

CDL week 2 answers

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Generating PES using classical methods

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?

Examples of variational techniques are the Hartree-Fock (HF) method and the Full Configuration Interaction (FCI) method. One advantage of using a variational method is that it will always provide a valid answer which is constrained by the way on which the trial wavefunction $|\psi(\theta)\rangle$ is parameterized. Consequently, the energy E that variational methods converge to will never be lower than the actual ground state energy E_g of the system it is trying to solve.

$$E = \langle \psi(\theta) | \hat{H} | \psi(\theta) \rangle \geq E_g$$

In contrast, this property is not guaranteed for perturbative methods, where there is no mechanism which obstructs the theory from predicting an energy value that is too low.

Additionally, variational methods can take advantage of knowledge in quantum chemistry to design a first guess for the wavefunction. Selecting a clever basis can ease the optimization and reduce the computing time by narrowing down the parameter landscape to explore. However, variational methods can sometimes converge to local minima or not converge at all. This may happen when a good trial wavefunction is not known, in which case it might be necessary to use other methods instead.

Another aspect is that in the case of these two examples (HF and FCI), there is often demand to have a method that is more accurate than HF but less costly than FCI. Sometimes, finding the correct balance between accuracy and computational cost is the only way to obtain any meaningful results at all and it may just happen that a non-variational method precisely strikes that balance needed for the task.

Generating the qubit Hamiltonian

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

There are two requirements for a mapping to be valid:

1. The fermionic operators obey a set of anticommutation rules.

$$\begin{aligned}\{\hat{a}_i, \hat{a}_j^\dagger\} &= \delta_{ij} \\ \{\hat{a}_i, \hat{a}_j\} &= 0 \\ \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} &= 0\end{aligned}$$

The mapping needs to preserve the validity of those rules. More generally, every expression of fermionic operators which is true needs to remain true after all of those operators are mapped to qubit operators.

2. A mapping not only maps operators, but also quantum states. A typical choice is to map the vacuum of the Fock space to the qubit state where all qubits are in the $|0\rangle$ state, although in principle any choice is permissible. The qubit operators must be consistent with how the fermionic operators act on the vacuum. For example, whichever state on the quantum computer corresponds to the vacuum state in Fock space needs to be an eigenstate of every qubit operator corresponding to a fermionic annihilation operator, with eigenvalue 0.

$$\hat{a} |0\rangle = 0$$

For a mapping to be physically implementable, there is also a hardware requirement, that the quantum computer has a sufficient number of qubits. If the entire Fermionic Fock space, of dimension N is mapped such that all states are represented as orthogonal computational basis states, then this requires at least $\log_2 N$ qubits.

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?

In this case, the fermionic and qubit Hamiltonians share the same eigenspectrum. Therefore, the qubit Hamiltonian will also be real and each of the terms will always include an even number of Pauli Y matrices.

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

Pros:

- Some research suggests that the number of quantum gates needed for Trotterization may be significantly reduced when using the Bravyi-Kitaev transformation instead of the Jordan-Wigner transformation [1]. Trotterization can be used to implement the Quantum Phase Estimation algorithm.
- The Jordan-Wigner transformation encodes fermionic modes onto separate qubits, whereas the Bravyi-Kitaev transformation distributes all of the fermionic modes among the qubits. This can be beneficial from an error resilience perspective - even if one particular qubit on the hardware is malfunctioning, then the error that it translates to on the prediction about the physical system may still result in an answer which is at least qualitatively similar to the correct answer, when using the Bravyi-Kitaev transformation.
- In the case of the Bravyi-Kitaev transformation, fermionic operations which describe either a change in occupancy or parity within orbitals can be kept track of with $\log_2 N$ qubits, where N

is the number of orbitals involved in the operation. This means that the Bravyi-Kitaev transformation has smaller terms when compared to the Jordan-Wigner transformation, which needs N qubits for the same operation. This means that measuring the expectation values of the terms will most likely be easier with the Bravyi-Kitaev transformation, especially for more complicated operations on larger systems.

Cons (or equivalences):

- In early demonstrations of VQE, the Bravyi-Kitaev transformation was used to reduce the number of qubits for a given calculation [2, 3]. Discovered slightly later, there exist methods to do this also for the Jordan-Wigner transformation [4].
- The Jordan-Wigner transformation is more intuitive to work with, because when examining a state on the quantum computer, it is immediately obvious what state that corresponds to on the physical system, since each qubit is keeping track of a specific orbital. The Bravyi-Kitaev transformation would need to be inversely mapped each time to be made sense of.

