二、研究計畫內容

(一) 摘要

1. 摘要

隨著量子硬體 (Quantum Hardware) 的快速發展，許多量子計算化學領域 (Quantum Computational Chemistry) 的演算法得以實行。然而在量子誤差修正 (Quantum Error Correction) 方面的困難，導致現今唯有一相對完善的半量子式演算法 (Variational Quantum Eigensolver, VQE)，得以計算出給定 Hamiltonian 的最低本徵值，同時能運行於近代的量子硬體上。因此，爲了讓計算資源的利用達到最佳化，使用高效基底集 (basis sets) 來分析化學分子 Hamiltonian 的過程就在電子結構問題 (Electronic Structure Problem) 中成爲了重要手段。然而，當前特定的 VQE 演算法，包括以 Daubechies wavelet 基底集搭配高效率的編碼方式運行於參數化的量子電路 (Parameterized Quantum Circuits, PQCs) 之量子硬體上，或是以化學式啓發 (chemical-inspired) 所建構之 PQC 運行於模擬器上，都僅能在結構相對較小的分子上達到化學準度 (chemical accuracy)。因此，本研究引入量子神經網路 (Quantum Neural Network) 模型，同時搭配 Daubechies wavelet orbitals 之計算，來達成高效且準確的分子相關性質計算。本研究預期生成的模型準確率、所需量子位元數 (qubit number)、量子電路之深度、與量子雜訊容忍性能等層面都能與先前的研究相比擬或甚至更加突破；同時，將未監督式學習 (Unsupervised Learning) 結合 Daubechies wavelet molecular orbitals 之方法亦是前所未有的嘗試，有望爲相關的問題開創新的研究方向。

2. Abstract

As the rapid evolution of quantum hardware industry, various algorithms in quantum computational chemistry are put forward for rigorous implementation. However, due to lack of quantum error correction, a promising hybrid quantum-classical algorithm to find the lowest eigenvalue of a given Hamiltonian for near-term quantum hardware is the variational quantum eigensolver (VQE). To get the best performance out of limited computational resources, using efficient basis sets to represent molecular Hamiltonian in electronic structure problems has become a crucial step. Some particular VQE calculations using Daubechies wavelet basis sets and efficient encoding schemes implemented via hardware-efficient parameterized quantum circuits (PQCs) on real quantum machines or via chemical-inspired PQCs on simulators to date are only accomplishing chemical accuracy on relatively small and simple-structure molecules. Hence, in this research we introduce a quantum neural network method while adopting the top pioneering basis sets of Daubechies wavelet orbitals for accurate and efficient quantum computations of molecular properties. It is expected that the results of this work would be comparable with or better than those of the previous works on model accuracy, required qubit number, circuit depth and quantum noise tolerance. Moreover, this work exploits the novelty of combining Daubechies wavelet molecular orbitals method with unsupervised learning on quantum neural networks, which may hold the potential to develop a new area of research

on relevant topics.

(二) 研究動機與研究問題

1. 研究動機

Due to the rapid evolution of quantum hardware industry, quantum computing has attracted much attention recently. Quantum computation of molecular properties is one of the most promising quantum computing applications. Among various methods in quantum computational chemistry, choosing a suitable and efficient basis set to represent the molecular Hamiltonian has played a key role in electronic structure problem.

One of the promising algorithms for near-term quantum hardware is the Variational Quantum Eigensolver (VQE) [1, 2, 3]. VQE is a hybrid quantum-classical algorithm as it uses the quantum computer for a state preparation and measurement subroutine, and the classical computer to process the measurement results and update the quantum computer according to an update rule. This exchanges the long coherence times needed for phase estimation for a polynomial overhead due to measurement repetitions and classical processing [3]. Currently the minimal STO-3G basis set is commonly used in benchmark studies because it requires the minimum number of spin orbitals, and thus minimum number of qubits and minimum circuit depth. Calculations using minimal basis sets are of limited accuracy, and thus can not provide useful prediction on the system properties (e.g. ground state energy, bond length and angle, molecular vibration frequency).

