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Application of Variational Quantum Eigensolver for Ground State Energies Calculation in Hydrogen and Helium Atomic Sequences

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ABSTRACT

Exponential scaling presents a significant challenge in electronic structure calculations performed on classical computers. This paper explores how quantum computer algorithms can accurately represent quantum systems. Variational Quantum Eigensolver (VQE) algorithm is used to compute the ground state energy of hydrogen and helium sequences by implementing variational principle and quantum gates as trial wavefunction. This technique combines classical optimization with quantum computing calculations to simulate quantum systems on noisy and resource-limited computers. The resulting calculated energy is highly consistent to the corresponding exact values and Hartree-Fock calculations with a trend of when the number of atoms increases the calculated energy becomes more negative, leading to a decrease in the percentage error. Moreover, the convergence of the ground state energy of hydrogen and helium atoms was effectively optimized. The desired energy was reached, proven by adjusting the expectation value, and gradually achieving unity in state overlap. These findings demonstrate the VQE method's accuracy in calculating simple quantum systems and its scalability for larger atomic and molecular system, such as those in quantum chemistry and material science. However, challenges in quantum computer simulations, such as limited in qubit numbers and the presence of noise, require further advancements. Therefore, implementing a larger basis sets, advanced qubit mapping, specific chemistry ansatz, and flexible optimization techniques is one way to improve overall calculation.

Keywords: electronic structure, ground state energy, quantum computing, variational quantum eigensolver

INTRODUCTION

Quantum computing began with Feynman's proposal in 1981, as classical computers lacked the efficiency to simulate quantum systems [1]. That proposal inspired scientists to make new devices that have a quantum advantage. Currently, quantum computing is in the Noisy Intermediate-Scale Quantum (NISQ) era [2-4], employing technologies like superconducting, photonics, and trapped-ions [5-7]. In the NISQ era, quantum computers still encounter challenges like qubit size, hardware error rates, and noise [4]. Despite these limitations, NISQ systems show potential in addressing complex problems, particularly in electronic structure calculations.

As molecular systems increase in complexity, the computational resources required by classical methods also grow exponentially. This resource demand often comes at the cost of reduced accuracy due to the use of an approximation method, especially in representing electron correlation effects within the system [8, 9]. Quantum computing, by contrast, has the potential to scale efficiently with molecular complexity while accurately modeling quantum interactions [10-12].

To address electronic structure problems, both classical and quantum methods are employed. Classical approaches, such as the Hartree-Fock method, have been applied with 1-D basis functions to hydrogen sequences [13] and helium sequences [14], as well as for hydrogen molecules using Optimized Huzinaga basis functions [15]. Quantum approaches, including quantum phase estimation (QPE) [16, 17], provide a more direct method for calculating ground states but currently face scalability issues due to qubit and quantum gate demands, even for relatively small systems [18]. Hybrid techniques, such as the Variational Quantum Eigensolver (VQE), combine classical and quantum components, offering a promising alternative that leverages the strengths of both computing techniques [19-21].

VQE was first developed by Peruzzo in 2014. This method uses variational principles and the Rayleigh-Ritz functional to calculate the expectation value of a trial wavefunction [21]. The process started with the preparation of a parameterized ansatz (a combination of quantum gates) to make the trial wavefunction. Then, that ansatz is optimized using classical methods until the ground state energy of a quantum system is found. Other than that, VQE could be used to obtain excited states [22, 23], simulate periodic materials [24], and solve optimization problems [25]. Even though VQE can run on an NISQ computer, there is still a problem simulating larger molecules because of the increasing number of parameters to optimize and the limitation number of qubits [18]. However, calculations on small and simple quantum systems, such as one- and two-electron systems, are still possible and represent an understudied area in current quantum computing applications.

Choosing an atom system with one electron (hydrogen sequences) and two electrons (helium sequences) has its advantages, one of which is that their Hamiltonian is simple. The Hamiltonian is only made from kinetic energy and electron-nucleus potential energy in the hydrogen sequences. Additionally, electron-electron potential energy is used in the helium sequences. On top of that, the hydrogen sequences have analytical solutions, which are known to have an energy of E = $-Z^2/2$ [26, 27]. While helium sequences are the simplest many-body system [28].

