Exploration of the Variational Quantum Eigensolver Applied to Calculation of Ground and Excited State Energies for Molecules

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I. Introduction

At Quantum Thought, we want to bring promising quantum computing technology to commercial fruition. One area of focus is molecular modeling and general materials simulation. Many companies model materials for a number of purposes, from creating new medicines to rethinking transportation vehicles. Upon talking with materials scientists that focus on computational modeling, a limitation we have heard repeatedly is that these simulations (for example, density functional theory or DFT calculations) are extremely time intensive. This is the pain point we are focusing on alleviating at Quantum Thought.

Quantum computers can perform fundamental calculations, like finding ground state and excited state energies of various molecules, exponentially faster than even the most powerful classical computers. As different quantum computing hardware platforms expand their capabilities, we are closer and closer to the point where quantum computing can have a meaningful impact on materials science. Quantum Thought is ensuring that when the hardware reaches this point, the software is ready for companies to immediately make groundbreaking progress for various materials science applications.

Quantum Thought is developing an easy-to-use graphical user interface in tandem with the variational quantum eigensolver (VQE) technique (described in the technical details section below) to efficiently execute relevant calculations for selected molecules. We begin by calculating ground state and excited state energies for small molecules, creating a path for scaling to larger molecules as the number of qubits available and the capabilities of quantum computers expand. We additionally have the resources to customize this baseline platform to generate calculations for different types of companies, based on their specific needs. A detailed description of our procedure for ground state energy calculations can be found in the following section.

II.   Quantum computation of ground state energy of a molecule

Variational quantum eigensolver (VQE) is a promising tool for studying molecules in chemistry. It is a hybrid quantum- classical algorithm [1]. The quantum element of this algorithm is in the state preparation in the form of a tunable ansatz (guess for the quantum state), which is computationally expressed in terms of a quantum circuit. Computation of the molecular Hamiltonian and optimization of parameters are done classically. The ansatz parameters are adjusted variationally until the expectation value of the Hamiltonian reaches the minimum. Figure 1 shows a schematic of the VQE algorithm.
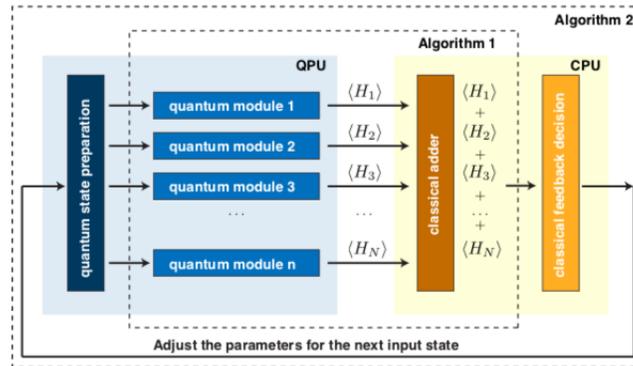

FIG. 1.   A schematic of the variational quantum eigensolver. Figure copied without permission from Ref.[1]

We demonstrate the implementation of VQE to find the ground state energies of small molecules such as H2, LiH, BeH2, H2O, and CH4 for given bond lengths. We use IBM's qiskit programming language to simulate VQE in a classical computer. Technical details of the implementation can be found in Ref.[2], where the results for H2, LiH, and BeH2 are also reported. An advantage of using Qiskit is the integration of the PySCFDriver and FermionicOperator libraries, which contain relevant molecular data, within the package.

Constructing the molecular Hamiltonian is the first step:

$$\hat{H} = \sum_{p,q} h_{pq}\hat{a}_p^{\dagger}\hat{a}_q + \sum_{p,q,r,s} h_{pqrs}\hat{a}_p^{\dagger}\hat{a}_q^{\dagger}\hat{a}_r\hat{a}_s, \tag{1}$$

