's WavefunctionSimulator. Unlike VQE in actual quantum circuit, WavefunctionSimuator evaluates the expectation value by directly calculating the wavefunction amplitude, thereby avoiding sampling from large number of data. The result is then fed into the classical routine that minimizes the expectation value by finding the optimum parameters $\boldsymbol{\theta}$. `Scipy` package's function `minimize` with *L-BFGS-B* method is used.

Speed of the algorithm is evaluated by the number of quantum gates in the circuit, multiplied by the number of times the `minimize` function calls the circuit until convergence. Accuracy of the algorithm is

evaluated by comparing the ground state energy calculated by VQE to the exact solution of Schrodinger's equation calculated classically by Psi4's FCI method.

VQE is also implemented on Quantum Virtual Machine (QVM). QVM classically simulates Quantum Processing Unit (QPU), which calculates the expectation value of the Hamiltonian by sampling large number of measurements. Since the measurements are always performed in the Z-basis, rotation gates corresponding to each Pauli term of the Hamiltonian should be appended to the quantum program.

Finally, we attempted to implement VQE on an actual QPU. QPU can be accessed by Rigetti's quantum cloud service, which provides access to superconducting quantum chip 'Aspen-4'. If implemented, the results would have been affected by qubit noise and gate errors, which are not considered in our QVM simulation.

3   Results and Discussion

3.1   Performance of Hardware Ansatz VQE

We evaluate the hardware ansatz VQE by its performance on calculating the ground state energy of H_2 of various interatomic distances. Hardware anstaz state is defined as

$$|\psi_{HA}(\boldsymbol{\theta})\rangle = \prod_{l=1}^{L} \left(\Big(\sum_{q=1}^{N} U^{q,l}(\boldsymbol{\theta}) \Big) \times U_{ENT} \right) |0\rangle^{\otimes N} \tag{1}$$

where $U^{q,l}(\boldsymbol{\theta}) = RZ(\theta_1^{q,l})RX(\theta_2^{q,l})$, RZ and RX are rotation gates of qubit with respect to z and x axes, and L is the number of layers [1]. $|\psi_{HA}(\boldsymbol{\theta})\rangle$ depends on $2NL$ parameters ($\boldsymbol{\theta} \in \mathbb{R}^{2NL}$), where N is the number of qubits and L is the number of layers. The number of gates required to build $|\psi_{HA}(\boldsymbol{\theta})\rangle$ is $(2N + (N-1))L$, where $2N$ is the number of rotation gates and $N-1$ is the number of two-qubit gates in U_{ENT}, per each layer. For H2, $N = 4$.

As L increases, the available state space expands, so we expect that VQE becomes more likely to find the ground state energy accurately. However, the computational cost also increases, as the number of gates per each iteration of circuit increases, and the number of calls to the circuit also increases because there are more parameters to optimize.
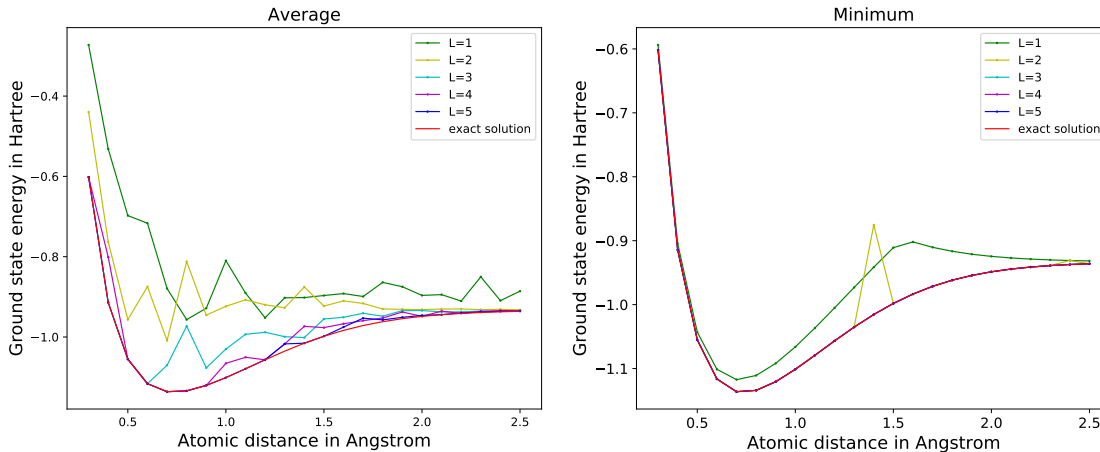

Figure 1: Average and minimum of ten calculations of H2 ground state energy obtained by hardware ansatz VQE simulated on WavefunctionSimulator. As the number of layers L increases, the ground state energy curve becomes closer to the exact solution. When minimum is taken, VQE and exact solution curves overlap perfectly when $L \geq 3$

Figure 1 shows the average and minimum of ten calculations of H2 ground state energy, obtained by VQE simulated on WavefunctionSimulator. We chose the initial parameters $\boldsymbol{\theta}^0$ as random angles between

0 and 2π. The results are compared with exact solution of Schordinger equation, obtained classically by FCI method. As expected, the ground state energy curve becomes closer to the exact solution curve as L increases.