In this paper, the VQE method will be used to calculate the ground state energy of hydrogen sequences from H to O^{7+} and helium sequences from H^- to O^{6+} with the STO-3G basis set. The calculation will be run using the Qiskit library [29] from IBM. The main outcomes will consist of the calculated energy values and the optimized parameters. Next, expectation values and state overlaps are obtained based on the optimized parameters. Furthermore, the accuracy of VQE in determining ground state energies for atomic systems will be assessed. This will involve comparing the VQE energy outputs with exact solutions for hydrogen sequences and Hartree-Fock calculations for helium sequences. These comparisons will allow us to assess VQE's effectiveness in accurately capturing electronic structure systems.

HYDROGEN AND HELIUM SEQUENCES HAMILTONIAN

Atomic systems that have only 1 electron are called hydrogen atom sequences, such as H, He^+, Li^{2+}, and so on, while those with 2 electrons are called helium atom sequences, such as H^-, He, Li^+, etc. The Hamiltonian of hydrogen sequences consists only of the kinetic energy of the electron and the potential energy of the nucleus against the electron. Likewise, with helium sequences, there is an addition of potential energy between electrons [30].

$$H_{hydrogen} = -\frac{1}{2}\nabla_1{}^2 - \frac{Z}{r_1} \tag{1}$$

$$H_{helium} = -\frac{1}{2}\nabla_1{}^2 - \frac{1}{2}\nabla_2{}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_{12}|} \tag{2}$$

Where H is the Hamiltonian of the atomic systems, Z is the atomic number, r_1 and r_2 are the distance between each electron to nucleus, and r_{12} is the distance between two electrons. Subsequently, the second quantization formulization expresses the atomic Hamiltonians in the following way:

$$H_{hydrogen} = h_{00}a_0^\dagger a_0 + \frac{1}{2}\left(h_{0110}a_0^\dagger a_1^\dagger a_1 a_0 + h_{1001}a_1^\dagger a_0^\dagger a_0 a_1\right) \tag{3}$$

$$H_{helium} = h_{00}a_0^\dagger a_0 + h_{11}a_1^\dagger a_1 + \frac{1}{2}\left(h_{0110}a_0^\dagger a_1^\dagger a_1 a_0 + h_{1001}a_1^\dagger a_0^\dagger a_0 a_1\right) \tag{4}$$

Where h_{00} and h_{11} are one-body integral coefficient, h_{0110} and h_{1001} are two-body integral coefficient, $a_0^\dagger$ and a_0 are fermionic operator. To employ the second quantized Hamiltonian in a qubit-based quantum simulator, Jordan-Wigner Mapper [31, 32] must convert Eqs. (3) and (4) into qubit Hamiltonians.

$$\begin{aligned} H_{hydrogen} = {} & \frac{h_{00}}{2}(II - IZ) + \frac{h_{0110}}{8}(II - IZ - ZI + ZZ) \\ & + \frac{h_{1001}}{8}(II - ZI - IZ + ZZ) \end{aligned} \tag{5}$$

$$H_{helium} = \frac{h_{00}}{2}(II - IZ) + \frac{h_{11}}{2}(II - ZI) + \frac{h_{0110}}{8}(II - IZ - ZI + ZZ) + \frac{h_{1001}}{8}(II - ZI - IZ + ZZ) \quad (6)$$

Where *I* is an identity matrix and Z is Pauli-Z matrix.

VARIATIONAL QUANTUM EIGENSOLVER (VQE)