Some particular VQE calculations using different basis sets or encoding schemes [4, 5] implemented via hardware-efficient parameterized quantum circuits (PQCs) [3] on real quantum machines or via chemical-inspired PQCs [3] on simulators to date are only accomplishing chemical accuracy on relatively small and simple-structure molecules (e.g. H_2, LiH). There is still room for improvement on efficiently harvesting the power of resource-saving basis functions (e,g. Daubechies wavelet orbitals) and novel variants of the VQE method.

Thus, to further enhance the overall performance in model accuracy, required qubit number, circuit depth and quantum noise tolerance, this work aims to apply hybrid quantum-classical neural networks to the quantum circuit with chosen basis sets [6]. With the help of unsupervised learning on neural networks, some characteristics that are not considered by previous chemical-inspired UCCSD-VQE based method may be included into the model, while some other redundant features could be discarded. As a result, both model accuracy and circuit complexity would outperform previous researches.

2. 研究問題

In this work, we follow the problem formulation used in [6]. The molecular "potential

energy surface" problem can be described as follows:

Input: The bond lengths of the considered molecules. The cost function to be minimized in the lowest eigenvalue problem of the VQE algorithm is defined as

$$f = \sum_j \langle \phi_j | H_j | \phi_j \rangle , \tag{1}$$

where $|\phi_j\rangle$ is the final state of the proposed hybrid quantum-classical neural networks with the j^{th} bond length as input, with H_j being the corresponding Hamiltonian.

Output: A sequence of "potential energy surface" that plots the ground state energy of the molecule with respect to a range of bond lengths.

Evaluation: The accuracy of the method is validated by comparing the results using the generated sequence of ground state energy and those performing the actual laboratory experiment, within the error bound of 1 kcal/mol regarded as chemical accuracy. In addition to the chemical accuracy, the circuit size, the runtime on real machine and qubit number used during the model generation and calculation are also crucial indicators. Note that there exists a trade-off among the indicators.

(三) 文獻回顧與探討

1. Encoding Hamiltonians

(1) The Second Quantization

Observables must be independent of the representation used. Therefore, the expectation values of second quantized operators must be equivalent to the expectation values of the corresponding first quantized operators. As first quantized operators conserve the number of electrons, the second quantized operators must contain an equal number of creation and annihilation operators. We can use these requirements to obtain the second quantized form of the electronic Hamiltonian [7, 8]:

$$H = \sum_{p,q} H_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} H_{pqrs} a_p^\dagger a_q^\dagger a_r a_s, \tag{2}$$

with

$$h_{pq} = \int d\mathbf{x} \phi_p^*(\mathbf{x}) \left(\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \right) \phi_q(\mathbf{x}), \tag{3}$$

$$h_{pqrs} = \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\phi_p^*(\mathbf{x}_1) \phi_q^*(\mathbf{x}_2) \phi_r(\mathbf{x}_2) \phi_s(\mathbf{x}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{4}$$

The first integral represents the kinetic energy terms of the electrons and their Coulomb interaction with the nuclei. The second integral is due to the electron-

electron Coulomb repulsion.

(2) **The Daubechies wavelet (DW) molecular orbitals**
Atomic orbitals are an intuitive choice of basis set for isolated molecular systems. However, basis sets constructed from atomic orbitals suffer from non-orthogonality and hence require additional computations of the overlap matrices. Daubechies wavelets provide an alternative option for basis sets in computational quantum chemistry [9, 11, 10]. In wavelet theory, there are a scaling function $\phi(x)$ and a wavelet $\psi(x)$,

$$\phi(x) = \sqrt{2} \sum_{j=1-m}^{m} h_j \phi(2x - j), \tag{5}$$

$$\psi(x) = \sqrt{2} \sum_{j=1-m}^{m} g_j \phi(2x - j), \tag{6}$$

where the coefficients h_j and $g_j = (-1)^j h_{-j+1}$ are elements of the filter characterizing the m^{th} order of the wavelet family. There are several advantages of Daubechies wavelets: (1) the wavelets are localized in both real and reciprocal space, which is conducive for providing an accurate representation of molecular Hamiltonian in spatially localized grid points. (2) the completeness of the Daubechies wavelet basis set eliminates the superposition error induced by the incompleteness of other previously used basis sets (e.g. STO-3G). (3) the DW method has its adaptivity within programming, making chemical accuracy achievable at affordable computational cost.

