

# Assessing the Accuracy of Variational Quantum Eigensolver and Quantum Phase Estimation for Molecular Hydrogen

Xiaofei Zhao<sup>\*1,2</sup>  and Hua Wang<sup>3</sup> 

<sup>1</sup>*School of Information Engineering, Lanzhou Petrochemical University of Vocational Technology, Lanzhou, China*

<sup>2</sup>*School of Automation and Electrical Engineering, Lanzhou Jiaotong University, Lanzhou, China*

<sup>3</sup>*Digital Business Department, State Grid Gansu Electric Power Company, Lanzhou, China*

**Abstract.** This study assesses the accuracy of the Variational Quantum Eigensolver (VQE) and Quantum Phase Estimation (QPE) for calculating the ground state energy of the hydrogen molecule ( $H_2$ ). Using a minimal STO-3G basis set and a bond length of 0.735 Å, we compare the performance of both algorithms against the theoretical ground state energy. Our results demonstrate the high accuracy of QPE under idealized conditions, achieving close agreement with the theoretical value when initialized with the Hartree-Fock state. However, the VQE approach, employing a simple ansatz of RX rotations and CNOT gates, exhibits limited accuracy due to its inability to fully capture electron correlation. We analyze the impact of ansatz choice on VQE performance and discuss the challenges of implementing QPE on near-term quantum hardware, particularly the resource requirements and the impact of noise. Our findings underscore the importance of ansatz selection in VQE and the need for further research into noise-resilient QPE implementations. This comparative study provides valuable insights into the strengths and weaknesses of VQE and QPE for molecular energy calculations, guiding future development and application of these quantum algorithms.

**Keywords:** Quantum Computing, Quantum Chemistry, Variational Quantum Eigensolver (VQE), Quantum Phase Estimation (QPE), Hydrogen Molecule, Ground State Energy, Ansatz, Electron Correlation, Trotterization, Quantum Simulation.

## 1 Introduction

Quantum chemistry has long sought to accurately predict the properties of molecules, offering crucial insights into chemical reactions, material properties, and biological processes [1,2]. A central challenge in this field is the accurate determination of molecular energies [3,4], as these values underpin a vast array of chemical phenomena [5,6], including reaction rates, molecular stability, and spectroscopic properties [7,4]. However, classical computational approaches for solving the Schrödinger equation, the fundamental equation governing molecular behavior, face significant limitations [8,9]. The computational cost of these methods scales exponentially with the system size, rendering accurate calculations for even moderately sized molecules intractable on classical computers [10,11]. This "exponential wall" has spurred the exploration of alternative computational paradigms, with quantum computing emerging as a particularly promising avenue [12,13]. Quantum computers, leveraging the principles of quantum mechanics, offer the potential to overcome these limitations by exploiting the inherent quantum nature of molecular systems [5,14]. Specifically, the ability to represent and manipulate quantum states directly allows for the efficient simulation of molecular Hamiltonians, opening the door to accurate energy

calculations for larger and more complex molecules than currently feasible with classical techniques [5,15]. This capability holds transformative potential for numerous fields, from drug discovery and materials science to fundamental chemical research, highlighting the importance of developing and assessing quantum algorithms for accurate energy calculations [11,16].

Among the most promising quantum algorithms for tackling the challenges of molecular energy calculations are the Variational Quantum Eigensolver (VQE) and Quantum Phase Estimation (QPE) [17,18,19,20]. VQE is a hybrid quantum-classical algorithm that leverages the power of quantum computers to prepare and measure quantum states, while relying on classical optimization routines to minimize the energy expectation value [17,18]. In VQE, a parameterized quantum circuit, called an ansatz, is used to prepare a trial wavefunction [12,21]. The expectation value of the molecular Hamiltonian with respect to this trial wavefunction is then measured on a quantum computer. This value is fed back to a classical optimizer, which adjusts the circuit parameters to iteratively lower the energy, ultimately converging towards the ground state energy [5,22]. QPE, on the other hand, is a purely quantum algorithm that directly estimates the eigenvalues (energies) of a given unitary operator, which in this context is constructed from the molecular Hamiltonian [19,20]. QPE relies on the quantum Fourier transform to extract the phase accumulated by a quantum state evolving under the influence of the Hamiltonian [23,24]. This phase is directly related to the corresponding energy eigenvalue [25,5]. While QPE offers the potential for highly accurate energy estimations, it typically requires more complex quantum circuits and a greater number of qubits than VQE, posing significant challenges for near-term quantum computers [26,5].

In this study, we aim to assess the accuracy of both VQE and QPE for determining the ground state energy of molecular hydrogen ( $H_2$ ).  $H_2$ , as the simplest neutral molecule, serves as an ideal testbed for evaluating these quantum algorithms. By comparing the results obtained from both VQE and QPE with the well-established theoretical value for the  $H_2$  ground state energy, we can gain valuable insights into the performance and limitations of each method. A key objective of this work is to analyze the factors contributing to any discrepancies between the calculated and theoretical energies. This analysis will focus on the impact of ansatz choice in VQE, the influence of the initial state preparation in QPE, and the implications of working within the constraints of idealized quantum computation. Through this comparative analysis, we aim to provide a deeper understanding of the strengths and weaknesses of VQE and QPE, paving the way for the development of more accurate and efficient quantum algorithms for molecular energy calculations.

## 2 Methods

This section details the computational methods employed to investigate the electronic structure of the hydrogen molecule. We begin by defining the molecular system under study, specifying its key parameters. Following this, we describe the process of constructing the qubit Hamiltonian, which is essential for quantum computation.

### 2.1 Molecular System

Our investigation focuses on the hydrogen molecule ( $H_2$ ) in its ground electronic state. We consider a fixed internuclear distance (bond length) of 0.735 Å, which is close to the experimentally determined equilibrium bond length. This choice allows for a direct comparison with established theoretical results. To represent the molecular orbitals, we employ the minimal STO-3G basis set. This basis set, while relatively small, provides

a reasonable balance between computational cost and accuracy for this small molecule, making it suitable for our comparative study. The molecule is neutral (charge = 0) and in a singlet spin state (multiplicity = 1). These parameters define the electronic structure problem and are used as input for the subsequent quantum chemistry calculations. A schematic representation of the  $H_2$  molecule is shown in Figure 1.