where h_{pq} and h_{pqrs} are some one- and two- body integral values which can be looked up in the PySCFDriver. The parameters for the built-in PySCFDriver function include the atoms which make up the molecule, molecular geometry, and the basis type to be used. The function then returns the self consistent field integrals values h_{pq} and h_{pqrs}. The molecular geometry is a function of the bond length and is expressed in cartesian coordinate system. The basis we used for all our test cases is the standard STO-3G (Slater-type orbital with 3 orbitals expressed as Gaussian wavefunctions) [3, 4], which are functions used as atomic orbitals to describe molecular properties and charge distributions. The Born-Oppenheimer model is assumed where the atomic nuclei are treated stationary with respect to the fast-moving surrounding electrons. This implies separable and independent energy computations between the nucleus and electrons. Molecular Hamiltonian in Eq. (1) only represents the electronic components while the repulsion energy from the nucleus can be easily extracted from the PySCFDriver.

Conversion of the second-quantized Hamiltonian in Eq. (1) to qubit Hamiltonian is done through the Fermionic-Operator function. The function maps the creation and annihilation operators $\hat{a}^{\dagger}$ and $\hat{a}$ onto spin or quantum gate operators. The three most commonly used transformations are parity [5, 6], Jordan-Wigner [7, 8], and Bravyi-Kitaev [9, 10], which are included in the FermionicOperator library. Results from three different mappings do not vary significantly for our test molecules. The number of qubits is equal to the number of spin orbitals. By symmetry or conservation of electron number and spin, the number of qubits can be reduced by two since the Hamiltonian does not act on these two qubits [11, 12]. This reduction is a computational advantage and does not affect the final result.

The initial state for the variational form is set to a particle number conserving Hartree-Fock state which is a spin orbital occupational number representation of the molecule. Next, a basic parametrized variational form of the trial ground state can be constructed from a series of rotations around Y and Z axes of each qubit where the angles and phases are the parameters. A more formal, standard, and more robust choice, however, is the UCCSD (unitary coupled cluster with single and double excitations) which creates a parametrized ansatz by considering excitations above the initial reference state [15]. This can be easily implemented by using the available UCCSD function. The

depth of this ansatz is set to one for all the test molecules. The qubit Hamiltonian and the ansatz state make up the quantum circuit of the VQE algorithm which is to be executed in a quantum processor. Measurement can then be performed to evaluate the energy of the prepared trial state. The measured energy is fed to a classical optimizer that returns the next quantum circuit parameters that further reduce the energy. Iterations between the quantum circuit executions and classical optimizations are performed until the lowest energy is reached. The VQE algorithm is designed to be implemented in a real quantum machine. However, for simulation purposes, we choose the `statevector_simulator` as backend to run the quantum circuit. This simulator evaluates the expectation values by calculating the wave function amplitude without sampling from large number of data and assuming noiseless circuits. The classical optimizers `L_BFGS_B()` and `SLSQP()` are used. We also note that running VQE on IBM's QPU remotely (by selecting `ibmq_qasm_simulator` as backend) takes a long time and yields inaccurate result even for small number of qubits. This may be caused by communication bottleneck which results from the quantum device and classical machines not being physically located in the same place [16].

Table I shows the ground state energy results of implementing VQE for different small molecules. The first (molecule), second (geometry), and fifth (bond length) columns are user-defined. If the number of spin orbitals is M, then the maximum number of qubits needed to compute the ground state energy is $M-2$, where the reduction of two qubits is due to symmetry and spin conservation [11, 12]. The number of qubits can be further reduced by freezing the spin orbitals where the non-bonding electrons reside. For instance, LiH has two non-bonding electrons, thus a total of four qubit reduction. The reduction from freezing orbitals results in a difference in the sixth significant digit of the ground state energy of LiH and about ten times longer run time. We find the number of parameters and run times increase with number of qubits. Therefore, qubit reduction without compromising the efficiency and accuracy of the results will make VQE more powerful.