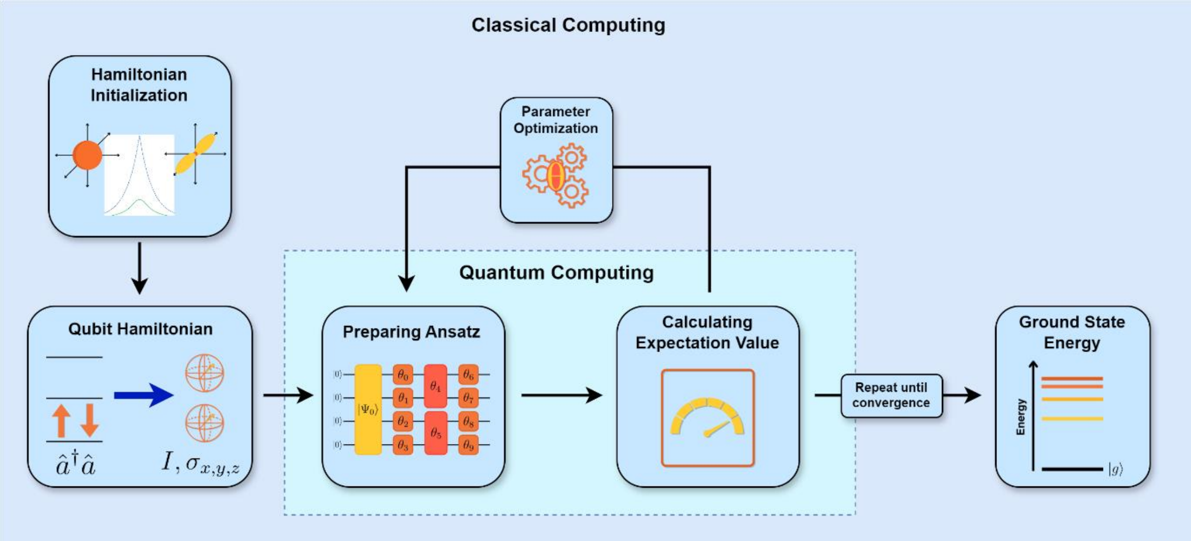


FIGURE 1. Variational Quantum Eigensolver Diagram

The VQE algorithm is a technique used to find the minimum ground state energy of a quantum, E_0, system by applying the variational principle with optimization method [19]. This process starts by preparing a qubit Hamiltonian, $\widehat{H}_q$, and a trial wave function, $\psi(\theta)$, which are implemented using quantum gates (ansatz). Next, the expectation value of the Hamiltonian will be determined using an ansatz with a set of parameters, θ.

$$\frac{\langle\psi(\theta)|\widehat{H}_q|\psi(\theta)\rangle}{\langle\psi(\theta)|\psi(\theta)\rangle} \geq E_0 \quad (7)$$

To reach the lowest energy state, one needs to select an appropriate ansatz that explores the correct Hilbert space and identifies the specific parameters values [21]. For instance, the Hardware Efficient Ansatz (HEA) consisting of a set of rotation gates (R_y gate) and entangling gates (C_x gate) [20]. The rotation gates create room to search for the optimal state, while the entangling gates allow correlations between qubits, greatly expanding the potential of quantum algorithms. HEA requires less circuit complexity and fewer parameterized functions compared to other ansatz type, which make the optimization process quicker and more feasible for NISQ devices [33]. However, this simplicity comes at a cost, as HEA does not provide physical insight into the wave function's structure, meaning it may not capture detailed correlations or interpretative aspects of quantum states.

Each qubit Hamiltonian is measured on the Pauli-Z measurement basis. So, for Pauli-X and Pauli-Y measurement we need to rotate x and y axes into z axis. For the Pauli-X it requires a

Hadamard gate before measurement, the Pauli-Y needs a Hadamard gate and S dagger gate, while the I matrix and Pauli-Z are already aligned with the Z basis [34].

$$\langle\psi(\theta)|aX+bY+cZ+dI|\psi(\theta)\rangle = a\langle\psi(\theta)|HXH|\psi(\theta)\rangle + b\langle\psi(\theta)|HS^{\dagger}YSH|\psi(\theta)\rangle + \langle\psi(\theta)|cZ+dI|\psi(\theta)\rangle \tag{8}$$

When working with two or more qubits, each individual qubit must be combined using a tensor product for every term in the calculation. The obtained matrix is then analyzed to determine the value of each classical bit. Next, the expectation values are computed by adding up the results of all the classical bits. The probability of each classical bit can be calculated by dividing the experimental result by the total number of measurements (shots).

$$I \otimes I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{9}$$

$$\langle\psi(\theta)|I \otimes I|\psi(\theta)\rangle = P(00) + P(01) + P(10) + P(11) \tag{10}$$

$$P(\text{classical bit}) = \frac{\text{Experimental Results}}{\text{Total Shots}} \tag{11}$$

Then, this process is optimized iteratively until convergence of the ground state energy is achieved from the set of parameters. This algorithm is known as a hybrid algorithm because it performs classical optimization to obtain the optimal state and measures the trial wave function using qubit for computation [19, 35].

