Proof-of-concept Quantum Use Case

Simulation – Summary

In the current **NISQ (noisy intermediate-scale quantum) era**, the most feasible and promising use cases for quantum computing are **optimization**, **simulation**, and **machine learning**. This is a summarized version of the proof-of-concept use case in optimization produced by DeiC's Quantum Department as part of the Q-Access initiative to make quantum use-case development more accessible to Danish academia and industry. Find the full proof-of-concept use case and more at https://github.com/DeiC-Quantum/Proof-of-concept-Quantum-Use-Cases.
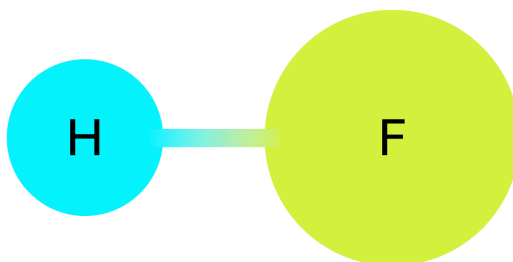
Simulation

Simulating quantum systems is a notoriously difficult but powerful tool for solving problems in *chemistry*, *physics*, *material science*, and the *pharmaceutical industry*.

To tackle problems in these areas, most NISQ algorithms take a hybrid approach by using *classical optimization techniques* to tune the parameters of *variational quantum circuits*. In this proof-of-concept use case, we will consider an **simulation problem in chemistry** and then walk through, step by step, a variational quantum algorithm which solves the problem.

Problem: Estimating the Ground-State Energy of a Small Molecule

Suppose that we have a small molecule with a particular geometry, and we would like to calculate its lowest energy level, or **ground-state energy**. In chemistry, this is an essential reference for quantitative predictions of molecular stability, reactivity, and spectroscopic signatures. In this case, we will consider the extremely dangerous hydrogen flouride atom HF at its equilibrium bond length, depicted below.

We will consider the Bohr-Oppenheimer approximation, which treats the nuclei as fixed and treats the electrons as dynamic, and we will set the bond length between the hydrogen and flourine atoms to the equilibrium bond length. With this setup, there is a variational quantum algorithm called a **variational quantum Eigensolver (VQE)**, which can estimate the ground-state energy. VQE was originally proposed in [1] and can be applied to a variety of problems ranging from the chemistry problem we are considering to problems in optimization and machine learning.

Precise Formulation of Our Problem

A **Hamiltonian** H in quantum mechanics is an operator that represents the total energy of a system. From a "spectral decomposition" of the Hamiltonian, one can find the possible energy levels of the system, which will be a finite set $\{E_0, E_1, E_2, ..., E_n\}$ typically ordered from smallest to largest. The **ground state** $|\Psi_0\rangle$ of a quantum system is the lowest energy state, which will have energy E_0 and satisfy

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle. \tag{1}$$

The **excited states** $\{|\Psi_1\rangle, |\Psi_2\rangle, ..., |\Psi_n\rangle\}$ are the states with energy greater than the ground state, and they satisfy $H|\Psi_i\rangle = E_i|\Psi_i\rangle$.

So, if we want find the ground state and corresponding ground-state energy of our atomic system, we must find its spectral decomposition, also known as its "eigendecomposition." Indeed, this problem is a special

case of the more general problem of finding **eigenvalues** (corresponding to the energy levels) and **eigenvectors** (corresponding to the states). Finding the full eigendecomposition is computationally expensive, but we are only looking for the smallest eigenvalue and its corresponding eigenvector, which is exactly what a variational quantum eigensolver (VQE) is designed to do.

VQE can be applied to wide range of Hamiltonians, and for the purpose of this summary we will assume that the Hamiltonian is given. Indeed, to obtain this form of the Hamiltonian for H^{HF} from our problem, we will use the Qiskit Nature library [2]. For this we only need to specify the 3-dimensional coordinates of the hydrogen and flourine atoms in our system, which will be given in angstroms (Å) as follows.

