

Quantum Simulation of Excited States of Molecules

UTKARSH SARASWAT

Technical university of Munich

Seminar report: Advanced Topics in Quantum Computing

1 Introduction

As part of the “Seminar: Advanced topics in Quantum Computing”, we studied two approaches for electronic structure simulation of small molecules using quantum algorithms, namely i) Variational Quantum Deflation and ii) Quantum Equation of Motion. We will discuss in detail the implementation and briefly cover the results and further improvements for both methods.

2 Methodology

2.1 Variational Quantum Deflation

Matrix deflation is a mathematical tool used in Principal Component Analysis (PCA) to eliminate the influence of a particular eigenvector. We can understand this with a simple example. Let there be a square matrix \mathbf{M} . The eigenvalue decomposition of \mathbf{M} will be $M = U\lambda U^{-1}$ where rows of U are the eigenvectors of \mathbf{M} and λ is a diagonal matrix with eigenvalues of \mathbf{M} .

Now if \mathbf{M} is a hermitian matrix, i.e, $M^\dagger = M$ then U can be written as a unitary matrix $U^\dagger U = I$ and it also implies each of the columns of U will be orthogonal to every other column. We can hence write M as

$$M = \lambda_1 v_1 v_1^t + \lambda_2 v_2 v_2^t + \dots \quad (1)$$

where v_i are eigenvectors (column), v_i^t are transpose of corresponding eigenvector (row) and λ_i being corresponding eigenvalues. If we want to get rid of a particular Eigen component from this matrix, we can perform the following transformation

$$M = M - \lambda_i v_i v_i^t \quad (2)$$

Essentially reducing the rank of the matrix (which can be thought of as deflation of a matrix). There are multiple approaches to deflation. For example, in Hotelling’s deflation, we start with M , find the largest eigencomponents of the matrix, perform deflation operation, and find the next highest eigencomponent, and we can perform it recursively up to any times (based on the size of the matrix).

In the context of Variational quantum deflation, we want to find excited states of a given Hamiltonian. By default, the standard Variational Quantum Eigensolver is designed to find the ground state of a Hamiltonian, or in other words, the lowest eigenvalue of the Hamiltonian matrix. We can utilize the deflation technique to get rid of the ground states from the Hamiltonian recursively and find excited states. The deflation methodology used here is based on constrained optimization. Let’s say if we have an objective function $f(\theta)$ we want to minimize w.r.t θ and under the constraint that $g(\theta) = 0$ We can achieve this by rewriting the objective function as

$$F(\theta) = f(\theta) + \beta g(\theta) \quad (3)$$

With β being an additional parameter w.r.t which we have to optimize. The corresponding equation in VQD is written as

$$F(\lambda_i) = \langle \Psi(\lambda_k) | H | \Psi(\lambda_k) \rangle + \sum_{i=1}^{k-1} |\beta_i \langle \Psi(\lambda_i) | \Psi(\lambda_k) \rangle|^2 \quad (4)$$

Here, the first part is taken from the standard VQE algorithm, which minimized the expectation value of a given ansatz of choice with respect to a given Hamiltonian. The counterpart of θ from equation (3) is λ_i in this case, which are the state parameters in our ansatz.

The VQD is based on this technique with the exception that β is not continuously optimized with state parameter λ but can be tuned separately to converge to an accurate value. To see how this scheme works we can look at a simple example

Let's say we have ground state hamiltonian and we used VQE to find ground state λ_0 . Our next step will be

$$F(\lambda_1) = \langle \Psi(\lambda_1) | H | \Psi(\lambda_1) \rangle + |\beta_1 \langle \Psi(\lambda_0) | \Psi(\lambda_1) \rangle|^2 \quad (5)$$

We know that both of the expressions will have positive values (assuming the Hamiltonian \mathbf{H} is positive semi-definite), therefore the lower bound of the above expression will be

$$\min(\langle \Psi(\lambda) | H | \Psi(\lambda) \rangle) + \min(|\beta_1 \langle \Psi(\lambda_0) | \Psi(\lambda_1) \rangle|^2) \geq 0 \quad (6)$$

We also know that $\min(\langle \Psi(\lambda) | H | \Psi(\lambda) \rangle) = E_0$ (based on the fact E_0 , the ground state is always the lowest eigenvalue of \mathbf{H}) and $\min(|\beta_1 \langle \Psi(\lambda_0) | \Psi(\lambda_1) \rangle|^2) = 0$.

