Project 2: Variational Quantum Eigensolver: Constructing Potential Energy Surfaces for Small Molecules

Introduction

Currently, the Variational Quantum Eigensolver (VQE) [1] is the most feasible technique for solving the electronic structure problem on a near-term noisy quantum computer. Yet, one needs to understand that VQE is a quite general framework that requires several choices to be made by the user to be efficient. In what follows, we will illustrate state-of-the-art techniques to make VQE efficient for obtaining potential energy surfaces (PESs) for small molecules.

A set of molecules suggested for investigation is: H_2, LiH, H_4, H_2O, N_2. They are of the increasing level of difficulty. A simple qualitative rule from chemistry is: the system PES is harder to calculate accurately if more chemical bonds are destroyed at the same time. Therefore, H_2 and LiH are the easiest systems (single bond), H_4 and H_2O are harder (two bonds), and N_2 is the hardest (triple bond). (Actually, 1-2% of the entire worldwide energy is spent on breaking N_2 bonds to make ammonia (NH_3) that is turned into fertilizers. Thus being able to model such processes is a necessary step for computational development of new catalysts for the ammonia production.) As a smaller correction to this qualitative picture of computational hardness, one can add a number of electrons in the system, the larger the number of electrons the more computationally demanding is the study. Thus, LiH is harder than H_2 and H_2O is harder than H_4.

Another qualitative indicator of hardness is whether classical computing approximate methods for electronic structure that have a polynomial scaling are able to treat the system with chemical accuracy (1 kcal/mol). Turns out, if one breaks more than a single bond state-of-the-art approaches like coupled cluster single and double (CCSD) cannot achieve chemical accuracy for all points of PES. Thus, quantum computing methods based on VQE were thought as a viable alternative to treat such so-called strongly correlated systems.

More on the topic:

- Lecture 1: Electronic Structure `https://www.youtube.com/watch?v=0cYq9yJFYkc`

- Lecture 2: Second Quantization `https://www.youtube.com/watch?v=_q4j9_D6AEg`

- Lecture 3: Fermion-qubit Mappings `https://www.youtube.com/watch?v=W8SW3qp3RzY`

- Lecture 4: Variational Approach `https://www.youtube.com/watch?v=bX5Y8mPa9oQ`

- Lecture 5: VQE `https://www.youtube.com/watch?v=UBkb54_MOLo`

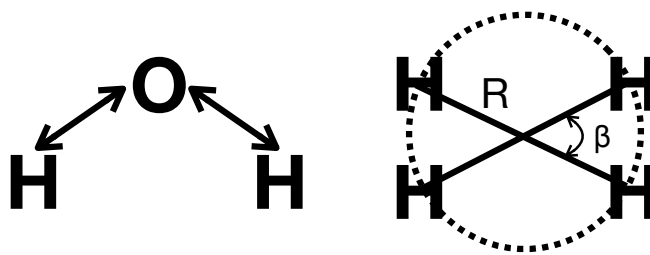- Lecture 6: Unitary Transformations `https://www.youtube.com/watch?v=981jc3Xdgvc`

Figure 1: Recommended distortions: H_2O, symmetric OH bond length changes around R(O-H)=0.75 Å and fixed $\angle$ HOH = 107.6°; H_4, change of β in the range $[85°, 95°]$ keeping planar configuration with fixed $R = 1.738$ Å.

- Lecture 7: Measurements `https://www.youtube.com/watch?v=U4xX5251b-E`

- Lecture 8: Constraints and Symmetry Projections `https://www.youtube.com/watch?v=mhlgldoCfx4`

Your task

Using H_2 and H_2O examples, we will illustrate main steps of the VQE process from the setup of the Hamiltonian till obtaining the circuit for the IBM quantum computer. Your task will be to repeat those steps for one or two other molecules so that you can obtain the ground state PES of your molecules both on a classical computer using classical methods and VQE simulator, and on a quantum computer.

Recommended bonds elongation for H_4 and H_2O are depicted in Fig. 1. Tequila is a free software package where all calculations will be illustrated.

Another component of this project will be to address questions posed at each step. Some of these questions are marked *Optional*, it is recommended to do the *Optional* questions only if you have time after finishing the required ones.

Step #0: Setting up your computer environment

Instructions: `S0_Setup.pdf`.

Step #1: Generating PES using classical methods

Hartree-Fock (HF), Configuration Interaction Singles and Doubles (CISD), Coupled Cluster Singles and Doubles (CCSD), and the exact answer within the chosen basis Full Configuration Interaction (FCI) [2]. All these methods can easily be used for all molecules in minimal atomic basis, STO-3G. Comparing accuracy of PES generated for different species using different methods you can see the difference between weakly correlated (H_2, LiH) and strongly correlated (H_4, H_2O, N_2) systems. Even though the FCI method provides the exact answer it scales exponentially with the number of basis functions and thus cannot be used for larger systems (system size can be either correlated with the number of electrons or number of basis functions). All approximated methods (HF, CISD, CCSD) scale polynomially with the system size but fail to deliver chemical accuracy along PESs.