All the programs in this paper are developed using Python, utilizing core libraries like Qiskit [29], Qiskit Nature, Qiskit Aer, and PySCF [36] to perform quantum simulations and electronic structure calculations. Calculations are executed in a Jupyter Notebook environment on a cloud-based computing platform. The Qiskit Aer simulator is employed for running noise-free quantum simulations, providing a controlled environment to test the VQE without hardware-induced noise.

PERFORMANCE METRICS

Determining the accuracy and efficiency of VQE in calculating ground state energies for atomic systems involves comparing percentage errors between calculated and reference energies, assessing the convergence of ground state energy and expectation value, and evaluating the unity state overlap between calculated and actual states. In ground state energy calculations, percentage errors are determined by comparing the calculated energies to the reference values and expressing the difference as a percentage of the reference value. When percentage errors are smaller, it means that the calculated energies are closer to the reference value, showing higher accuracy in the calculations.

$$\text{Percentage errors} = \frac{|\text{Calculated} - \text{Reference}|}{\text{Reference}} \times 100\% \tag{12}$$

Monitoring the ground state energy and expectation value throughout the optimization process is crucial. It ensures that the system is correctly navigating the Hilbert space toward the ground state and can reveal any deviations or fluctuations that might indicate instability or inaccuracies in the algorithm. Additionally, observing the speed of convergence helps us understand the optimization process and the suitability of chosen parameters. When convergence slows down or stops, it might indicate the need to adjust the Hamiltonian initialization, select the correct ansatz structure, and consider changing the optimization method [21, 37]. These changes result in a more reliable calculation of the ground state energy.

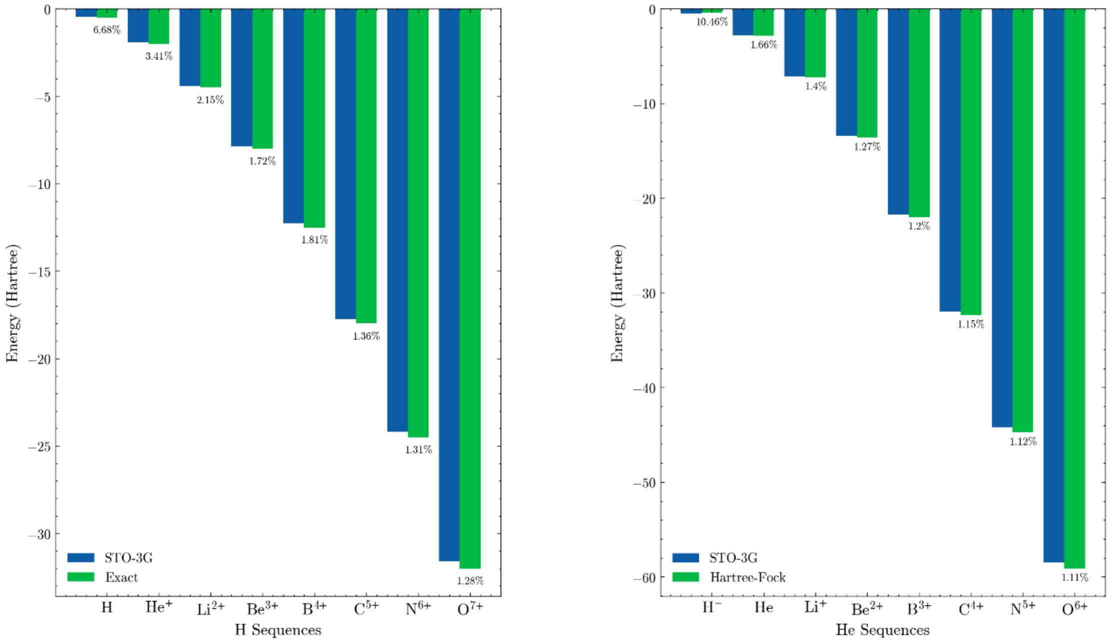
The convergence of ground state energy relies on the overlap between the current state, $|\psi_i\rangle$, and the actual state, $|\psi_g\rangle$[38]. To find the state overlap, $|\langle\psi_i|\psi_g\rangle|$, set of parameter θ is calculated using the VQE algorithm and used to derive $|\psi_i\rangle$ and $|\psi_g\rangle$. $|\psi_i\rangle$ is obtained by calculating the probability of each classical bit result using a set number of shots used in the experiment, while $|\psi_g\rangle$ is derived from an ideal calculation representing the theoretical output of a quantum circuit [19]. Subsequently, calculating the inner product of both states yields $|\langle\psi_i|\psi_g\rangle|$ and to get the real part of the state overlap must be squared. This overlap is crucial in determining how close the current state is to the actual ground state, impacting the accuracy of the ground state energy calculation.