There are two ways to arrive at the next largest minima. First we have $\lambda = \lambda_0$, the value of $|\beta_1 \langle \Psi(\lambda_0) | \Psi(\lambda_1) \rangle|^2$ will be β_1 and hence total value will be $E_0 + \beta_1$. Second, at $\lambda = \lambda_1$, the value will be E_1 (since all eigenstates are orthogonal to each other). However, E_0 is known already, and we instead want to find E_1 ; therefore, it must imply that if we want convergence of the optimization algorithm at E_1 , we have to make sure it is the point of minima, or in other words

$$E_1 < E_0 + \beta \quad \text{or} \quad \beta > E_1 - E_0 \quad (7)$$

Since we don't have a priori knowledge about E_1 , we can initialize β to a guess value. At any point of convergence, we can simply perform a check if $\min(f(\lambda_1))$ is equal to $E_0 + \beta_1$ and accordingly keep on increasing value of β_1 , until the point where minima is independent of choice of β_1 . It is easy to see that we can implement this algorithm inductively for any excited state λ_i . For example, if we have found optima up to $k - 1$ excitation, we have

$$F(\lambda) = \langle \Psi(\lambda) | H | \Psi(\lambda) \rangle + \sum_{i=1}^{k-1} |\beta_i \langle \Psi(\lambda_i) | \Psi(\lambda) \rangle|^2 \quad (8)$$

Two possible minima of the above equation will be E_i at $\lambda = \lambda_i$, or $E_0 + \beta_0$ at $\lambda = \lambda_0$, or $E_k + \beta_k$ at any $k < i$. To ensure the optimizer converges at $\lambda = \lambda_i$ we have to make sure $\beta_k > E_i - E_k$, or as a safer option, we can make $\beta_k > E_i - E_0$ for every case ensuring convergence at every step.

2.2 Quantum Equation of Motion

The Quantum Equation of Motion method, or qEOM, is based on the classical method Equation of Motion (EOM). The fundamental idea behind EOM is to express excitation energy directly as a function of the excitation state.

We start with excitation and de-excitation operators as

$$O_n^\dagger = |n\rangle \langle 0|; \quad O_n = |0\rangle \langle n| \quad (9)$$

It's easy to see that from the above definition, it follows

$$\begin{aligned} O_n^\dagger |0\rangle &= |n\rangle; \quad O_n |0\rangle = 0 \\ O_n^\dagger |n\rangle &= 0; \quad O_n |n\rangle = |0\rangle \end{aligned} \quad (10)$$

Our objective is to calculate the excitation state energy E_n . We can define a new quantity E_{0n} as $E_{0n} = E_n - E_0$ and knowing E_{0n} and E_0 would be sufficient to calculate E_n . Since the energy of any state can be expressed in terms of the Hamiltonian as

$$H |0\rangle = E_0 |0\rangle \quad H |n\rangle = E_n |n\rangle \quad (11)$$

Based on equations (11) and (10), we can write the commutator

$$\begin{aligned} [H, O_n^\dagger] |0\rangle &= HO_n^\dagger |0\rangle - O_n^\dagger H |0\rangle = H |n\rangle - E_0 O_n^\dagger |0\rangle = (E_n - E_0) |0\rangle = E_{0n} |0\rangle \\ [H, O_n] |n\rangle &= HO_n |n\rangle - O_n H |n\rangle = E_0 O_n |n\rangle - E_n O_n |n\rangle = -E_{0n} O_n |n\rangle = -E_{0n} |0\rangle \end{aligned} \quad (12)$$

Additionally, we can also derive

$$\begin{aligned} [O_n, [H, O_n^\dagger]] |0\rangle &= O_n [H, O_n^\dagger] |0\rangle - [H, O_n^\dagger] O_n |0\rangle \\ &\implies E_{0n} O_n |n\rangle = E_{0n} |0\rangle \\ &\implies \langle 0 | [O_n, [H, O_n^\dagger]] |0\rangle = E_{0n} \\ [[O_n, H], O_n^\dagger] |0\rangle &= [O_n, H] O_n^\dagger |0\rangle - O_n^\dagger [H, O_n] |0\rangle = E_{0n} |0\rangle \\ &\implies \langle 0 | [O_n, [H, O_n^\dagger]] |0\rangle = E_{0n} \end{aligned} \quad (14)$$