2. **Quantum Machine Learning (QML)**

(1) **Parameterized Quantum Circuits (PQCs)**
A parameterized quantum circuit (PQC) is a quantum circuit consisting of data encoding gates, entangling gates and parameterized gates (i.e., gates with tunable parameters) with fixed depth. In general, an n-qubit PQC can be written as

$$U(\vec{\theta}) \left|\psi\right\rangle = \left(\prod_{i=1}^{m} U_i \right) \left|\psi\right\rangle, \tag{7}$$

where $U(\vec{\theta})$ is the set of universal gates, m is the number of quantum gates, $\vec{\theta}$ is the set of parameters $\{\theta_0, \theta_1, \cdots, \theta_{k-1}\}$ with k being the total number of tunable parameters, and $\left|\psi\right\rangle$ is the initial quantum state. The operation of U can be modified by changing parameters $\vec{\theta}$. Thus, by optimizing the cost function with the parameters used in $U(\vec{\theta})$, PQC approximates the wanted quantum states.

(2) **Constructions of the Circuit**

Our PQC consists of three parts: the data encoding part, the variational circuit part, and the measurement part. One can use the hardware-efficient ansatze [3] and the variational encoding [12] technique to decrease the depth of the quantum circuit so that it can be implemented on noisy intermediate-scale quantum (NISQ) [13] devices. The classical part of the circuit is enabled by measuring the expectation values of the concerned operators. Notice that non-linearity is introduced into the circuit via direct measurement operation, which is crucial in boosting the function space of the neural network. The construction of the proposed hybrid quantum-classical neural network is illustrated in Figure 1 where the linear part in the classical neural network is replaced by the quantum circuit and the nonlinear part is replaced by the quantum measurement.

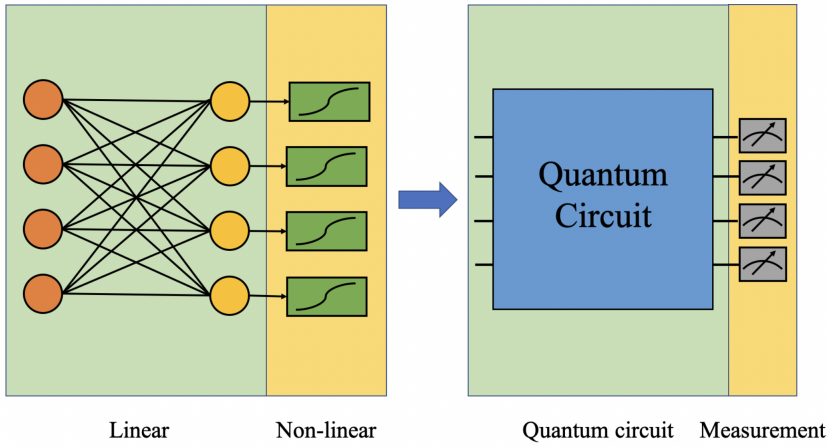

Figure 1: Quantum-classical hybrid neural network, the linear part in the classical neural network is replaced by the quantum circuit and the nonlinear part is replaced by the measurement. From [6].

(四) 研究方法及步驟

1. 研究方法

(1) **Orbital Integrals**

We will calculate the orbital integrals in the second quantization Hamiltonian by Daubechies wavelet (minimal) basis orbitals with [14] as reference, and with other sets of basis (e.g. STO-3G) for final result comparison.