Atom	x	y	z
H	0.0	0.0	0.0
F	0.0	0.0	0.9168

With this geometry, the hydrogen and flourine are 0.9168Å apart, which is the equilibrium bond length according to the NIST Computational Chemistry Comparison and Benchmark DataBase [3]. The full expression for H^{HF} is given in terms of 631 Pauli strings on 12 qubits, which is too long to display here, but its general form is given below along with a few terms.

$$H^{\mathrm{HF}} = \sum_{P_i \in \{I,X,Y,Z\}^{\otimes 12}} c_i P_i = \begin{cases} -65.947\, I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \\ +16.182\, I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes Z \\ +2.338\, I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes Z \otimes I \\ \vdots \\ +0.004\, Y \otimes Z \otimes Z \otimes Z \otimes Z \otimes Y \otimes Y \otimes Z \otimes Z \otimes Z \otimes Y \otimes I \\ \vdots \\ +0.155\, Z \otimes Z \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \end{cases} \tag{2}$$

Flourine has 5 spatial orbitals and Hydrogen has 1. For each spatial orbital, there is either a spin-up or spin-down electron, which is why the above Hamiltonian acts on 12 qubits. Now, since we are considering neutral HF, Flourine will contribute 9 electrons and Hydrogen 1 for 10 total electrons. Moreover, since HF is a "spin singlet" it will have an equal number of spin-up and spin-down electrons. If we just filled up the orbitals with 5 spin-up and 5 spin-down electrons in order of their energy from lowest to highest in the basis provided by Qiskit Nature, we would obtain the Hartee-Fock state, given below.

$$\Psi^{\mathrm{Hartree\text{-}Fock}} = |111110111110\rangle \tag{3}$$

Now, to solve our problem, we need to find an approximation of ground state $\left|\Psi_0^{\mathrm{HF}}\right\rangle$ and ground-state energy E_0^{HF} for H^{HF}, which satisfies

$$H^{\mathrm{HF}}\left|\Psi_0^{\mathrm{HF}}\right\rangle = E_0^{\mathrm{HF}}\left|\Psi_0^{\mathrm{HF}}\right\rangle. \tag{4}$$

The Hartree-Fock state is generally not the ground state of the full interacting Hamiltonian, but it will serve as a good starting point for our approximation.

Motivation from Variational Quantum Simulation

The variational principle is the basis for VQE and is a useful tool for establishing upper bounds on ground-state energies and, along with classical optimization of tunable parameters, can be used to approximate ground-state energies.

<div align="center">**Variational Principle**</div>

For a Hamiltonian H that describes the a quantum system and a "trial state" $|\Psi\rangle$ with $\langle\Psi|\Psi\rangle = 1$, the ground-state energy E_0 is always less than or equal to the expectation value of the energy of the state of $|\Psi\rangle$. That is, we have the following.

$$E_0 \leq \langle\Psi|H|\Psi\rangle \tag{5}$$

Moreover, if we have

$$E_0 = \langle\Psi|H|\Psi\rangle \tag{6}$$

then $|\Psi\rangle = |\Psi_0\rangle$ is the ground state of the system described by H. Thus, by **varying** Ψ until the expectation value $\langle\Psi|H|\Psi\rangle$ is minimized, we can obtain approximations of the ground-state and the ground-state energy.

Now, we want to consider a tunable trial state, so we will introduce parameters $\boldsymbol{\theta} = (\theta_1, ..., \theta_N)$ and consider a state $|\Psi(\boldsymbol{\theta})\rangle$ that depends on these parameters. This in turn gives us a tunable energy function

$$E(\boldsymbol{\theta}) = \langle\Psi(\boldsymbol{\theta})|H|\Psi(\boldsymbol{\theta})\rangle. \tag{7}$$

Our problem then becomes to find an approximation of the set of parameters which minimizes this energy function, i.e.

$$\boldsymbol{\theta}_{\text{optimal}} \approx \underset{\boldsymbol{\theta}}{\operatorname{argmin}} E(\boldsymbol{\theta}). \tag{8}$$

This optimal set of parameters gives us an approximation of the ground-state energy

$$E_0^{\text{HF}} \approx E(\boldsymbol{\theta}_{\text{optimal}}) \tag{9}$$

and an approximation of the ground-state

$$\left|\Psi_0^{\text{HF}}\right\rangle \approx \left|\Psi(\boldsymbol{\theta}_{\text{optimal}})\right\rangle. \tag{10}$$

In order to prepare such a tunable state for VQE, we will use a variational quantum circuit.

Variational Quantum Eigensolver (VQE)

The VQE algorithm is a straightforward implementation of the variational principle discussed above.

<div align="center">**Outline of VQE**</div>

Goal: Find an approximation of the ground-state energy E_0 of a given Hamiltonian H.