Note that VQE with fewer layers can also calculate the ground state energy very accurately by chance. However, with fewer layers, it is more likely for the VQE to converge to a local minima, as the state space of $|\psi_{HA}(\boldsymbol{\theta})\rangle$ is not large enough. This explains the 'cusps' in Figure 1.

For practical use of VQE, minimum value obtained from repeated calculations of ground state energy should be taken, instead of average value. For the case of H2, minimum of ten repeated calculations with $L = 3$ is sufficient enough to obtain very accurate (relative error $<$ 1e-10) ground state energies. For more complicated molecules with larger N, we expect the required number of layers and repetitions to increase.

Figure 2 shows the computation cost and accuracy of hardware ansatz VQE with number of layers 1 to 5. Computation cost is represented by the total number of gates until VQE converges to minimum. Number of calls to the circuit is multiplied with number of gates in the circuit, which is $36 + (3N - 1)L$. Note that the exact number of calls may depend on the optimization method, which is L-BFGS-B in this research. Accuracy is represented by the relative error of average energy calculated by VQE to energy calculated by exact solution.
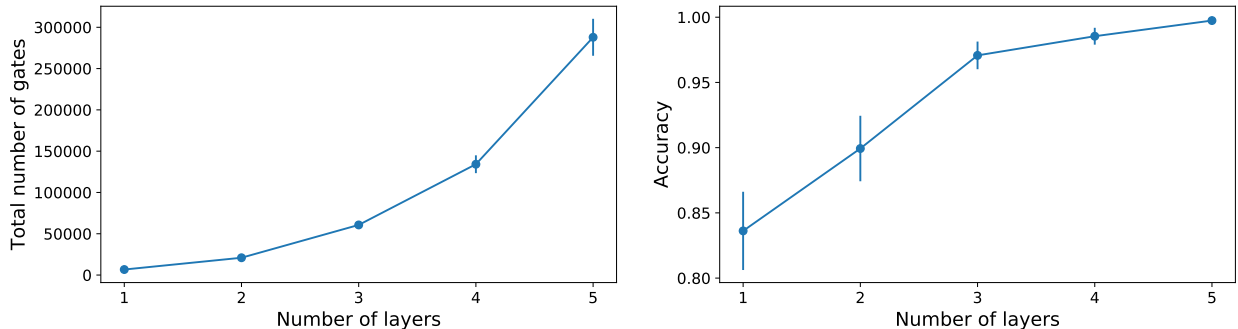

Figure 2: Computation cost and accuracy of hardware ansatz VQE simulated on WavefunctionSimulator, with number of layers 1 to 5. Computation cost is represented by the total number of gates, and accuracy is measured as $1 - |E_{VQE} - E_{exact}|/E_{exact}$. The average and standard error is taken over all repeated calculations at all atomic distances. As expected, both computation cost and accuracy increases as number of layers increases.

Computation cost grows quadratically with number of layers. This is because both the number of gates (used to prepare $|\psi_{HA}(\boldsymbol{\theta})\rangle$) in the circuit and the number of calls both increase. Average accuracy reaches $> 97\%$ at $L = 3$. For practical use, minimum value from repeated calculations should be obtained, which will give much higher accuracy.

For future research, performance of hardware ansatz VQE with larger number of qubits N should be investigated. Although the number of parameters is linear with N, we do not know how the minimum number of layers L required for obtaining accurate ground state energy scales with N. This will help estimate the resources required to perform hardware ansatz VQE for more complicated molecules.