Unitary transformations

1) Standard Hamiltonian symmetries are

1. number of electrons $\hat{N}_e = \sum_k \hat{a}_k^\dagger \hat{a}_k$
2. electron spin \hat{S}^2
3. electron spin projection \hat{S}_z
4. time-reversal symmetry
5. point-group symmetry for symmetric molecules

Which of these symmetries are conserved in a) UCC and b) QCC ?

All of these symmetries are conserved in UCC. The QCC ansatz conserves just the time-reversal symmetry, the other symmetries have to be enforced with additional methods.

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

If we construct a unitary operator which commutes with these symmetries, then are able to ensure that the final state is in the same symmetry sector as the initial state. This allows us to specify properties of the final state (such as particle number) by choosing an initial state that has the same properties.

Symmetries can reduce the initial Hilbert space to a subset and it is always easier to map a subset to its own with fewer terms. Therefore the unitary maps carry fewer terms in a subset.

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

In the context of variational algorithms, a penalty term can be added to the Hamiltonian. This

penalty term would persuade the classical optimizer to modify the parameters of the unitary transformation such that the symmetry is not violated.

It is also possible to attempt to perform another unitary transformation within the circuit which would restore the symmetry. However, to construct a corrective transformation, it would be necessary to know beforehand in which way the symmetries were broken in the first place. In the case of UCC, it is also possible to create linear combinations of the Hermitian and anti-Hermitian generators to ensure spin conservation.

If the problem appears at the level of measurement, meaning that some specific samples from the output of the quantum computer break the symmetries, then we can consider applying some post-selection methods, where we discard results that break symmetries and only keep the ones that don't.

Hamiltonian measurements

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

$$|\langle \psi | \hat{H}_n | \psi \rangle - \bar{H}_n| \leq \sqrt{\frac{\langle \psi | \hat{H}_n^2 | \psi \rangle - \langle \psi | \hat{H}_n | \psi \rangle^2}{N}} = \sqrt{\frac{\sigma_{H_n}^2}{N}} \quad (1)$$

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

$$\left(\langle \psi | \hat{H} | \psi \rangle - \bar{H} \right)^2 \leq \sum_n \frac{\sigma_{H_n}^2}{N_n} \quad (2)$$

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 n gives the error

$$|\langle \psi | \hat{H} | \psi \rangle - \bar{H}| \leq \sum_n \sqrt{\frac{\sigma_{H_n}^2}{N_T}} \quad (3)$$

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.)

Suppose we choose the splitting

$$N_n = \frac{N_T \sigma_{H_n}}{\sum_m \sigma_{H_m}} \quad (4)$$

We can see that this is a valid splitting, because

$$\sum_n N_n = \frac{N_T \sum_n \sigma_{H_n}}{\sum_m \sigma_{H_m}} = N_T \quad (5)$$

If we take the square root of equation (2) and insert the splitting (4), we obtain

$$\begin{aligned} |\langle \psi | \hat{H}_n | \psi \rangle - \bar{H}_n| &\leq \sqrt{\sum_n \frac{\sigma_{H_n}^2}{N_n}} = \sqrt{\sum_n \frac{\sigma_{H_n}^2 \sum_m \sigma_{H_m}}{N_T \sigma_{H_n}}} = \sqrt{\frac{\sum_n \sigma_{H_n} \sum_m \sigma_{H_m}}{N_T}} \\ &= \sqrt{\frac{(\sum_n \sigma_{H_n})^2}{N_T}} = \sum_n \sigma_{H_n} \sqrt{\frac{1}{N_T}} = \sum_n \sqrt{\frac{\sigma_{H_n}^2}{N_T}} \end{aligned} \quad (6)$$

Without needing to prove that (4) is the optimal splitting, we can still say that the optimal splitting, by definition of "optimal" must have an error that has an equal or lower bound than the one derived for this choice of splitting.

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.

Let's take H_2 as the model system. This has 5 QWC fragments and 2 FC fragments. To calculate anything, we have to have some estimate for the variance of a single fragment. Let's say it is $\sigma_{H_n} = 10\text{mHa}$. The number of measurements required by each of these to achieve 1mHa accuracy for this system is

$$N_T^{\text{QWC}} = ((1\text{mHa})^{-1} \cdot 5 \cdot 10\text{mHa})^2 = 2500 \quad (7)$$

$$N_T^{\text{FC}} = ((1\text{mHa})^{-1} \cdot 2 \cdot 10\text{mHa})^2 = 400 \quad (8)$$

Use of quantum hardware

2) Can the error-mitigation protocol described in Ref.[5] be used for more complicated symmetries, like \hat{S}^2 ?

Yes, it is mentioned in the paper that this is possible, although it hadn't been implemented in that work.