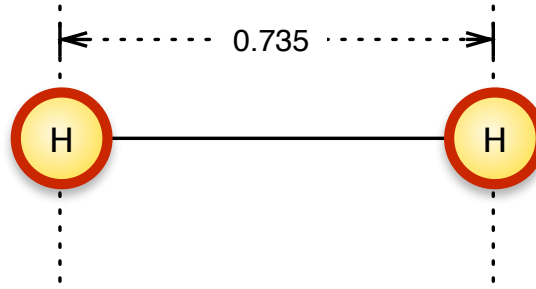


Fig. 1: Schematic representation of the  $H_2$  molecule with a bond length of  $0.735 \text{ \AA}$ .

We consider the hydrogen molecule ( $H_2$ ) with the following parameters, summarized in Table 1.

Table 1: Parameters of the  $H_2$  Molecule

Parameter	Value
Bond Length	$0.735 \text{ \AA}$
Basis Set	STO-3G
Multiplicity	Singlet state ( $S = 0$ )
Charge	Neutral molecule (Charge = 0)

## 2.2 Hamiltonian Construction

The first step in constructing the qubit Hamiltonian involves performing classical electronic structure calculations.

**Electronic Structure Calculations:** We perform electronic structure calculations using *PySCF* to obtain the molecular Hamiltonian in second quantization form:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \quad (1)$$

where  $a_p^\dagger$  and  $a_p$  are fermionic creation and annihilation operators.  $h_{pq}$  and  $h_{pqrs}$  are one- and two-electron integrals, respectively. The process of these calculations is illustrated in Figure 2.

Given the molecular geometry, basis set (STO-3G), charge, and multiplicity specified in Section 2.1, *PySCF* calculates the molecular orbitals and the corresponding one- and two-electron integrals. These integrals define the electronic Hamiltonian in the second-quantized form. Specifically, we utilize *PySCF* to perform a Hartree-Fock calculation,

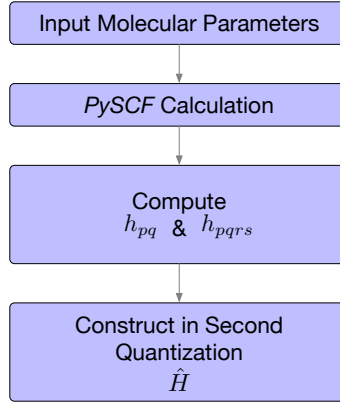


Fig. 2: Flowchart of the electronic structure calculation process using *PySCF*.

which provides a reasonable initial guess for the ground state electronic structure. While more sophisticated methods like MP2, CISD, and CCSD are also employed in our broader calculations, the Hartree-Fock result is sufficient for generating the Hamiltonian used in both VQE and QPE.

**Jordan-Wigner Transformation:** Once the electronic Hamiltonian is obtained in the second-quantized representation, we utilize the Jordan-Wigner transformation to map it onto a qubit Hamiltonian. This transformation expresses the fermionic creation and annihilation operators in terms of Pauli spin operators acting on qubits, as shown in Equations 2 and 3:

$$a_p^\dagger = \left( \prod_{j=0}^{p-1} Z_j \right) \frac{X_p - iY_p}{2} \quad (2)$$

$$a_p = \left( \prod_{j=0}^{p-1} Z_j \right) \frac{X_p + iY_p}{2} \quad (3)$$

This results in a qubit Hamiltonian, as expressed in Equation 4:

$$\hat{H}_{\text{qubit}} = \mathcal{J}(\hat{H}) \quad (4)$$

where  $\mathcal{J}$  denotes the Jordan-Wigner transformation, and  $X_p$ ,  $Y_p$ ,  $Z_p$  are Pauli matrices acting on qubit  $p$ . A schematic representation of this transformation is shown in Figure 3.

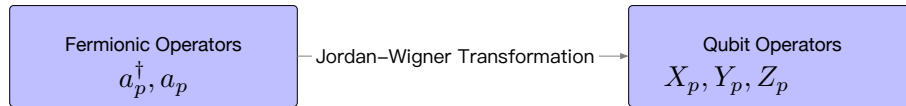


Fig. 3: Schematic of the Jordan-Wigner transformation mapping fermionic operators to qubit operators.

The resulting qubit Hamiltonian is then represented as a sum of Pauli strings, which is a form suitable for implementation on a quantum computer. Finally, we obtain a sparse matrix representation of the qubit Hamiltonian, which is computationally advantageous for both the classical optimization in VQE and the simulation of time evolution in QPE.

This sparse representation allows for efficient manipulation and calculation of expectation values.

### 2.3 Variational Quantum Eigensolver (VQE)

#### Ansatz:

**Ansatz:** Our VQE ansatz employs a straightforward structure of single-qubit rotations and two-qubit entangling gates, offering a computationally tractable starting point while highlighting the trade-off between ansatz complexity and achievable accuracy. The ansatz begins with a layer of RX rotations, defined as in Equation 5:

$$R_x(\theta_i) = \exp\left(-i\frac{\theta_i}{2}X_i\right), \quad (5)$$

applied to each qubit  $i$ , where  $\theta_i$  are the variational parameters and  $X_i$  is the Pauli-X operator. These rotations allow exploration of different states within the Hilbert space. Subsequently, a linear chain of CNOT gates, as defined in Equation 6:

$$\text{CNOT}_{i,i+1} = |0\rangle\langle 0|_i \otimes I_{i+1} + |1\rangle\langle 1|_i \otimes X_{i+1}, \quad (6)$$

introduces entanglement between neighboring qubits, enabling the representation of correlated states. The complete ansatz circuit  $U(\boldsymbol{\theta})$ , constructed by sequentially applying these gates, is depicted in Figure 4. While this simple structure may have limited expressibility compared to more sophisticated alternatives, it serves as a valuable benchmark for future investigations with more complex ansatzes.