RESULTS AND DISCUSSION

The computed ground state energy for the hydrogen and helium sequences determined by the VQE and HEA ansatz is shown in FIGURE 2. The calculated energies using the STO-3G basis set are represented in the blue line, while the exact values and Hartree-Fock (HF) calculations using 6-31G basis set are shown in the green line. The energy difference is expressed as a percentage error displayed in black font below the reference energy line. In both systems, the calculated energy values become more negative relative to the reference energy as the charge of the ion increases from Z = 1 to Z = 8. Moreover, the computed energy is consistent with the trend of exact hydrogen energies formula, $E = -Z^2/2$. This phenomenon can be attributed to the significant increase in the ionic energies compared to the electron-electron repulsion energies, making the system more tightly bound, as documented in the referenced studies [14, 28].

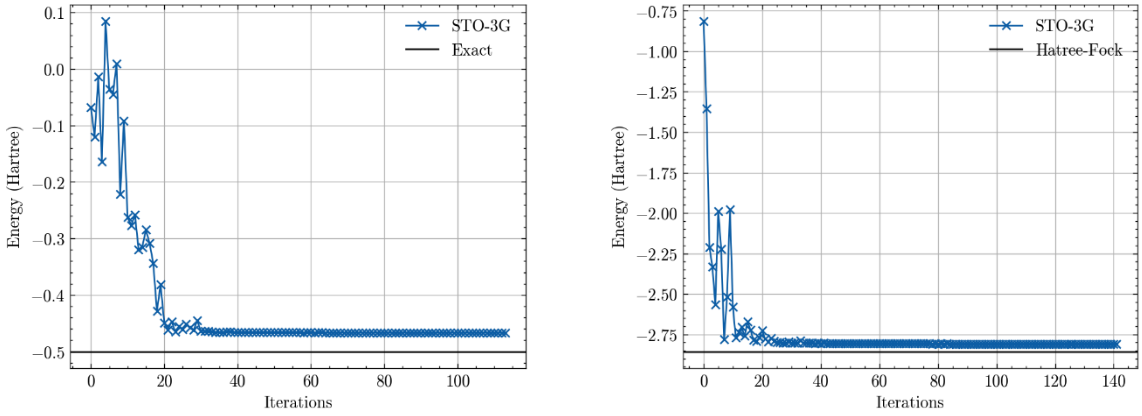
On hydrogen sequences using the STO-3G basis set, approximate the exact values reasonably well, with percentage error decreasing from 6.68% (H) to 1.28% (O^{7+}). While in the helium sequences, the calculated energies provide a closer approximation to the HF 6-31G calculation, particularly for lighter systems with percentage error systematically decreasing from 10.46% (H^-) to 1.11% (O^{6+}). Suprisingly, the H^- VQE calculation is more negative than the reference value. This is because the VQE algorithm can capture missing electron correlation effects even with a minimal basis set by mapping the second quantization Hamiltonian. The decreasing percentage errors indicate that the STO-3G basis set is more suitable for systems with higher nuclear charges.