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 .

For each term in \hat{H} , we could select a measurement basis in which both the term and \hat{A} could be measured. Then, when we are performing the measurements that are meant to construct the expectation value of the term, we also calculate the eigenvalue of \hat{A} for each measurement result and discard results in which the eigenvalue is not equal to a .

Further Challenges (optional)

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.

Excited states can be obtained for example through an approach called variational quantum deflation. In this approach, after the ground state $|\psi_0\rangle$ has been found, a penalty term is added to the hamiltonian in the form of

$$\beta |\psi_0\rangle \langle \psi_0| \quad (9)$$

where β is a real-valued parameter which has a sufficiently high value (larger than the gap between the ground state and first excited state). The existence of this term forces the VQE to optimize within the space that is orthogonal to the ground state, thus finding the next lowest energy state. This method can be used repeatedly, excluding states that have already been found from the search. In principle, this would enable the VQE to find all of the eigenstates of the Hamiltonian, although with each added term, an error accumulates owing to the fact that the obtained state is not exact and may be also difficult to accurately retrieve from the quantum computer by state tomography.

Another method to computing molecular excitation energies on a noisy quantum processor is to use equation of motion [6]. Within this approach, excited states $|n\rangle$ are generated by applying an excitation operator of the general form $\hat{O} = |n\rangle\langle 0|$ to the ground state $|0\rangle$ of the system. The commutation of the Hamiltonian and the excitation operator leads to an expression for the excitation energy:

$$[\hat{H}, \hat{O}]|0\rangle = \hat{H}\hat{O}|0\rangle - \hat{O}\hat{H}|0\rangle = E_n\hat{O}|0\rangle - E_0\hat{O}|0\rangle = E_{n0}\hat{O}|0\rangle \quad (10)$$

Given that $E_{n0} = E_n - E_0$. Restricting excitation to single and double excitations helps to make an ansatz for the operator \hat{O} in terms of $\hat{a}_m^\dagger \hat{a}_i$ and $\hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_i \hat{a}_j$ so that electrons make transition from an orbital labelled by i, j to another orbital labelled by m, n . This helps to make estimates on the excitation energy gap with the ground state E_n0 .

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

One alternative is the Iterative Phase Estimation Algorithm (IPEA), which is a NISQ-friendly version of the Quantum Phase Estimation (QPE) algorithm, able to work with shallow circuits at the expense of multiple iterations [7].

Another alternative is to not use the quantum circuit model at all, but instead perform analog quantum computation or attempt to use adiabatic state preparation to find the ground state [8].

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?

- For drug design, one important aspect is to make sure that a prospective drug is soluble in certain liquids such as water or blood. The solubility of compounds can be modelled

through quantum chemistry simulations, and VQE is able to help with that. If the solvent is treated as a perturbation to the molecular Hamiltonian, VQE can determine the electronic structure of the molecule in the solvent. The energy values can be used as input to classical thermodynamic models, which can calculate quantities such as partition coefficients and solubility.

- In materials and drug manufacturing, catalysts are often used. VQE could help design better manufacturing processes by improving the knowledge about catalysts. Catalysts reduce the potential energy barrier between a reaction pathway, thereby increasing the reaction rate. VQE can be used to map out the potential energy surfaces of molecules in the presence of various catalysts and find out what the new reaction rate would be. This would be useful for catalyst design and discovery.
- With many drugs and materials, photodegradation is an issue. The way in which light may cause unwanted changes in a compound or material is largely governed by the energy spectrum of those materials. VQE can calculate the energy values in that spectrum, which would enable us to predict what kind of lighting conditions a drug or material should be stored in to maintain an optimal lifetime.

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

- Proteins play a huge role in molecular biology, but are difficult to model with classical computing simply due to their sheer size. Proteins govern many functions of biological systems and can also be used as bases for new drugs.
- Systems where the primary mechanism of reaction is proton transfer are hard to simulate classically, because the Born-Oppenheimer approximation cannot be used. Quantum approaches might be more amenable to not making that approximation. These systems are of interest to fuel cell development.
- Chemical elements with high atomic number are difficult to simulate, because orbital basis sets to describe them are lacking or inaccurate. Nuclear energy is one example of a field that relies heavily on our understanding of those elements. Modern approaches to nuclear energy include compact molten salt reactors, in which uranium or plutonium are included in a complicated mix of molten salt. For those use cases it would be very valuable to be able to optimize such mixtures.
- High-temperature superconductors are poorly understood and are difficult to model classically due to their inherent quantum nature. Discovering superconducting materials that operate at higher temperatures could revolutionize energy applications.

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