Strategy
1. Construct a variational quantum circuit $Q(\boldsymbol{\theta})$ depending on N parameters $\boldsymbol{\theta} = (\theta_1, ..., \theta_N)$.
2. Optimize the parameters $\boldsymbol{\theta}$, by repeatedly running the circuit from Step 1 to estimate the energy

$$E(\boldsymbol{\theta}) = \langle\Psi(\boldsymbol{\theta})|H|\Psi(\boldsymbol{\theta})\rangle. \tag{11}$$

   where

$$|\Psi(\boldsymbol{\theta})\rangle = Q(\boldsymbol{\theta})|0\rangle \tag{12}$$

   and by updating the parameters to lower the energy.
3. Estimate the ground-state energy E_0 by sampling the final optimized circuit.

There are numerous classical optimization algorithms which could be used for Step 2 above, but we will not delve into these and instead rely on existing implementations from the open-source Python library SciPy [4]. However, this leaves a big question unanswered. How do we construct an appropriate

variational quantum circuit $Q(\boldsymbol{\theta})$? There are several potential considerations for designing the variational form, or **ansatz**, for our quantum circuit. Ultimately, we will use a chemistry-tailored ansatz that keeps the number of spin-up and spin-down electrons fixed.

Finally, in variational methods like VQE ideally we start with a state that is already a decent approximation. For our problem of approximating the ground-state energy of HF, we will start with the Hartree-Fock approximation of HF from Equation (3).

We have implemented the VQE algorithm tailored to this problem using iskit [5], Qiskit Nature [2], and SciPy [4], which is available at https://github.com/DeiC-Quantum/Proof-of-concept-Quantum-Use-Cases along with the full proof-of-concept use case tutorial.

Results

From the VQE implementation in the above Qiskit code, we obtain the following estimate for the ground-state energy.

$$E_0^{\text{VQE}} = \left\langle \Psi_0^{\text{VQE}} \middle| H^{\text{HF}} \middle| \Psi_0^{\text{VQE}} \right\rangle \approx -103.764 \tag{13}$$

where $\left| \Psi_0^{\text{VQE}} \right\rangle = \left| \Psi^{\text{VQE}}(\boldsymbol{\theta}_{\text{optimal}}) \right\rangle = Q^{\text{VQE}}(\boldsymbol{\theta}_{\text{optimal}})|0\rangle$. In this case, we can also compute E_0^{HF} and $\left| \Psi_0^{\text{HF}} \right\rangle$ exactly and see how well our implementation of VQE performed.

$$E_0^{\text{HF}} = \left\langle \Psi_0^{\text{HF}} \middle| H^{\text{HF}} \middle| \Psi_0^{\text{HF}} \right\rangle \approx -103.791 \tag{14}$$

So, our approximation is quite good without having to tune any meta-parameters! We can also compute the fidelity of our approximation for the ground state, which is given as follows.

$$\left| \left\langle \Psi_0^{\text{VQE}} \middle| \Psi_0^{\text{HF}} \right\rangle \right|^2 \approx 0.983 \tag{15}$$

A perfect fidelty would be 1, so the fidelity is also quite good.

References

[1] A. Peruzzo *et al.*, "A variational eigenvalue solver on a quantum processor," *Nature Communications*, vol. 5, 4213, Jul. 2014, doi: 10.1038/ncomms5213.

[2] The Qiskit Nature developers and contributors, *Qiskit Nature 0.6.0 (0.6.0)*. doi: 10.5281/zenodo.7828767.

[3] NIST Computational Chemistry Comparison and Benchmark DataBase, "Experimental data for HF (Hydrogen fluoride)." [Online]. Available: https://cccbdb.nist.gov/exp2x.asp?casno=7664393&charge=0

[4] P. Virtanen *et al.*, "SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python," *Nature Methods*, vol. 17, no. 3, pp. 261–272, Feb. 2020, doi: 10.1038/s41592-019-0686-2.

[5] A. Javadi-Abhari *et al.*, "Quantum computing with Qiskit," *arXiv*, May 2024, doi: 10.48550/arXiv.2405.08810.

[6] P. J. J. O'Malley *et al.*, "Scalable quantum simulation of molecular energies," *Physical Review X*, vol. 6, 31007, Jul. 2016, doi: 10.1103/PhysRevX.6.031007.

Appendix: Data and Resources

The Python code implementing the VQE algorithm tailored to this problem using Qiskit [5], Qiskit Nature [2], and SciPy [4] is available at https://github.com/DeiC-Quantum/Proof-of-concept-Quantum-Use-Cases.