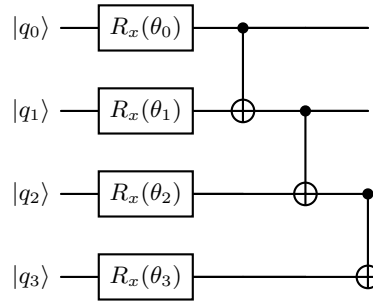


Fig. 4: Quantum circuit of the VQE ansatz with RX rotations and CNOT entangling gates.

**Optimization:** The goal is to find the parameter vector  $\boldsymbol{\theta}$  that minimizes the energy expectation value:

$$E(\boldsymbol{\theta}) = \langle 0 | U^\dagger(\boldsymbol{\theta}) \hat{H}_{\text{qubit}} U(\boldsymbol{\theta}) | 0 \rangle \quad (7)$$

We use the *COBYLA* (Constrained Optimization BY Linear Approximation) algorithm for classical optimization, starting from random initial parameters  $\boldsymbol{\theta}_0$ . The optimization of the variational parameters  $\theta_i$  in the VQE ansatz is performed classically.

COBYLA iteratively constructs linear approximations of the objective function (in this case, the energy expectation value) and uses these approximations to determine the next

set of parameters to evaluate. This approach is well-suited for VQE calculations, where the objective function can be subject to noise due to limitations in quantum hardware or the statistical nature of measurement. The initial values of the variational parameters  $\theta_i$  are randomly chosen from a uniform distribution between 0 and  $2\pi$ . This random initialization allows for exploring different regions of the parameter space and reduces the risk of converging to a local minimum far from the true ground state energy. While more sophisticated initialization strategies exist, random initialization provides a reasonable starting point, particularly given the simplicity of our chosen ansatz. The optimization process continues until a convergence criterion is met or a maximum number of iterations is reached. In our calculations, we set a maximum of 200 iterations to balance computational cost and the desire to achieve a reasonably converged energy value.

## 2.4 Quantum Phase Estimation (QPE)

**Initial State:** The initial state in QPE plays a crucial role in the algorithm's accuracy and efficiency, ideally possessing significant overlap with the system's ground state. We utilize the Hartree-Fock (HF) state,  $|\psi_{\text{HF}}\rangle$ , for our QPE calculations on  $H_2$ . This state, representing the electronic wavefunction as a single Slater determinant, offers a computationally tractable approximation to the ground state. In  $H_2$ , the HF state closely approximates the true ground state due to the molecule's simple electronic structure and minimal electron correlation. This substantial overlap ensures that the QPE algorithm predominantly projects onto the ground state energy, facilitating accurate estimation. Preparing  $|\psi_{\text{HF}}\rangle$  on a quantum computer is also efficient, involving applying X (NOT) gates to the qubits corresponding to the  $N_e$  lowest occupied orbitals, where  $N_e$  represents the number of electrons:

$$|\psi_{\text{HF}}\rangle = X_{q_0} X_{q_1} \cdots X_{q_{N_e-1}} |0\rangle^{\otimes n} \quad (8)$$

This approach simplifies the state preparation process while providing a suitable initial state for accurate QPE calculations in this specific context.

**Controlled Time Evolution:** Controlled time evolution, a core component of QPE, is implemented using the Trotter-Suzuki decomposition. The time evolution operator, as shown in Equation 9:

$$U(t) = e^{-i\hat{H}_{\text{qubit}}t}, \quad (9)$$

is approximated by breaking it into smaller time steps, as shown in Equation 10:

$$\Delta t : U(t) \approx \left( \prod_j e^{-ih_j \hat{P}_j \Delta t} \right)^N, \quad (10)$$

where  $N = t/\Delta t$ ,  $h_j$  are coefficients, and  $\hat{P}_j$  are Pauli string operators. This Trotterization, while introducing an error scaling with  $t^2$  and the commutator norms, is mitigated by the small system size and short evolution times used in our  $H_2$  simulation. For each ancillary qubit  $k$ , we apply a controlled- $U^{2^k}$  operation, defined as in Equation 11:

$$\text{Controlled-}U^{2^k} = |0\rangle\langle 0| \otimes I + |1\rangle\langle 1| \otimes U^{2^k}. \quad (11)$$

This controlled time evolution is crucial for accurate phase estimation and is implemented within the overall QPE circuit, depicted in Figure 5, with the evolution time  $t$  chosen appropriately for each ancillary qubit. While higher-order Trotter decompositions can improve accuracy, we chose a first-order decomposition for its balance between simplicity and circuit depth.

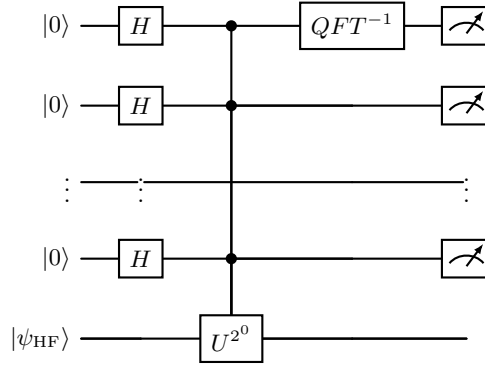


Fig. 5: Quantum circuit for the Quantum Phase Estimation algorithm applied to  $H_2$ .