Equation (14) inspires us to define the ternary commutator as

$$[O_n, H, O_n^\dagger] = \frac{[[O_n, H], O_n^\dagger] + [O_n, [H, O_n^\dagger]]}{2} \quad (15)$$

And hence we get an expression for the Excitation energy difference in terms of the ground state as

$$E_{0n} = \langle 0 | [O_n, H, O_n^\dagger] |0\rangle \quad (16)$$

The above result assumes the states are normalized or $\langle 0|0\rangle = 1$; however, this may not always be the case. Therefore, a more generic result will be

$$E_{0n} = \frac{\langle 0 | [O_n, H, O_n^\dagger] |0\rangle}{\langle 0 | [O_n, O_n^\dagger] |0\rangle} \quad (17)$$

ensuring normalization.

Since the excited state $|n\rangle$ is still unknown, we need to express it in an ansatz form and optimize it with respect to the ansatz parameters in order to calculate the excitation energy from equation (17). In Quantum subspace expansion, the O_n^\dagger is written as

$$O_n^\dagger = \sum_{\alpha} \sum_{\mu_{\alpha}} X_{\mu_{\alpha}}^{\alpha}(n) E_{\mu_{\alpha}}^{\alpha} \quad (18)$$

Where $X_{\mu_{\alpha}}^{\alpha}(n)$ all possible excitation to the state $|n\rangle$ of the order α and μ_{α} represents all possible excitation of order α . In case of qEOM, we add an additional term

$$O_n^\dagger = \sum_{\alpha} \sum_{\mu_{\alpha}} X_{\mu_{\alpha}}^{\alpha}(n) E_{\mu_{\alpha}}^{\alpha} - Y_{\mu_{\alpha}}^{\alpha}(n) E_{\mu_{\alpha}}^{\alpha \dagger} \quad (19)$$

It is not clear from the paper how the de-excitation operator O_n is defined. One would assume that the term $Y_{\mu_{\alpha}}^{\alpha}(n) E_{\mu_{\alpha}}^{\alpha \dagger}$ is the de-excitation part, but we will not get the same result on substituting this value into the equation (17). But it is clear that by including $Y_{\mu_{\alpha}}^{\alpha}(n) E_{\mu_{\alpha}}^{\alpha \dagger}$ term in the excitation operator, we make sure that all possible de-excitation are also taken into account while calculating the energies. It can be shown that on limiting the terms in equation (19) to only single and double excitation, substituting equation (19) into (17), and solving the optimization equation obtained by differentiating the new equation w.r.t the ansatz parameters, one will obtain a solution

$$\begin{pmatrix} M & Q \\ Q^* & M^* \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \end{pmatrix} = E_{0n} \begin{pmatrix} V & W \\ -W^* & -V^* \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \end{pmatrix} \quad (20)$$

where **M**, **Q**, **V**, **W** are $n * n$ matrices with each element as

$$\begin{aligned} M_{\mu_{\alpha}\nu_{\beta}} &= \langle 0 | [E_{\mu_{\alpha}}^{\alpha}, H, E_{\nu_{\beta}}^{\beta}] | 0 \rangle \\ Q_{\mu_{\alpha}\nu_{\beta}} &= -\langle 0 | [E_{\mu_{\alpha}}^{\alpha}, H, E_{\nu_{\beta}}^{\beta}] | 0 \rangle \\ V_{\mu_{\alpha}\nu_{\beta}} &= \langle 0 | [E_{\mu_{\alpha}}^{\alpha}, E_{\nu_{\beta}}^{\beta}] | 0 \rangle \\ Q_{\mu_{\alpha}\nu_{\beta}} &= \langle 0 | [E_{\mu_{\alpha}}^{\alpha}, E_{\nu_{\beta}}^{\beta}] | 0 \rangle \end{aligned} \quad (21)$$

The expression obtained above is similar to the measurement step in VQE. Hence, the quantum advantage of this algorithm lies in the calculation of the four matrices **M**, **Q**, **V**, and **W**. For classical matrix calculation, without any concurrent algorithm, the complexity of matrix calculation can be calculated as $O(m^2)O(n^2)$ where m is the size of the Hamiltonian and n is the rank of these matrices, which is equal to all possible single and double excitation. It is mentioned in the paper that quantum complexity of the matrix calculation is $O(N^4)$ where the N is said to be number of terms in Hamiltonian. It is not exactly clear whether N is the same as m or a different quantity. As for the calculation of energy, the right-hand matrix of equation (20) can be diagonalised and the corresponding eigenvalues can be calculated classically, which will result in excitation energy.