Illustrative code: `S1_Classical_Methods.ipynb`.

Questions:

1) Among classical methods, there are techniques based on the variational approach and those that are not. Identify variational methods among those that were used and explain advantages of the variational approach. Are there any arguments for using non-variational techniques?

2) *Optional*: There is another division between classical methods, it is based on so-called separability or size-consistency. Simply speaking, if one investigates two molecular fragments (A and B) at a large distance from each other (~ 100 Å) then the total electronic energy should be equal to the sum $E_{A+B} = E_A + E_B$, where the energy of each fragment (E_A or E_B) can be obtained in a calculation that does not involve the other fragment. If this condition is satisfied for a particular method, this method is separable or size-consistent. Check separability of HF, CISD, and CCSD by taking 2 H_2 fragments at a large distance from each other and comparing the total energy with 2 energies of one H_2 molecule. Explain your results.

3) *Optional*: If one is interested in converging to the exact non-relativistic electronic energies, there are two independent coordinates: 1) accuracy of accounting for many-body effects beyond the Hartree-Fock method (electronic correlation) and 2) accuracy of representation of one-electron states, or convergence with respect to the one-electron basis size. Convergence along the first coordinate can be illustrated by monitoring reduction of the energy deviations from the Full CI answer in a particular basis set for a series of increasingly accurate approaches, e.g. HF, CCSD, CCSD(T), CCSDT. Convergences along the second coordinate requires the basis set extension from STO3G to a series like cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z. Explore for a small system like H_2 both convergences. Which energies should be expected to be closer to experimentally measured ones?

Step #2: Generating the qubit Hamiltonian

To proceed to VQE one needs to generate the qubit Hamiltonian, the easiest path is via first generating the electronic Hamiltonian in the second quantized form and then transform it into the qubit form using one of the fermion-to-qubit transformations: Jordan-Wigner or Bravyi-Kitaev [3]. Next, some qubit operators can be substituted by numbers (± 1) because their states are stationary for the specific electronic state (e.g. ground state). This reduction is very useful for fitting larger problem in a fewer qubit description and is based on Hamiltonian symmetries, which are discussed in Refs. [4, 5, 6]

Illustrative code: `S2_Hamiltonian_gen.ipynb`.

Questions:

1) What are the requirements for a function of qubit operators to be a valid mapping for the fermionic operators?

2) The electronic Hamiltonian is real (due to time-reversal symmetry), what consequences does that have on the terms in the qubit Hamiltonian after the Jordan-Wigner transformation?

3) *Optional*: What are the cons and pros of the Bravyi-Kitaev transformation compared to the Jordan-Wigner transformations?

Step #3: Unitary transformations

There are three main paths : 1) historically first, the unitary coupled cluster (UCC) approach has originated from the ideas of the classical electronic structure theory [7, 8], 2) hardware-efficient, direct optimization of gates and their sequence [9], and 3) the qubit coupled cluster (QCC) based approach [10]. We will illustrate the first and third approaches, since the second one frequently runs into difficulties with energy optimization [11]. Even though UCC follows directly from a classical molecular orbital picture, it doesn't provide an efficient framework for generating gates for a quantum circuit later. In contrast, QCC can efficiently optimize energy and generate efficient circuits.

In this step, we will look at how to generate elementary unitary operations in the UCC and QCC schemes for model systems and to optimize their continuous parameters (amplitudes).

Illustrative code: `S3_U_ansatz.ipynb`.

Questions:

1) Standard Hamiltonian symmetries are i) number of electrons $\hat{N}_e = \sum_k \hat{a}_k^\dagger \hat{a}_k$, ii) electron spin $\hat{S}^2$, iii) electron spin projection $\hat{S}_z$, iv) time-reversal symmetry, and v) point-group symmetry for symmetric molecules. Which of these symmetries are conserved in a) UCC and b) QCC ?

2) Why symmetries are helpful for constructing a unitary operator which rotates the initial state $|\bar{0}\rangle$ to the eigenstate $|\Psi\rangle$?

3) What are the ways to restore symmetries if your unitary transformation break them?

Step #4: Hamiltonian measurements

To obtain the expectation value of the qubit Hamiltonian it needs to be measured at the end of the VQE circuit. The problem is that the entire Hamiltonian cannot be measured using current hardware. In this step, we show how to partition the Hamiltonian to a minimal number of groups, whose elements can be all measured simultaneously [12, 13].

Illustrative code: `S4_Measurement.ipynb`.