FIGURE 3 shows the convergence of the ground state energy of the hydrogen and helium atoms in the optimization run. The calculated energies using VQE are shown in the blue line, and the exact values and HF calculation are shown in the black line. The numerical optimization results achieve an energy convergence of -0.4666 Hartree and -2.8078 Hartree. Initially, the energy calculations are less accurate due to the unoptimized parameters that are given randomly. During the optimization process, the calculated energy fluctuated as the algorithm searched for parameter values that minimize the energy. Additionally, the algorithm might overshoot or undershoot the optimal parameters. After approximately 20 iterations, the optimization process stagnates, making only minimal progress. This indicates that the optimizer has found parameters close to the global minimum of the variational energy. Upon convergence, the energies stabilize, closely aligning with the reference values for hydrogen (-0.5 Hartree) and helium (-2.8552 Hartree). Overall, the optimization process effectively achieved reasonable energy values for both hydrogen and helium atoms using minimal basis set.



(a) (b)

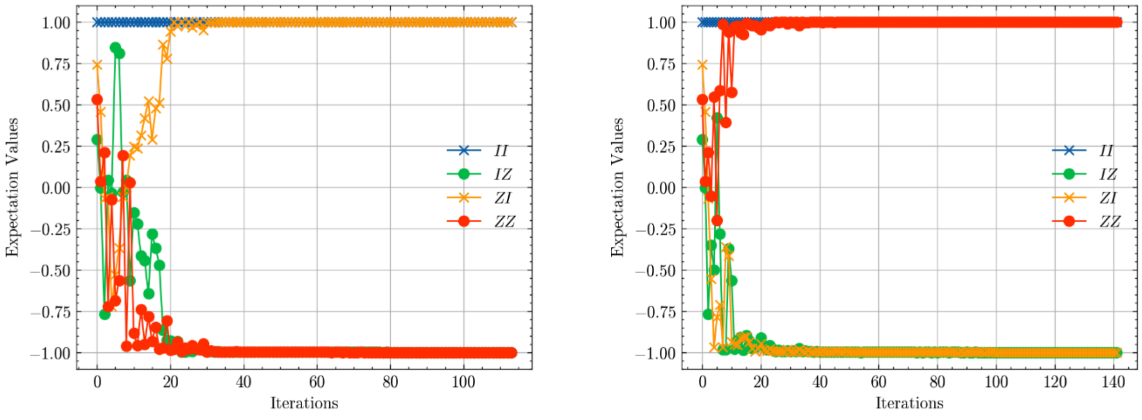
FIGURE 2. The ground state energy calculated using VQE. (a) Hydrogen sequences and their exact energy. (b) Helium sequences and Hartree-Fock calculations.



(a) (b)

FIGURE 3. The convergence of ground state energy as a function of iteration calculated using VQE. (a) Hydrogen atom and the exact energy. (b) Helium atom and the Hartree-Fock Calculation.

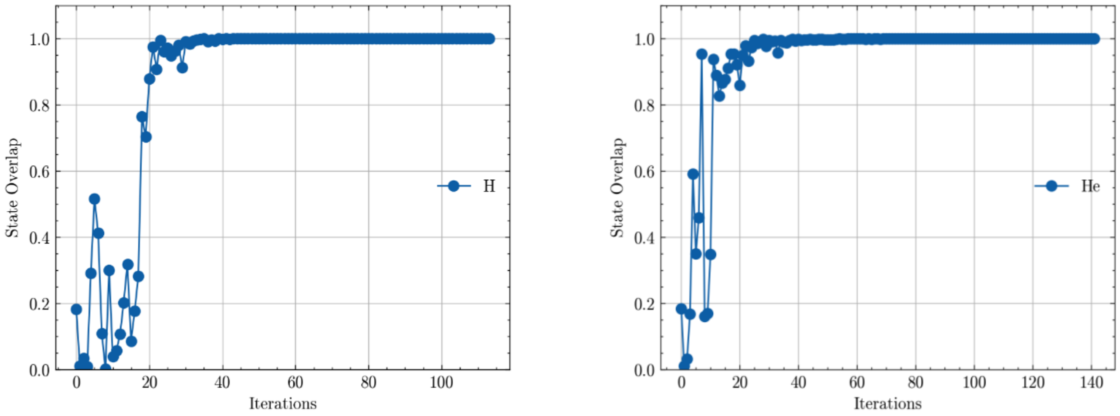
FIGURE 4 highlights the importance of optimizing the expectation values of individual qubit Hamiltonians for hydrogen and helium atoms. As expected, operator *II* in both systems remains at a constant value of 1 during the optimization process. Conversely, the others vary based on the qubit Hamiltonian's coefficient to achieve minimum ground state energy. Operator *ZI* shows an expected value of one in the hydrogen atom, while operators *IZ* and *ZZ* both converge to minus one. Subsequently, operators *IZ* and *ZI* become negative ones in the helium atom, but operator *ZZ* turns out to be the value of 1. These results indicate that the optimization process effectively adjusts the expectation value of every term in the qubit Hamiltonian to minimize the ground state energy for each atom. The variation in values among different operators underscores the distinct electronic structure characteristics of hydrogen and helium atoms in quantum computing calculations.