3 Results

Both algorithms have given highly accurate results for different excited states within chemical accuracy. The two images in Figure 1 depict the results of the respective algorithms.

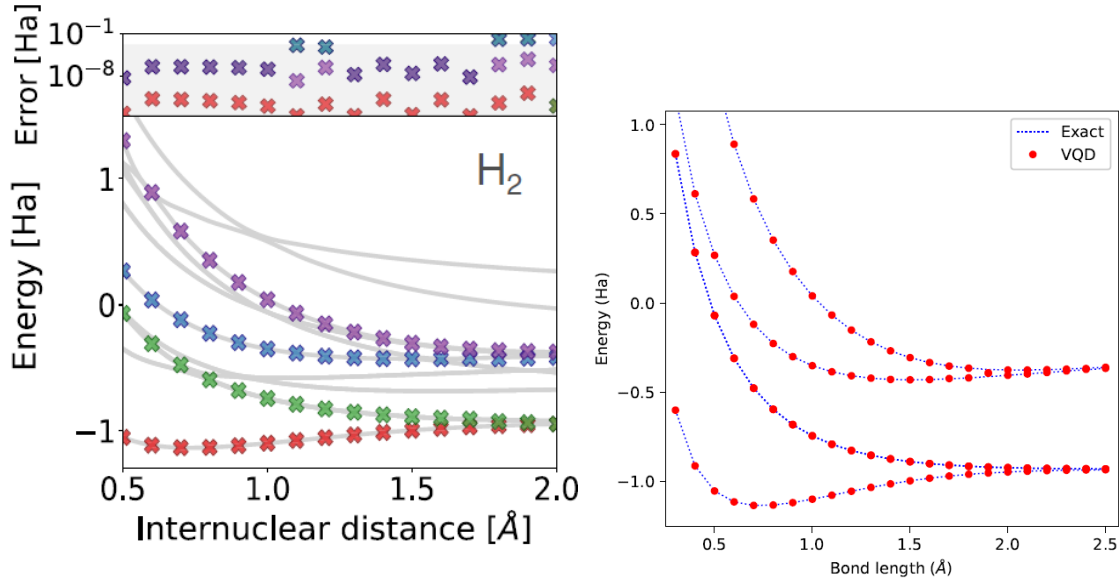


Figure 1: Left: Results for qEOM H_2 molecule simulation, grey line represents actual values and colored cross represents qEOM values. Right: Results for QD H_2 molecule simulation

It is not obvious to conclude performance of which algorithms is better, however VQD was performed only for H_2 molecule while qEOM was also performed on heterogeneous molecule like H_2O and LiH . Additionally, QEOM also provided a method to reduce the number of orbitals in the active space (i.e, performing simulation only for orbitals active in molecular interaction and ignoring the low-lying frozen orbitals). In the case of LiH , the active space was reduced from 10 to 4, which significantly reduced the computational cost.

4 Further improvements

While there aren't any specific suggestions given for qEOM for more accurate/faster results, in case of VQD, a symmetry-constrained optimization is recommended. It was observed that the error amplifies with the increasing number of excitation states in the case of VQD. Using symmetry-constrained optimization, we can tweak equation (4) as

$$F(\lambda_i) = \langle \Psi(\lambda_k) | H | \Psi(\lambda_k) \rangle + \sum_{i=1}^{k-1} (|\beta_i \langle \Psi(\lambda_i) | \hat{C}_i | \Psi(\lambda_k) \rangle|^2 - c_i) \quad (22)$$

Here, the \hat{C}_i is a symmetry operator and c_i is the expected value of the symmetry operation. The fundamental idea behind equation (22) is that the space of the molecular energies is much smaller compared to the Hilbert solution space of the energy equation. Electronic distribution of molecules often follows a symmetrical pattern, and by constraining our solution to a particular symmetry, we are not only reducing solution space but also making it more accurate.

5 Conclusion

In this seminar, we first understand the Variational Quantum Eigensolver algorithm, which served as the foundation of the VQD and qEOM algorithms of our study. We later attempted to understand methodologies and explain in detail the mathematics behind these methods. We also established a relationship between the VQD and the qEOM with the standard qEOM algorithm and explained the quantum advantage achieved. Finally, we also briefly covered results and possible ways for error mitigation in the VQD method.

References

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