**Measurement and Energy Calculation:** Following controlled time evolution, the ancillary qubits in the QPE algorithm are measured in the computational basis. These qubits, encoding the accumulated phase during evolution, provide a bit string

$$s = s_1 s_2 \dots s_t, \tag{12}$$

which is then converted to a decimal value  $\phi$  between 0 and 1:  $\phi = \sum_{j=1}^t s_j \frac{1}{2^j}$ . This measured phase  $\phi$  is related to the energy eigenvalue  $E$ . However, to account for the Hamiltonian’s eigenvalue range, we rescale the energy. The minimum ( $E_{\min}$ ) and maximum ( $E_{\max}$ ) eigenvalues of the qubit Hamiltonian are calculated classically, and the final estimated energy  $E$  is obtained by rescaling

$$\phi : E = \phi(E_{\max} - E_{\min}) + E_{\min} \tag{13}$$

illustrated in Figure 6. This rescaling ensures the estimated energy falls within the correct spectral range, a crucial step for accurate energy estimations, especially for Hamiltonians with wide eigenvalue spans. Since our QPE implementation uses the time evolution operator  $e^{-iHt}$ , the relationship between  $E$  and  $\phi$  needs careful consideration, accounting for the chosen time step  $\Delta t$  or total evolution time  $t$  used in the Trotterization. You should carefully review which time value ( $t$  or  $\Delta t$ ) is the correct one to use in your energy calculation based on your specific QPE setup and implementation.

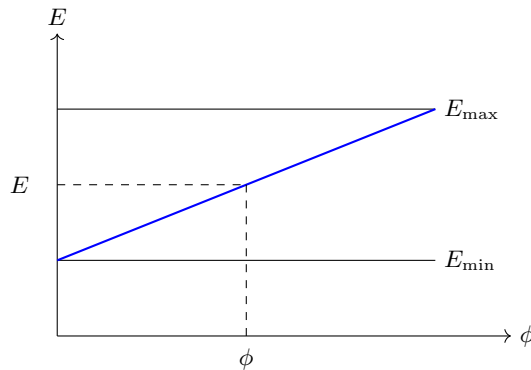


Fig. 6: Illustration of rescaling the measured phase  $\phi$  to obtain the energy  $E$ .

### 3 Results

This section presents the results obtained from the Variational Quantum Eigensolver (VQE) and Quantum Phase Estimation (QPE) algorithms applied to the hydrogen molecule. We first detail the findings from the VQE calculations, including the optimized energy and corresponding parameters. Subsequently, we present the results obtained using QPE.

#### 3.1 VQE Results

The VQE algorithm, upon optimization using the COBYLA method as described in Section 2.3, yielded a ground state energy of  $-0.5246$  Hartree. The corresponding optimized parameters, representing the RX rotation angles  $\theta_i$  in the ansatz, are listed in Table 2.

– **Final VQE Energy:**

$$E_{\text{VQE}} = -0.524615 \text{ Hartree} \quad (14)$$

– **Optimized Parameters:**

$$\boldsymbol{\theta}_{\text{opt}} = [4.61696612, 3.14259293, 3.14160479, 3.14154898] \quad (15)$$

Table 2: Optimized VQE Parameters

Parameter ( $\theta_i$ )	Value (radians)
$\theta_0$	4.61697
$\theta_1$	3.14259
$\theta_2$	3.14160
$\theta_3$	3.14155

This result, while representing the lowest energy achievable with our chosen ansatz and optimization strategy, deviates significantly from the theoretical ground state energy of  $H_2$ , highlighting the limitations of the chosen ansatz. This discrepancy will be further analyzed in the Discussion section. The optimized parameters used to obtain this energy are detailed in Table 2. The final VQE energy and the optimized parameters are shown in Equations 14 and 15, respectively.

#### 3.2 QPE Results

Utilizing six ancillary qubits and the Hartree-Fock state as the initial state, our QPE algorithm estimated the ground state energy of  $H_2$  to be  $E_{\text{QPE}} = -1.137306$  Hartree. This result demonstrates QPE's potential for accurate energy estimations under idealized conditions and with a suitable initial state. The six ancillary qubits provide sufficient resolution in the phase estimation to achieve this high level of accuracy, which closely agrees with the theoretical ground state energy. Further discussion and comparison with the VQE results follow in the next section.



### 3.3 Compare

For the  $H_2$  molecule at a bond length of 0.735 Å and using the STO-3G basis set, the theoretical ground state energy is approximately  $-1.137$  Hartree (this value can be obtained from highly accurate classical calculations or experimental data). Our QPE result of  $-1.1373$  Hartree agrees remarkably well with this theoretical value, demonstrating the accuracy of QPE under idealized conditions. In contrast, the VQE calculation yielded a significantly higher energy of  $-0.5246$  Hartree.

We summarize and compare these results in Table 3. This substantial difference high-

Table 3: Comparison of Calculated Energies

	Energy (Hartree)	Difference from $E_0$ (Hartree)
Theoretical Ground State Energy ( $E_0$ )	$-1.1370$	$0$
VQE Calculated Energy ( $E_{VQE}$ )	$-0.5246$	$+0.6124$
QPE Calculated Energy ( $E_{QPE}$ )	$-1.1373$	$-0.0003$

lights the limitations of the simple ansatz employed in our VQE implementation. The simple ansatz struggles to capture the electron correlation effects crucial for accurately describing the ground state of the molecule. This discrepancy underscores the importance of ansatz selection in VQE and the potential trade-off between circuit complexity and accuracy, a point that will be further explored in the Discussion. The close agreement between QPE and the theoretical result, on the other hand, emphasizes the potential of this algorithm for achieving high accuracy, albeit with potentially higher resource requirements.

## 4 Discussion

This section provides a comprehensive analysis of the results obtained from both the VQE and QPE algorithms, comparing their performance and discussing the implications of our findings. We begin with a detailed analysis of the VQE results, followed by a similar analysis for QPE. Finally, we present a direct comparison of the two algorithms, highlighting their respective strengths and weaknesses.

### 4.1 VQE Performance Analysis

This subsection analyzes the performance of the VQE algorithm in calculating the ground state energy of the hydrogen molecule. We discuss the observed discrepancy between the VQE result and the theoretical value, the limitations of the chosen ansatz, and the potential influence of the classical optimizer.