TABLE I. VQE results

Molecule	Geometry	No. of spin orbitals	No. of qubits	Bond length (Angstroms)	Ground state energy (Hartree)	Est. runtime (seconds)	No. of parameters
H2	linear	4	2	0.735	-1.137	0.63	3
LiH	linear	12	8	1.5	-7.882	41	24
BeH	linear	14	10	1.3	-15.594	665	92
H2O	bent (angle 105 deg)	14	8	0.952	-75.995	220	54
CH4	tetrahedral	18	12	1.09	-39.777	3866	204

A previously exploited quantum efficient method of finding the lowest eigenvalue of a large system, which may be classically intractable, is the quantum phase estimation (QPE). The success of this method and precision of resulting energy estimate rely on the initialization of the main qubit register $|\Psi\rangle$ and the number of qubits in the ancilla register [11]. Ideally, the initial state of the main qubit register has to have a nonzero overlap with the true ground state of the molecule. The Hadamard gate is then applied to each ancilla qubit, $|x\rangle$ resulting in a superposition state of the ancilla register. A controlled rotation gate, $e^{-2\pi iHx}$ is applied to the target state $|\Psi\rangle$. The inverse quantum Fourier transform is applied to the ancilla qubits to extract the phase which encodes the information about the energy eigenvalue. A measurement of the ancilla qubits in the Z basis is performed. This yields the ground state eigenvaule as a binary bitstring, and collapses the main register into the corresponding energy eigenstate. Shown in Fig. 2 is the quantum circuit with three ancillary qubits employed in QPE implementation. For chemical problems, the adiabatic state preparation is commonly employed and the ground state of the Hartree-Fock Hamiltonian is a standard choice for initialized $|\Psi\rangle$. The Hamiltonian H is time evolved successively and coherently for times $t_0 = 2\pi$, $t_1 = 4\pi$, ..., $t_{\omega-1} = 2^\omega\pi$, where the total coherent time evolution is $T = 2^{\omega+1}\pi$ and ω is the number of ancillary qubits. It is shown that to obtain a success probability of $p = 0.5$, with a binary precision $\epsilon = 1/2^n$, a $\omega = n+2$ ancillary qubits are required, which is equivalent to a total of $16\pi/\epsilon$ calls to the unitary gate operator e^{-iH} [13, 14]. The long gate circuit and the number of qubits required by this algorithm may not be realized using a near-term hardware.
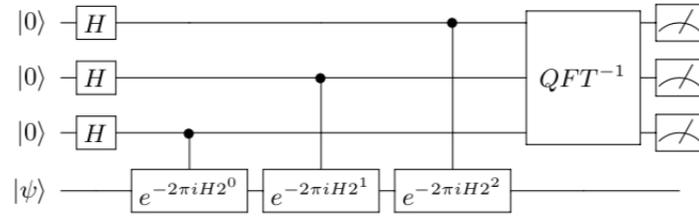
FIG. 2.   Quantum phase estimation circuit with three ancillary qubits. Figure copied without permission from Ref.[11]

III. Quantum computation methods for excited state energies

One way to probe a molecule is using light. Molecule-light interaction may cause the molecule to vibrate and rotate. Electrons orbiting the atoms making up the molecule may absorb the light photons. When this happens, the electrons are promoted from a low energy orbital to a higher one. Properties of these excited states are a key to understand better the chemistry of molecules including the reaction rates and pathways. However, determining these properties is not a trivial task because the electrons of an excited state can be highly entangled. Expressing the statevector of the excited electronic configuration of molecule which captures the entanglement may be computationally expensive using classical computers. Quantum computers has the power to handle this difficulty and to simulate excited states.

Extensions of the VQE algorithm, which is designed to solve for the lowest eigenvalue of a Hamiltonian on a quantum computer, have been proposed to find the excited state energies. For instance, the variational quantum deflation algorithm finds the excited states by including some overlap terms into the cost function or energy of $k-$th excited state to be minimized [17]. These additional terms are treated as a constraint to the excited state $|\Psi(\theta_k)\rangle$, where θ_k is a set of parameters that optimizes the cost function, such that $|\Psi(\theta_k)\rangle$ is orthogonal to the the states $|\Psi(\theta_j)\rangle$, where $j \neq k$. Only one state can be computed at a time because knowledge of $(k-1)$th states is required to find $|\Psi(\theta_k)\rangle$ which makes the algorithm slow. Another method built on VQE algorithm is the quantum subspace expansion (QSE) [18]. Once the ground state wavefunction $|\Psi_0\rangle$ is approximated via VQE, a basis set is formed by computing $\hat{a}_i^\dagger \hat{a}_j |\Psi_0\rangle$. Working in the qubit representation, the Hamiltonian can then be expressed as a matrix with elements

$$H_{ij} = \langle \Psi_0 | \sigma_i^\dagger H \sigma_j | \Psi_0 \rangle, \tag{2}$$

where σ_k's are the Pauli matrices. This matrix can then be diagonalized classically to obtain the low-lying excited state energies and a refined ground-state estimate.