3.2 Performance of Unitary Coupled Cluster VQE

We evaluate the Unitary Coupled Cluster VQE by its performance on calculating the ground state energy of H2 of various interatomic distances. The UCC state is defined as $|\psi_{UCC}\rangle = e^{\hat{T}-\hat{T}^\dagger}|G\rangle$, where

$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots$, and

$$\hat{T}_1(\boldsymbol{\theta}) = \sum_{i_1 \in occ, a_1 \in virt} \theta_{i_1}^{a_1} \hat{a}_{a_1}^\dagger \hat{a}_{i_1} \tag{2}$$

$$\hat{T}_2(\boldsymbol{\theta}) = \frac{1}{(2!)^2} \sum_{i_1,i_2 \in occ, a_1,a_2 \in virt} \theta_{i_1,i_2}^{a_1,a_2} \hat{a}_{a_1}^\dagger \hat{a}_{a_2}^\dagger \hat{a}_{i_1} \hat{a}_{i_2} \tag{3}$$

$|G\rangle$ is the reference state, usually chosen as the Hatree-Fock ground state, and $\hat{a}$ is the Fermion annihilation operator acting on the subscript site. The *occ* and *virt* spaces are the sites occupied and unoccupied by $|G\rangle$ [5, 6].

For UCC state with degree 1 ($\hat{T} = \hat{T}_1$), there are two parameters, and with degree 2 ($\hat{T} = \hat{T}_1 + \hat{T}_2$), there are three parameters. Note that $|G\rangle = |1100\rangle_{occ}$ in the Fermion occupation basis should be converted into $|G\rangle = |1010\rangle$ in the Bravyi-Kitaev qubit basis.
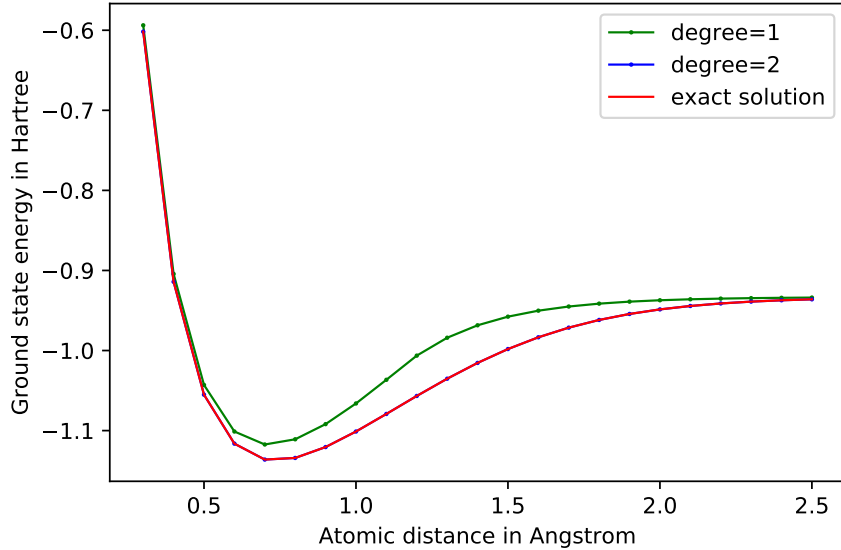

Figure 3: Average of ten calculations of H2 ground state energy obtained by UCC ansatz VQE simulated on WavefunctionSimulator. Degree=2 curve overlaps perfectly with the exact solution curve.

Figure 3 shows the average of ten calculations of H2 ground state energy, obtained by VQE simulated on WavefunctionSimulator. We chose the initial parameters $\boldsymbol{\theta}^0$ as random numbers between -0.25 and 0.25. The results are compared with exact solution of Schordinger equation obtained classically.

1-UCC VQE predicts the ground state energies with average accuracy 0.9777, and 2-UCC VQE ground state energy curve perfectly agrees with the exact solution. This is expected, as 2-UCC state encodes all the one-body and two-body interactions under symmetries such as number of fermions and total spin conservation.

Table 1 shows the computation cost and accuracy of VQE with both hardware ansatz and UCC. Computation cost is represented by total number of gates, which is average number of calls to the circuit multiplied with number of gates in the circuit. Accuracy is represented by the average relative error to exact solution. Note that the exact number of calls may depend on the optimization method, which is L-BFGS-B in this case.

When solving the H2 molecule, computation cost is significantly lower with UCC than hardware ansatz. This is because UCC exploits the symmetries of the molecule and has much fewer parameters than hardware ansatz. However, this is not guaranteed to be true for more complicated molecules, as the number of parameters of 2-UCC state scales with number of qubits N in the order of $O(N^4)$.

	Number of calls	Total number of gates	Accuracy
4-layer HA	1973	134181	0.9854
5-layer HA	3788	287900	0.9974
1-UCC	34	2402	0.9777
2-UCC	44	6227	1

Table 1: Computation cost and accuracy of hardware ansatz and UCC VQE simulated on Wavefunction-Simulator. Total number of gates is number of calls times number of qubits in the circuit. The numbers are averaged over all atomic distances. The relative error of 2-UCC is less than 1e-10, which is dominated by floating point error.