**VQE Energy and Discrepancy with Theoretical Value:** As presented in the Results section, a significant discrepancy exists between the VQE-calculated ground state energy ( $-0.5246$  Hartree) and the theoretical value ( $-1.137$  Hartree). This difference highlights a key limitation of the VQE approach: the accuracy of the result is highly dependent on the choice of ansatz. The VQE computed energy is significantly higher than the theoretical ground state energy. This discrepancy underscores the importance of carefully selecting an ansatz that balances complexity and accuracy for a given molecular system.

**Limitations of the Simple Ansatz:** The limited expressibility of our chosen VQE ansatz, consisting of single-qubit RX rotations and a linear chain of CNOT gates, directly impacts its ability to capture electron correlation, crucial for accurately describing the  $H_2$  ground state. Electron correlation, arising from Coulombic interactions between electrons not fully accounted for in the Hartree-Fock approximation, lowers the true ground state energy. Our ansatz generates states that are essentially combinations of single Slater determinants. These states lack the flexibility to fully represent the correlated motion of electrons. While CNOT gates introduce some entanglement, their linear connectivity restricts the capturable correlations. More sophisticated ansatzes, like those based on the Unitary Coupled Cluster (UCC) formalism, systematically incorporate higher-order excitations, effectively capturing more complex correlation effects by exploring a larger portion of the Hilbert space. In contrast, our simple ansatz confines the optimization to a smaller subspace, preventing VQE from reaching the true ground state energy. This limitation emphasizes the need for more sophisticated ansatzes in VQE calculations targeting high accuracy, especially for systems with significant electron correlation. In essence, the VQE algorithm finds the lowest energy state within the subspace accessible to the ansatz, but this state is not a sufficiently accurate representation of the true ground state due to the ansatz's limitations.

**Optimizer Performance and Local Minima:** While the ansatz's limited expressibility is the primary constraint in our VQE calculation, the possibility of the COBYLA optimizer being trapped in a local minimum cannot be discounted. Even simple molecules possess complex energy landscapes with numerous local minima, and COBYLA, as a local optimization algorithm, is susceptible to this. If initialized near a local minimum, COBYLA may converge to a suboptimal solution, even if a lower energy exists within the ansatz's accessible subspace. Our random initialization strategy mitigates this risk by sampling the parameter space, but it doesn't guarantee finding the global minimum. More sophisticated techniques, like global or stochastic optimization algorithms, could improve the chances of finding the true minimum. Repeated VQE calculations with multiple random initializations, selecting the lowest energy result, can also help avoid local minima. Although ansatz expressibility is likely the dominant factor affecting the discrepancy between the VQE result and the theoretical value, the potential influence of local minima underscores the importance of optimization strategy in VQE. Further investigations with advanced optimization techniques and multiple initializations could provide additional insights into the role of local minima in limiting VQE performance.

## 4.2 QPE Performance Analysis

This subsection analyzes the performance of the QPE algorithm, focusing on its high accuracy in idealized conditions and the crucial role of the initial state.

**High Accuracy in Ideal Conditions:** Our QPE calculation yielded a highly accurate estimate of the  $H_2$  ground state energy, closely matching the theoretical value. This impressive performance, particularly within our idealized simulation setting, highlights QPE's potential for molecular energy calculations. Unlike VQE, QPE directly estimates Hamiltonian eigenvalues, making it less susceptible to wavefunction representation limitations. The Hartree-Fock state's substantial overlap with the true ground state in  $H_2$  enabled efficient projection onto the ground state energy during QPE. This good initial state is crucial for QPE's success, and its impact is discussed further. Our simulations, assuming ideal quantum computation and neglecting noise and decoherence, allow exploration

of QPE’s theoretical capabilities. While these ideal conditions contribute significantly to the observed accuracy ( $\Delta\phi = \frac{1}{2^t}$ , where  $t$  is the number of ancillary qubits), they don’t reflect the current realities of quantum computing. The challenges of implementing QPE on near-term hardware are addressed later.

**Role of Initial State and Overlap:** The choice of the Hartree-Fock state as the initial state was crucial for our QPE calculation’s success. QPE’s accuracy depends heavily on the overlap between the initial and target (ground) states. A larger overlap results in a stronger projection onto the desired eigenvalue during phase estimation. In  $H_2$ , the Hartree-Fock state closely approximates the true ground state due to the molecule’s simplicity and limited electron correlation. Consequently, the substantial overlap ensures effective isolation of the ground state energy by the QPE algorithm. A less suitable initial state, with poorer overlap, would likely reduce accuracy, as the measured phase would contain contributions from multiple eigenstates. This highlights a key consideration for applying QPE to more complex molecules: finding a good initial state balancing computational feasibility and sufficient overlap with the target state. When the Hartree-Fock state is a poor approximation, more sophisticated state preparation techniques are necessary. This dependence on the initial state is both a strength and limitation of QPE: while a good initial state enables high accuracy, finding such a state for complex systems can be challenging, as the probability of measuring the ground state energy is proportional to this overlap:

$$|\langle\psi_{\text{HF}}|\psi_0\rangle|^2 \approx \text{High}. \quad (16)$$

### 4.3 Comparison of VQE and QPE

This subsection provides a direct comparison of the VQE and QPE algorithms, considering their performance, resource requirements, inherent trade-offs, and practical implementation challenges.

**Performance and Resource Requirements:** Our findings reveal a stark contrast in the performance of VQE and QPE for calculating the ground state energy of  $H_2$ . QPE, under idealized conditions and with a suitable initial state, delivered a highly accurate result, closely matching the theoretical value. VQE, on the other hand, produced a significantly less accurate energy estimate due to the limitations of the simple ansatz employed. This difference in performance reflects a fundamental trade-off between the two algorithms. QPE, while offering higher accuracy, comes with greater resource demands. It requires a larger number of qubits, particularly ancillary qubits for phase estimation, and deeper circuits for implementing the controlled time evolution. The complexity of these circuits scales with the desired accuracy and the system size. VQE, in contrast, is less demanding in terms of quantum resources. It utilizes a smaller number of qubits and shallower circuits, making it more amenable to near-term quantum computers. However, the accuracy of VQE is strongly dependent on the choice of ansatz, and finding a suitable ansatz for complex molecules can be challenging.