Questions:

1) If we focus on a measurement of an expectation value $\langle \Psi | \hat{H}_n | \Psi \rangle$ for a single fragment, $\hat{H}_n$, since $|\Psi\rangle$ is not an eigenfunction of $\hat{H}_n$, we will need to do multiple preparations of $|\Psi\rangle$ and measurements. If we denote $\{H_{n,k}\}$ results of repeated measurements, then to obtain the estimate of $\langle \Psi | \hat{H}_n | \Psi \rangle$ we will need to average the obtained results $\bar{H}_n = \frac{1}{N} \sum_{k=1}^{N} H_{n,k}$. Using the central

limit theorem, the error of our estimator can be shown to be [1]

$$| \langle \Psi | \hat{H}_n | \Psi \rangle - \bar{H}_n | \leq \sqrt{\frac{\langle \Psi | \hat{H}_n^2 | \Psi \rangle - \langle \Psi | \hat{H}_n | \Psi \rangle^2}{N}} = \frac{\sqrt{\sigma_{H_n}^2}}{\sqrt{N}}. \tag{1}$$

The estimator for the expectation value of the entire Hamiltonian $\hat{H} = \sum_n \hat{H}_n$ can be organized by adding individual $\bar{H}_n$ estimates. Since measurements for different parts are independent the following relation holds

$$(\langle \Psi | \hat{H} | \Psi \rangle - \bar{H})^2 \leq \sum_n \frac{\sigma_{H_n}^2}{N_n}, \tag{2}$$

where N_n is the number of measurements for each fragment. The question arises how to split the entire number of measurements one can afford to do, $N_T = \sum_n N_n$, between each fragment so that the total error is the lowest? Show that if one knows fragment variances $(\sigma_{H_n}^2)$ the optimal splitting gives the error

$$| \langle \Psi | \hat{H} | \Psi \rangle - \bar{H} | \leq \frac{\sum_n \sqrt{\sigma_{H_n}^2}}{\sqrt{N_T}}. \tag{3}$$

How many measurements should one do per fragment, N_n, in this optimal splitting ? (Note that even though $\sigma_{H_n}^2$ is not known *a priori* one can use estimations based on classical approximations to $|\Psi\rangle$, for example the Hartree-Fock wavefunction.)

2) Using Eq. (3) calculate how many measurements N_T is needed to achieve 1 mili Hartree estimator error for the qubit-wise commuting (QWC) and fully commuting (FC) partitionings in one of the model systems.

3) *Optional*: Assuming that we could measure the entire $\hat{H}$ as a single operator, estimate using Eq. (1) (use $\hat{H}$ instead of $\hat{H}_n$) how many measurements would be needed to reach 1 mili Hartree estimator error for the same systems as in the previous question?

Step #5: Use of quantum hardware

To carry out the VQE algorithm on the actual quantum hardware one needs to present unitary transformations found in steps 3 and 4 as a sequence of gates (i.e. circuit). Here, we will illustrate circuit generation using compilers. Obtained circuits will allow one to either carry out the entire VQE optimization procedure by optimizing amplitudes of step 3 unitaries or its single step using amplitudes for step 3 obtained on a classical simulator (easier route).

Illustrative code: `S5_Circuits.ipynb`.

Questions:

1) Implement an error-mitigation protocol based on removing measurement results corresponding to a wrong number of electrons, which is described in Ref. [14](see Sec. 3.4. Post-processing

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[1]This covers 2σ's of the gaussian error distribution, so there is 68.27% chance that the error is lower than the given estimate. For a higher fidelity one can take this estimate multiplied by 3 (6σ's) to be 99.73% sure.

Procedure). How different are the results of simulations with and without error-mitigation?

2) Can the error-mitigation protocol described in Ref. [14] be used for more complicated symmetries, like $\hat{S}^2$?

3) *Optional*: Suggest an error-mitigation protocol if you know that the right wavefunction should be an eigenstate of a certain multi-qubit operator $\hat{A}$ with eigenvalue a.

Further Challenges (*Optional*)

Now you're on your own. Discuss ideas for expanding on the above steps with your group. Some possible directions for more advanced treatment:

1. How to obtain excited electronic states of the same or different symmetry? This task is highly relevant to any spectroscopic application of quantum computing because in real experiments and applications not absolute energy but their differences are measured and are important.

2. Hamiltonian measurements (Step #4): There are more advanced techniques to consider that are based on partitioning in the fermionic operator space and then bringing the fragments into the qubit space [15, 16].

3. Unitary transformations (Step #3): Some of the unitary transformations can be applied on the Hamiltonian instead of the wavefunction, this increases accuracy without increasing the circuit depth, but it increases the size of the Hamiltonian and thus introduces the measurement overhead. See Refs. [17, 18] for details.

4. Qubit Hamiltonian preparation (Step #2): Typical fermion-qubit transformations substitute a single molecular spin-orbit by a qubit, which restricts calculations to relatively small basis sets because of the current limitations in the number of qubits. There were several techniques proposed recently to compress larger basis sets into smaller number of qubits [19, 20].

5. What are alternatives to VQE for the electronic structure problem using quantum computers with shallow circuits without error-correction?

Business-related questions in the context of quantum entrepreneurship:

1. What other molecular properties one can obtain using VQE for the purpose of rational material and drug design?

2. What are the systems (molecules / materials) which are challenging for classical computing and whose modelling is valuable ?

3. What businesses can benefit from more accurate electronic structure calculations ?

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