Figure 4 shows the ground state energies of LiH and BeH2, obtained by VQE simulated on WavefunctionSimulator. Only degree 1-UCC is calculated, as optimization with degree 2-UCC is computationally too expensive. As in H2, the curves reasonably agree with the exact solutions, but is not exact, because the two-body interactions are not included in the 1-UCC state. Average accuracy of LiH and BeH2 calculation is 0.9967 and 0.9957, each, relative to the exact solution.
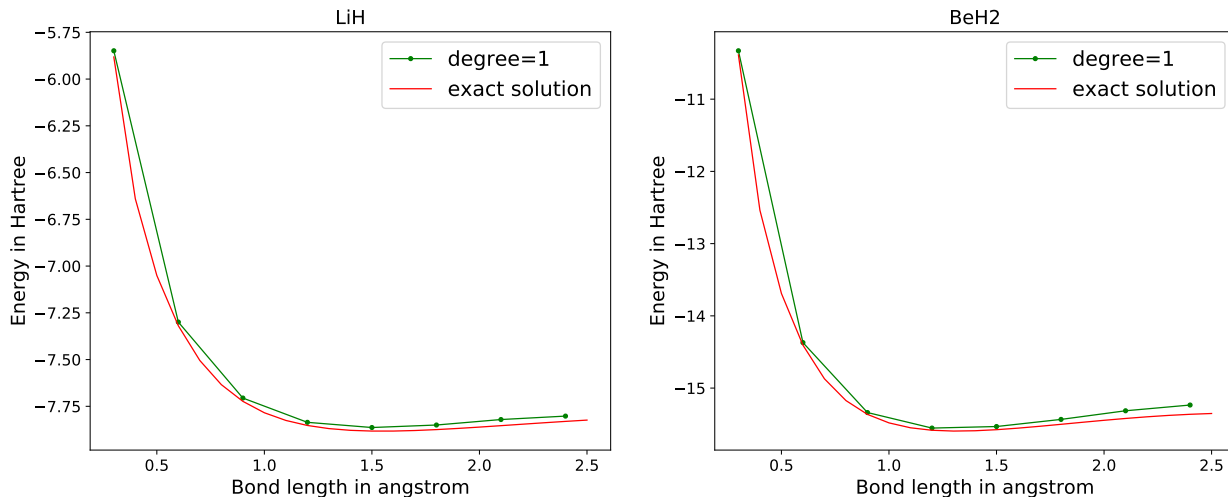

Figure 4: Calculations of ground state energies of LiH and BeH2, obtained by 1-UCC ansatz VQE simulated on WavefunctionSimulator. The curves are in decent agreement with the exact solution.

3.3 VQE on Quantum Virtual Machine and QPU

We implement the VQE on pyQuil's Quantum Virtual Machine. Unlike WavefunctionSimulator, QVM evaluates the expectation value of the Hamiltonian by taking the mean of large number of samples from repeated measurements.

According to [1], the error ϵ of mean energy $\langle H \rangle$ after taking S samples is given by:

$$\epsilon = \sqrt{\frac{\text{Var}[H]}{S}} \leq \sqrt{\frac{T|h_{max}^2|}{S}} \tag{4}$$