We summarize the resource requirements and characteristics of both algorithms in Table 4. This difference in performance reflects a fundamental trade-off between the two algorithms. QPE, while offering higher accuracy, comes with greater resource demands. It requires a larger number of qubits, particularly ancillary qubits for phase estimation, and deeper circuits for implementing the controlled time evolution. The complexity of these circuits scales with the desired accuracy and the system size. VQE, in contrast, is

Table 4: Comparison of VQE and QPE Resource Requirements

	VQE	QPE
Qubits Required	$n$ qubits	$n + t$ qubits (with $t$ ancilla qubits)
Circuit Depth	Relatively shallow; depends on ansatz	Deep; due to controlled unitary operations and QFT
Classical Optimization	Required; iterative	Not required
Initial State	Flexible; can be simple	Should have high overlap with target state
Susceptibility to Noise	Moderate; shorter circuits	High; long coherence times needed

less demanding in terms of quantum resources. It utilizes a smaller number of qubits and shallower circuits, making it more amenable to near-term quantum computers. However, the accuracy of VQE is strongly dependent on the choice of ansatz, and finding a suitable ansatz for complex molecules can be challenging.

**Fundamental Trade-offs Between Ansatz and Controlled Time Evolution:** The contrasting performance of VQE and QPE for  $H_2$  highlights a fundamental trade-off in quantum algorithm design for molecular energy calculations. VQE’s accuracy is intrinsically linked to ansatz complexity. More expressive ansatzes, capturing greater entanglement and electron correlation, generally yield better energy estimates. However, increased complexity also means more variational parameters, complicating classical optimization, and deeper quantum circuits, challenging near-term hardware. QPE, conversely, bypasses the parameterized ansatz, directly targeting Hamiltonian eigenvalues. This eliminates ansatz selection but introduces other complexities. QPE’s success hinges on a good initial state, significantly overlapping with the desired eigenstate, and accurate controlled time evolution. While the Hartree-Fock state sufficed for  $H_2$ , preparing suitable initial states for more complex molecules is non-trivial. Controlled time evolution, requiring deep circuits for accurate simulation, especially with long evolution times or complex Hamiltonians, presents further challenges. Trotterization, while practical, introduces approximation errors needing careful management. Therefore, choosing between VQE and QPE involves balancing ansatz complexity (VQE) against the difficulties of state preparation and controlled time evolution (QPE). This trade-off necessitates ongoing research in algorithm and hardware development to advance quantum chemistry calculations.

**Practical Implementation Challenges:** Our QPE simulation’s high accuracy relies on idealized conditions, neglecting the noise and decoherence inherent in real-world quantum computers. These factors can severely impact QPE performance, causing errors in the estimated phase and calculated energy. A key challenge for practical QPE is the depth of the circuits required for controlled time evolution. Trotterization, while necessary, introduces approximation errors mitigated by finer time steps, which in turn lead to deeper, noise-prone circuits. Furthermore, QPE requires numerous highly coherent ancillary qubits. Maintaining coherence throughout the procedure is crucial, but current quantum computers are limited in both qubit number and coherence time, making large-scale, fault-tolerant QPE currently infeasible. Our idealization also assumes perfect gate operations, neglecting the errors that accumulate in real quantum gates, further degrading accuracy. Addressing these challenges requires advances in both quantum hardware (improved qubit coherence times) and algorithm development (error mitigation techniques, fault-tolerant computing).

While our simulation showcases QPE's theoretical potential, bridging the gap to practical implementation remains a significant task. VQE, while also affected by noise and decoherence during measurements, is primarily sensitive to ansatz choice and the optimization landscape. QPE, conversely, faces the significant hurdles of deep circuits, exceeding current hardware's coherence times, and the difficulty of implementing precise controlled unitary operations.

## 5 Conclusion

Our investigation into the performance of VQE and QPE for calculating the ground state energy of  $H_2$  reveals key insights into the capabilities and limitations of these quantum algorithms. We found that QPE, under idealized conditions and using the Hartree-Fock state as the initial state, provides a highly accurate estimate of the ground state energy, closely matching the established theoretical value. This result underscores the potential of QPE for achieving high accuracy in molecular energy calculations when provided with a suitable initial state and in the absence of noise and decoherence. In contrast, the VQE approach, employing a simple ansatz composed of single-qubit rotations and a linear chain of CNOT gates, yielded a significantly less accurate energy. This discrepancy highlights the strong dependence of VQE's performance on the choice of ansatz and the limitations of simple ansatzes in capturing the electron correlation effects crucial for accurate molecular energy calculations. This comparative study demonstrates the trade-off between accuracy and resource requirements for these two prominent quantum algorithms. While QPE offers high accuracy, it demands greater quantum resources and is more susceptible to the detrimental effects of noise in real-world quantum devices. VQE, while less resource-intensive, requires careful ansatz selection to achieve reasonable accuracy. These findings provide valuable guidance for selecting and optimizing quantum algorithms for molecular energy calculations, emphasizing the need for tailoring the approach to the specific characteristics of the molecule and the available quantum resources.