A more robust strategy than QSE is the equation of motion (EOM) method which has been shown to be less sensitive to the approximate VQE ground state result [19]. This approach was first formulated by Rowe to study nuclear spectroscopy and works with the ground state expectation of operator equations [20]. Suppose the ground state $|0\rangle$ is known, then excited states $|n\rangle$ are generated by applying an excitation operator

$$\hat{O}_n^\dagger = |n\rangle\langle 0|, \tag{3}$$

whose counter de-excitation operator given by $\hat{O}_n = |0\rangle\langle n|$. Within this approach, the target measured quantity is not the actual excited state energy E_n, but the energy gap $E_n - E_0$ between the ground state energy E_0. The derived $E_{0n} = E_n - E_0$ quantity is given by[19]

$$E_{0n} = \frac{\langle 0 | \left[\hat{O}_n, \hat{H}, \hat{O}_n^\dagger \right] | 0 \rangle}{\langle 0 | \left[\hat{O}_n, \hat{O}_n^\dagger \right] | 0 \rangle}, \tag{4}$$

where $\left[\hat{A}, \hat{B}, \hat{C} \right] = \frac{1}{2} \left(\left[\left[\hat{A}, \hat{B} \right], \hat{C} \right] + \left[\hat{A}, \left[\hat{B}, \hat{C} \right] \right] \right)$. The operator $\hat{O}_n^\dagger$ is then expressed as a linear combination of products of Fermionic creation and annihilation operators:

$$\hat{O}_n^\dagger = \sum_\alpha \sum_{\mu_\alpha} \left[X_{\mu_\alpha}^{(\alpha)}(n) \hat{E}_{\mu_\alpha}^{(\alpha)} - Y_{\mu_\alpha}^{(\alpha)}(n) \hat{E}_{\mu_\alpha}^{(\alpha)\dagger} \right], \tag{5}$$

where α indicates the degree of excitations, and $\hat{E}_{\mu_1}^{(1)} = \hat{a}_m^\dagger \hat{a}_i$ (represents the excitation of a single electron from an occupied orbital i to a virtual orbital m), $\hat{E}_{\mu_2}^{(2)} = \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_i \hat{a}_j$ (represents the double excitation of a pair of electrons from the occupied orbitals i, j to virtual orbitals m, n), $\hat{E}_{\mu_1}^{(1)\dagger} = \hat{a}_i^\dagger \hat{a}_m$, and $\hat{E}_{\mu_2}^{(2)\dagger} = \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_m \hat{a}_n$. Inserting the expansion in Eq. (5) into Eq. (4) and applying the variational principle $\delta(E_{0n}) = 0$ lead to the secular equation

$$\begin{pmatrix} \mathbf{M} & \mathbf{Q} \\ \mathbf{Q}^* & \mathbf{M}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = E_{0n} \begin{pmatrix} \mathbf{V} & \mathbf{W} \\ -\mathbf{W}^* & -\mathbf{V}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}, \tag{6}$$

where the matrices $\mathbf{M}$, $\mathbf{Q}$, $\mathbf{V}$, and $\mathbf{W}$ are defined as

$$M_{\mu_\alpha \nu_\beta} = \langle 0| \left[\hat{E}_{\mu_\alpha}^{(\alpha)\dagger}, \hat{H}, \hat{E}_{\nu_\beta}^{(\beta)} \right] |0\rangle,$$

$$Q_{\mu_\alpha \nu_\beta} = -\langle 0| \left[\hat{E}_{\mu_\alpha}^{(\alpha)\dagger}, \hat{H}, \hat{E}_{\nu_\beta}^{(\beta)\dagger} \right] |0\rangle,$$