where T is the number of Pauli terms and $|h_{max}|$ is the absolute value of the largest Pauli coefficient. We use $S = 100$ and set the tolerance of minimization algorithm to 0.1, so that we calculate the energies with $\epsilon \approx 0.1$. Note that the sampling overhead can be reduced by using techniques such as simplifying the Hamiltonian and grouping Pauli operators [1].
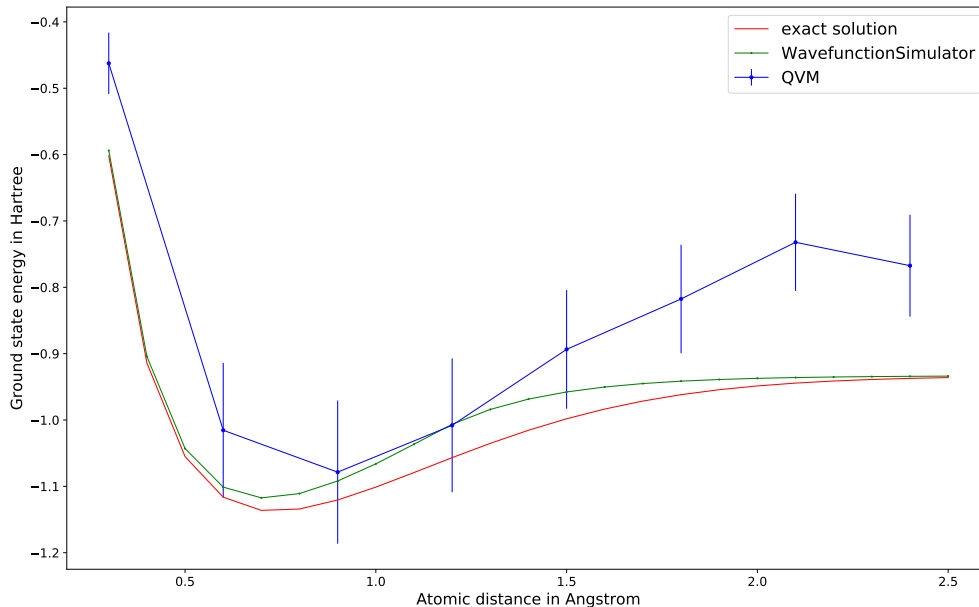
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Figure 5: Calculations of ground state energies of H2, obtained by degree 1-UCC ansatz VQE simulated on Quantum Virtual Machine. The results are compared with WavefunctionSimulator results and exact solution. Error bars represent the energy error ϵ due to small number of sampling.

The results of QVM simulation are displayed in Figure 5. The general tendency matches the solution, and some points agree with the WavefunctionSimulator results. The average accuracy relative to the exact solution is 0.8667, which is lower than WavefunctionSimulator accuracy 0.9974. We expect that the accuracy will increase to the WavefunctionSimulator level as we increase the number of samples S.

We attempted to run VQE on a QPU, accessed through Rigetti's quantum cloud service. However, the runtime was much slower than QVM simulation, so we could not perform the algorithm. Simulation with lattice QVM, which models the connections of Rigetti's quantum chip, indicates that limited connections of the chip leads to the program being compiled into more complicated circuit. This is because the chip lattice does not have four qubits that are all mutually connected to each other. We should either simplify the program so that it does not require all mutual connections, or use a quantum chip with better connectivity, in order to run the algorithm faster.

If VQE works with QPUs, quantum noise, gate errors, and readout errors will also contribute to fluctuations of expectation value, so larger S will be required. The accuracy will decrease from QVM results. However, as the number of qubit N increases, exponential speedup in evaluating the Hamiltonian will overcome the disadvantages.

4   Conclusion

Variational Quantum Eigensolver in quantum chemistry is one of the most promising and realistic applications of quantum computers in the near future. By using open source quantum chemistry packages such as Psi4 and OpenFermion, we implemented the molecular Hamiltonian into quantum circuit. Second quantization formalism and Bravyi-Kitaev transformation are used. Then, VQE is run with the circuit by the quantum programming language pyQuil to find the ground state energy of the Hamiltonian.

Hardware ansatz and Unitary Coupled Cluster are the ansatz states that are used in VQE to solve quantum chemistry problem. The computation cost and accuracy of VQE depends on the choice of ansatz state and its attribute (hardware ansatz: number of layer, UCC: degree). When VQE is simulated on Wavefunc-

tionSimulator to solve H2 molecule, hardware ansatz with three layers and UCC with degree 2 yield accurate ground state energies. UCC has significantly lower computational cost than hardware ansatz, but there is no guarantee that this is true for solving more complicated molecules. Ground state energies of LiH and BeH2 are also calculated using degree 1-UCC.

VQE is also performed on Quantum Virtual Machine, but due to limited number of sampling, we could only achieve $\sim 87\%$ accuracy. We could not perform VQE on actual QPU due to limited qubit connection of the chip.

In general, although we successfully calculated the ground state energies of simple molecules in VQE with various methods and parameters, the number of parameters, iterations, and gates grow fast with the size of molecule. Sampling overhead and noise are also possible obstacles. It is unclear how the computation cost and accuracy of VQE scales with the number of qubits N. Limited connectivity between qubits in the chip lattice also complicates the circuit.

However, note that we did not simplify the Hamiltonian to reduce N [1, 3], or use 'grouping Pauli operators' technique [1] to reduce the sampling overhead. For simple molecules such as H2, LiH, and BeH2, the size of the circuit can be reduced to scale that is tractable with existing quantum chips. Further research could be done on how to generalize these simplifying tricks for larger molecules, and how much computational resource is required for a VQE to outperform classical algorithms.

We agree that both our code and project report be posted publicly on the course website.

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