The limitations of the simple VQE ansatz employed in this study became evident in the significant discrepancy between the calculated and theoretical ground state energies of  $H_2$ . The restricted expressibility of the ansatz, consisting only of single-qubit rotations and a limited chain of CNOT gates, hindered its ability to accurately capture the electron correlation inherent in the molecule's ground state. This limitation underscores the crucial role of ansatz selection in VQE calculations and the need for more sophisticated ansatzes when targeting higher accuracy. The potential for improvement in VQE performance lies primarily in exploring more complex ansatzes. Ansatzes based on the Unitary Coupled Cluster (UCC) framework, for instance, offer a systematic approach to incorporating higher-order excitations and capturing more complex correlation effects. While such ansatzes introduce additional variational parameters and increase the complexity of the quantum circuits, they offer the potential to significantly improve the accuracy of VQE calculations. Further research into the design and implementation of efficient and expressive ansatzes is essential for advancing the capabilities of VQE for tackling more complex molecular systems. Beyond the ansatz itself, exploring alternative classical optimization strategies may also yield improvements in VQE performance. More robust optimization algorithms could help mitigate the risk of converging to local minima in the energy landscape, potentially leading to more accurate energy estimates even with the same ansatz. Thus, while our study revealed the limitations of a simple ansatz, it also pointed towards promising avenues for enhancing VQE's accuracy through more sophisticated ansatzes and optimization techniques.

While our QPE simulation demonstrated remarkable accuracy under idealized conditions, realizing this potential on current quantum hardware presents significant challenges. The depth of the circuits required for accurate controlled time evolution, particularly for larger molecules or longer simulation times, renders QPE highly susceptible to noise and decoherence, the detrimental effects inherent in current quantum devices. Maintaining qubit coherence throughout the lengthy QPE procedure remains a major hurdle. Furthermore, the need for a substantial number of ancillary qubits, each with high fidelity and long coherence times, poses a significant challenge for near-term quantum computers. These limitations underscore the importance of ongoing research in both quantum hardware development and algorithm design. Exploring error mitigation techniques, developing more noise-resilient QPE variants, and ultimately achieving fault-tolerant quantum computation are crucial steps towards harnessing the full power of QPE for accurate molecular energy calculations in the future.

## 6 Future Work

A primary avenue for future work is the exploration of more complex and expressive ansatzes within the VQE framework. As highlighted by the limitations of the simple ansatz used in this study, accurately capturing electron correlation requires a more sophisticated representation of the molecular wavefunction. The Unitary Coupled Cluster (UCC) family of ansatzes, particularly UCC with Singles and Doubles (UCCSD), offers a promising route for achieving higher accuracy. UCCSD systematically incorporates single and double electron excitations, allowing for a more complete description of electron correlation effects. While implementing UCCSD introduces additional variational parameters and increases the complexity of the quantum circuits, the potential gains in accuracy warrant further investigation. Exploring the performance of UCCSD and other advanced ansatzes for  $H_2$  and larger molecules will be crucial for assessing their effectiveness and practicality in the context of near-term quantum computers. Furthermore, developing strategies for efficiently optimizing the increased number of parameters associated with these more complex ansatzes is essential for their successful implementation. Investigating alternative optimization algorithms and developing tailored strategies for specific ansatzes are promising directions for future research.

Beyond exploring more sophisticated ansatzes, investigating advanced optimization techniques is crucial for enhancing the performance of VQE. The choice of classical optimizer significantly impacts the efficiency and accuracy of the variational parameter search. While COBYLA, the optimizer used in this study, provides a reasonable starting point, its susceptibility to local minima and relatively slow convergence can limit the achievable accuracy, especially for complex ansatzes with numerous parameters. Exploring alternative optimization algorithms, particularly those designed for noisy or non-smooth objective functions, is a promising avenue for future research. Gradient-based methods, such as stochastic gradient descent (SGD) and its variants like Adam, offer potential advantages in terms of convergence speed. However, their applicability to VQE depends on the efficient estimation of gradients on quantum hardware. Furthermore, investigating hybrid optimization strategies that combine elements of global and local optimization could prove beneficial. Global optimization algorithms can help escape local minima and explore a wider parameter space, while local optimization methods can refine the solution in the vicinity of a promising candidate. Developing optimization techniques tailored to the specific characteristics of VQE, such as the noise inherent in quantum measurements and the structure of specific ansatzes, could lead to significant improvements in both the speed and accuracy of VQE calculations.

For QPE to transition from a theoretical tool to a practical method for molecular energy calculations, the challenges associated with controlled time evolution and quantum error correction must be addressed. The accuracy and feasibility of QPE are intrinsically linked to the precise implementation of the time evolution operator  $e^{-iHt}$ . As discussed earlier, Trotterization provides a means to approximate this operator, but it introduces errors that scale with the evolution time and the Hamiltonian's complexity. Developing more efficient and accurate methods for controlled time evolution is crucial for realizing the full potential of QPE. Higher-order Trotter decompositions, alternative simulation algorithms, and techniques for optimizing the Trotter step size are promising areas for future research. Furthermore, the impact of noise and decoherence on QPE cannot be overlooked. Real-world quantum computers are inherently noisy, and these imperfections accumulate throughout the computation, degrading the accuracy of the phase estimation. Quantum error correction (QEC) offers a path towards mitigating these errors and achieving fault-tolerant quantum computation. Developing and implementing QEC schemes tailored to the specific requirements of QPE is essential for its practical application to molecular systems. This involves exploring efficient encoding and decoding strategies, optimizing error correction protocols, and integrating QEC into the overall QPE algorithm. Addressing these challenges in controlled time evolution and quantum error correction will pave the way for realizing the promise of QPE as a powerful tool for accurate and reliable molecular energy calculations on quantum computers.

## Acknowledgements

This research was supported by the Innovation Fund for Higher Education in China Gansu Province (No.2023B-295).