$$V_{\mu_\alpha \nu_\beta} = \langle 0| \left[\hat{E}_{\mu_\alpha}^{(\alpha)\dagger}, \hat{E}_{\nu_\beta}^{(\beta)} \right] |0\rangle,$$

$$W_{\mu_\alpha \nu_\beta} = -\langle 0| \left[\hat{E}_{\mu_\alpha}^{(\alpha)\dagger}, \hat{E}_{\nu_\beta}^{(\beta)\dagger} \right] |0\rangle. \tag{7}$$

The above equations are the key elements of finding the excited state energies in a quantum computer. Treating $\hat{E}_{\mu_\alpha}^{(\alpha)}$ as a quasi-creation operator since the direction of excitation is from occupied to virtual orbitals, and $\hat{E}_{\mu_\alpha}^{(\alpha)\dagger}$ as a quasi-annihilation operator where the direction of excitation is from virtual to occupied orbitals, one can assume that $\hat{E}_{\mu_\alpha}^{(\alpha)\dagger}|0\rangle = 0$ if $|0\rangle$ is the exact ground state. This simplifies Eqs. (6) and (7) where the matrices $\mathbf{Q}$ and $\mathbf{W}$ now vanish. The generalized eigenvalue problem to be solved then becomes

$$\mathbf{HX}_n = E_n \mathbf{SX}_n, \tag{8}$$

where

$$H_{\mu_\alpha \nu_\beta} = \langle 0| \hat{E}_{\mu_\alpha}^{(\alpha)\dagger} \hat{H} \hat{E}_{\nu_\beta}^{(\beta)} |0\rangle,$$

$$S_{\mu_\alpha \nu_\beta} = \langle 0| \hat{E}_{\mu_\alpha}^{(\alpha)\dagger} \hat{E}_{\nu_\beta}^{(\beta)} |0\rangle. \tag{9}$$

The above simplification is known as the Tamm-Dancoff approximation [21]. Equations (8) and (9) are useful when the exact $|0\rangle$ is given. But in practice, the ground state results from VQE are also an approximation.

To implement the EOM algorithm in a quantum computer, the ground state wavefunction $|0\rangle = |\Psi(\theta_0)\rangle$ is obtained via VQE. The matrix operators $\mathbf{M}$, $\mathbf{Q}$, $\mathbf{V}$ and $\mathbf{W}$ in Eq. (7) are then constructed by mapping the Fermionic operators $\hat{a}$ and $\hat{a}^\dagger$ which define the $\hat{E}$, $\hat{E}^\dagger$, and $\hat{H}$ onto qubit operators just like how the Hamiltonian $\hat{H}$ is transformed in VQE. The expectation values $\langle M \rangle$, $\langle Q \rangle$, $\langle V \rangle$, and $\langle W \rangle$ are then measured, and the generalized eigenvalue problem in Eq. (6) is solved classically. An outline of the EOM algorithm is depicted in Fig. 3. Within the Qiskit platform, the algorithm is executed using the function `QEomVQE()`.
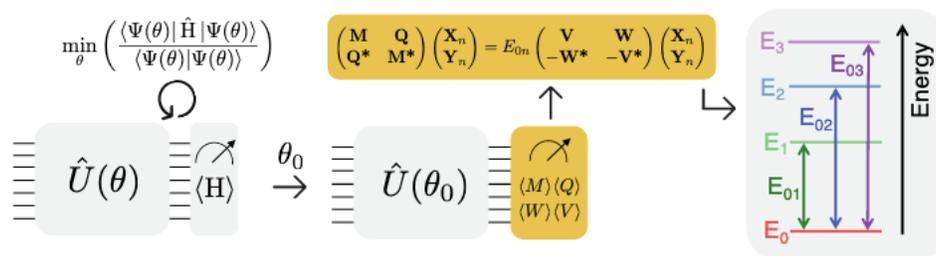

FIG. 3. Implementation of quantum equation of motion algorithm. Figure copied without permission from Ref.[19]

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