(a) (b)

FIGURE 4. The convergence of the expectation value of individual qubit Hamiltonians as a function of iteration. (a) Hydrogen atom. (b) Helium atom.

The rapid convergence is due to the swift discovery of the eigen function, as seen by the overlap $|\langle\psi_i|\psi_g\rangle|$ between the estimated state at each iteration i, $|\psi_i\rangle$, and the actual state of the system of hydrogen and helium atoms, $|\psi_g\rangle$, illustrated in FIGURE 5. Initially, there is a small and unstable overlap between the states, resulting in relatively poor energy estimations for both systems. However, $|\psi_i\rangle$ eventually discovers $|\psi_g\rangle$ that the $|\langle\psi_i|\psi_g\rangle|$ reaches unity after a certain number of iterations, which is determined by the parameter in the ansatz during optimization. The calculated state overlap is 1, meaning that the parameters are optimized and found to have the minimum energy. Furthermore, this implies that the system has reached its optimal state.



(a) (b)

FIGURE 5. State overlap $|\langle \psi_i | \psi_g \rangle|$ between calculated state and the actual state as a function of iteration (a) Hydrogen atom. (b) Helium atom.

The VQE implementation to find the ground state energy of atomic systems, like hydrogen and helium sequences, has the potential to enable calculations for more complex systems such as lithium sequences, beryllium sequences, and molecules. These advancements can lay the foundation for applications in fields such as quantum chemistry and materials science. Nevertheless, challenges persist in further research due to the limited number of qubits in current hardware and the presence of noisy environments in the simulation. Addressing these limitations will be crucial for scaling VQE to larger and more bigger systems. This can be achieved by applying more advanced technique, such as enhancing the Hamiltonian initialization, selecting suitable ansatz, and improving optimization methods.

CONCLUSION

The Schrödinger equation for the hydrogen and helium sequences is simulated using a quantum computer through the VQE method. The qubit Hamiltonians are obtained by mapping the second quantized Hamiltonians of both systems to qubits using the Jordan-Wigner transformation, a crucial step in quantum computing simulations. The energies, expectation values, and state overlap for the hydrogen and helium sequences are computed using a trial function of Hardware-Efficient Ansatz and a classical optimization algorithm.

The simulation achieved the minimum ground state energy for hydrogen and helium sequences, demonstrating close proximity to the reference energy. It was observed that as the ion's charge increases, the calculated energy becomes more negative, leading to a decrease in the percentage error. This shows that using VQE and a simple basis set is very efficient for systems with higher nuclear charges. However, the VQE calculation for H^- was more negative than the reference due to its ability to capture more electron correlation effects than the HF method. The convergence of the ground state energy for hydrogen and helium atoms were effectively optimized and reach the desired energy. The expectation values of each qubit were adjusted to achieve the lowest energy state for the systems under evaluation. Additionally, the state overlap gradually increases from a small non-zero value to a perfect match of 1 as the optimization process converges, indicating an exact correspondence between the calculated and actual states.

This discovery demonstrates that the VQE method is capable of simulating simple systems with a minimal basis set and has the potential to simulate larger systems. Moreover, this study provides a foundation for extending VQE to more complex quantum systems, such as molecular systems and periodic materials. These advancements could enable impactful applications in quantum chemistry and material science. However, difficulties remain in simulating quantum computers, including limitations in qubit numbers and the presence of noise. Addressing these challenges will be essential for scaling VQE to larger and complicated systems. Therefore, implementing a larger basis set, advanced qubit mapping, a specific chemistry ansatz, and an adaptable optimization method is one way to improve overall calculation accuracy.

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