## References

1. O. A. von Lilienfeld, K. R. Müller, and A. Tkatchenko, "Exploring chemical compound space with quantum-based machine learning," *Nature Reviews Chemistry*, vol. 4, no. 7, pp. 347-358, 2020.
2. K. J. A. Keith, V. Vassilev-Galindo, B. Cheng, et al., "Combining machine learning and computational chemistry for predictive insights into chemical systems," *Chemical Reviews*, vol. 121, no. 16, pp. 9816-9872, 2021.
3. M. Head-Gordon, "Quantum chemistry and molecular processes," *The Journal of Physical Chemistry*, vol. 100, no. 31, pp. 13213-13225, 1996.
4. P. E. M. Siegbahn and M. R. A. Blomberg, "Transition-metal systems in biochemistry studied by high-accuracy quantum chemical methods," *Chemical Reviews*, vol. 100, no. 2, pp. 421-438, 2000.
5. Y. Cao, J. Romero, J. P. Olson, et al., "Quantum chemistry in the age of quantum computing," *Chemical Reviews*, vol. 119, no. 19, pp. 10856-10915, 2019.
6. B. Bauer, S. Bravyi, M. Motta, et al., "Quantum algorithms for quantum chemistry and quantum materials science," *Chemical Reviews*, vol. 120, no. 22, pp. 12685-12717, 2020.
7. F. Neese, "Prediction of molecular properties and molecular spectroscopy with density functional theory: From fundamental theory to exchange-coupling," *Coordination Chemistry Reviews*, vol. 253, no. 5-6, pp. 526-563, 2009.
8. S. Jin, P. Markowich, and C. Sparber, "Mathematical and computational methods for semiclassical Schrödinger equations," *Acta Numerica*, vol. 20, pp. 121-209, 2011.
9. O. V. Prezhdo, "Mean field approximation for the stochastic Schrödinger equation," *The Journal of Chemical Physics* vol. 111, no. 18, pp. 8366-8377, 1999.
10. R. A. Friesner, "Ab initio quantum chemistry: Methodology and applications," *Proceedings of the National Academy of Sciences*, vol. 102, no. 19, pp. 6648-6653, 2005.
11. N. S. Blunt, J. Camps, O. Crawford, et al., "Perspective on the current state-of-the-art of quantum computing for drug discovery applications," *Journal of Chemical Theory and Computation*, vol. 18, no. 12, pp. 7001-7023, 2022.
12. H. Liu, G. H. Low, D. S. Steiger, et al., "Prospects of quantum computing for molecular sciences," *Materials Theory*, vol. 6, no. 1, p. 11, 2022.

13. C. R. Laumann, R. Moessner, A. Scardicchio, et al., "Quantum annealing: The fastest route to quantum computation?," *The European Physical Journal Special Topics*, vol. 224, no. 1, pp. 75-88, 2015.
14. M. R. Wasielewski, M. D. E. Forbes, N. L. Frank, et al., "Exploiting chemistry and molecular systems for quantum information science," *Nature Reviews Chemistry*, vol. 4, no. 9, pp. 490-504, 2020.
15. S. McArdle, S. Endo, A. Aspuru-Guzik, et al., "Quantum computational chemistry," *Reviews of Modern Physics*, vol. 92, no. 1, p. 015003, 2020.
16. S. Pathak, S. P. Kushwaha, S. Verma, et al., "Advances in Computational Chemistry for Drug Discovery," *Journal of Drug Discovery and Health Sciences*, vol. 1, no. 03, pp. 146-152, 2024.
17. A. Kandala, A. Mezzacapo, K. Temme, et al., "Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets," *Nature*, vol. 549, no. 7671, pp. 242-246, 2017.
18. J. Tilly, H. Chen, S. Cao, et al., "The variational quantum eigensolver: a review of methods and best practices," *Physics Reports*, vol. 986, pp. 1-128, 2022.
19. U. Dorner, R. Demkowicz-Dobrzanski, B. J. Smith, et al., "Optimal quantum phase estimation," *Physical Review Letters*, vol. 102, no. 4, p. 040403, 2009.
20. R. Demkowicz-Dobrzanski, U. Dorner, B. J. Smith, et al., "Quantum phase estimation with lossy interferometers," *Physical Review A: Atomic, Molecular, and Optical Physics*, vol. 80, no. 1, p. 013825, 2009.
21. H. L. Tang, V. O. Shkolnikov, G. S. Barron, et al., "qubit-adapt-vqe: An adaptive algorithm for constructing hardware-efficient ansätze on a quantum processor," *PRX Quantum*, vol. 2, no. 2, p. 020310, 2021.
22. P. J. Ollitrault, A. Miessen, and I. Tavernelli, "Molecular quantum dynamics: A quantum computing perspective," *Accounts of Chemical Research*, vol. 54, no. 23, pp. 4229-4238, 2021.
23. T. E. O'Brien, B. Tarasinski, and B. M. Terhal, "Quantum phase estimation of multiple eigenvalues for small-scale (noisy) experiments," *New Journal of Physics*, vol. 21, no. 2, p. 023022, 2019.
24. K. Yamamoto, S. Duffield, Y. Kikuchi, et al., "Demonstrating Bayesian quantum phase estimation with quantum error detection," *Physical Review Research*, vol. 6, no. 1, p. 013221, 2024.
25. J. R. McClean, R. Babbush, P. J. Love, et al., "Exploiting locality in quantum computation for quantum chemistry," *The Journal of Physical Chemistry Letters*, vol. 5, no. 24, pp. 4368-4380, 2014.
26. M. Cerezo, A. Arrasmith, R. Babbush, et al., "Variational quantum algorithms," *Nature Reviews Physics*, vol. 3, no. 9, pp. 625-644, 2021.

## Authors

**Xiaofei Zhao** an Associate Professor at Lanzhou Petrochemical University of Vocational Technology, is currently pursuing a Ph.D. at Lanzhou Jiaotong University. Her research interests encompass automation engineering, information engineering, related education, and information security. She is also exploring the application of quantum computing techniques to information security, with a focus on post-quantum cryptography and quantum key distribution.

**Hua Wang** is the Lead for Big Data Operations in the Digital Business Division of the State Grid Gansu Electric Power Company. Holds a master's degree from Lanzhou University of Technology. Her research interests focus on big data integration and mining in smart grids, the socio-economic impacts of grid data, related security issues, and the application of quantum computing in smart grids, particularly in areas such as optimization and security. She emphasizes leveraging data-driven approaches to promote sustainable development and infrastructure safety.