(2) **Mapping Operators**

Once the calculations of orbital integrals are done, we apply second quantized basis set encoding methods, such as the Jordan-Wigner or Bravyi-Kitaev encoding method, to map from operators that act on indistinguishable fermions to

operators acting on distinguishable qubits to obtain the corresponding Hamiltonian in the Hilbert space of the qubits [3]. One may utilize the OpenFermion package [15] during the encoding procedure.

(3) **Implementation of Quantum Neural Networks**
To train a quantum neural network model on a hybrid circuit, we need to define a reliable network architecture. The observation is that the state space in quantum computing increases exponentially with the number of qubits, while the complexity of a classical neural network increases exponentially with the number of neuron layers in the neural network. Since increasing the number of layers of the variational part circuit (composed of entangling gates and parametrized gates) would reach saturation and may not improve the performance when the number of layers is large enough [16], we aim not to increase the depth of the circuit, but to develop a hardware-efficient hybrid network which saves computational resources while maintaining essential non-linearity. In this work, we may choose the measurement operation as means of implementing non-linearity into the circuit and use the expectation values of operators on each qubit of the PQC to serve as the nonlinear operations connecting different quantum layers. The expectation values of operators capable of extracting useful information from the PQC are used as the input data for the encoding part of the next quantum circuit layer. As for the data encoding part, we may initialize the input state as $\left(\otimes_{i=0}^{n-1} R_y(a)H \right) |0\rangle^{\otimes n}$, where a is the bond length, H is the Hadamard gate, and R_y is the rotational-y gate. The number of qubits n is equal to the number of qubits of the corresponding Hamiltonian.

For the variational part of our PQC, we may construct a circuit consisting of R_y and CNOT gates, which can be written as [6]

$$\prod_{j=0}^{n-1} \left(\otimes_{i=0}^{n-1} R_y(w_{i+n\times j}) \right) \left(\mathrm{CNOT}_{n-3,n-2} \cdots \mathrm{CNOT}_{3,4} \mathrm{CNOT}_{1,2} \right) \cdot \left(\mathrm{CNOT}_{n-2,n-1} \cdots \mathrm{CNOT}_{2,3} \mathrm{CNOT}_{0,1} \right) \text{, for even } n, \quad (8)$$

and

$$\prod_{j=0}^{n-1} \left(\otimes_{i=0}^{n-1} R_y(w_{i+n\times j}) \right) \left(\mathrm{CNOT}_{n-2,n-1} \cdots \mathrm{CNOT}_{3,4} \mathrm{CNOT}_{1,2} \right) \cdot \left(\mathrm{CNOT}_{n-3,n-2} \cdots \mathrm{CNOT}_{2,3} \mathrm{CNOT}_{0,1} \right) \text{, for odd } n, \quad (9)$$

where w are adjustable parameters, and $\mathrm{CNOT}_{m,n}$ represents CNOT gate with m as the control qubit and n as the target qubit. This particular way of circuit construction is plotted below in Figure 2 where b_i in the data encoding part of the second quantum circuit layer is the measured expectation value of σ_z

operator from qubit i of the previous quantum circuit layer.

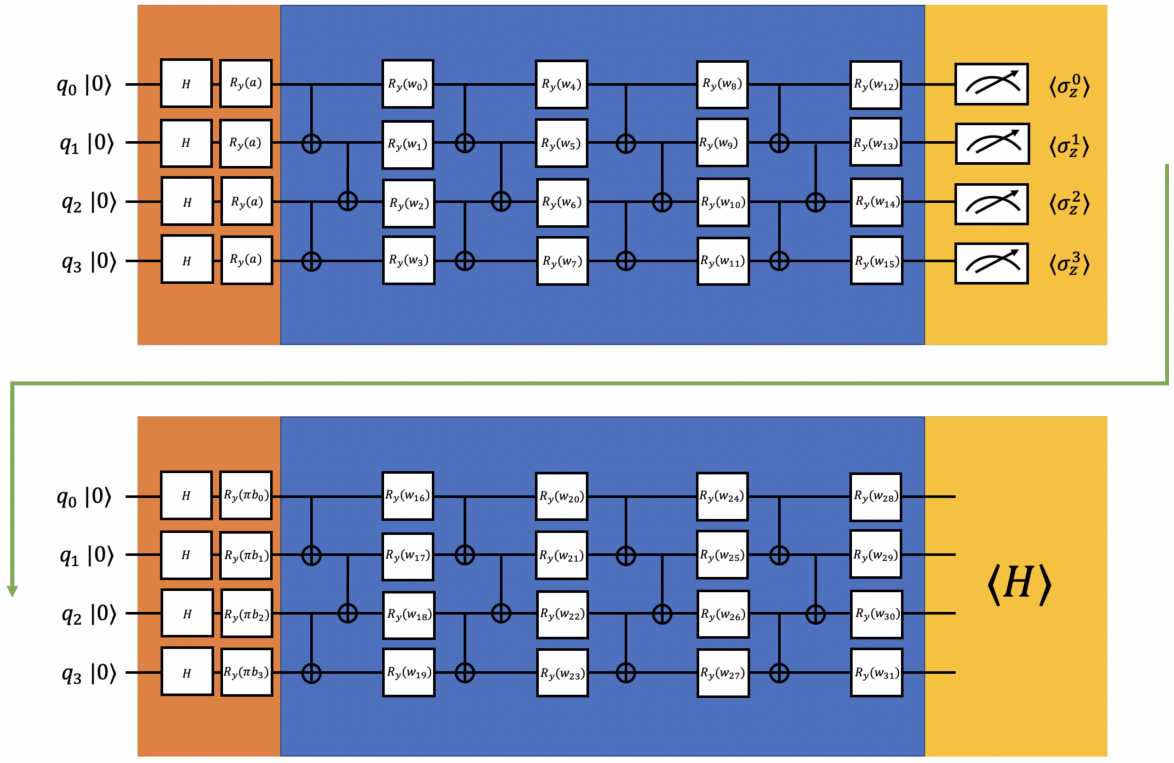

Figure 2: A 4-qubit quantum-classical neural network. The orange parts are data encoding, the blue parts are the variational (parametrized) quantum circuits, and the yellow parts are measurements. Notice that the first set of the measurements serve as nonlinear operations connecting the two PQCs. From [6].

Notice that the ways of arranging different gates and the numbers of qubits, repetition circuit units and circuit layers are not definite (i.e. there remains wide possibility and freedom for the construction of our hybrid neural network). For instance, we can adjust the types of the parameterized gates and the number of repetition units in our variational circuit (4 repetitions for the case in Figure 2), which would in turn affect our model expressibility and entangling capability.

(4) **The Noise Model**
To take the effect of quantum noise into consideration, we will investigate the performance of quantum simulations under noisy quantum computer configurations instead of running on noise-free simulator, which is more realistic to a NISQ [13] device. We will then implement the linear zero-noise extrapolation method for error mitigation [17, 4, 18].

2. **研究步驟**

(1) Review previous researches regarding molecular Hamiltonian encoding (espe-

cially the Daubechies wavele method) as well as quantum-classical hybrid neural networks, in order to come up with the research methods for this work.

(2) Get familiar with the algorithm flow of Variational Quantum Eigensolver and modify several parts within it to adapt to the hybrid neural network method.

(3) Calculate each term of the Hamiltonian of chosen molecules (e.g. H_2, LiH, H_2O) by performing a Hartree-Fock calculation using the BigDFT code [11, 19], an *ab initio* software package that employs Daubechies wavelet basis sets. Then, select a minimal number of spin orbitals from the BigDFT output to form a set of (minimal) basis Daubechies wavelet molecular orbitals for the subsequent quantum simulations.

(4) Train the proposed hybrid quantum-classical neural network on several indicated bond lengths.

(5) Apply the rest of the bond lengths to the trained network as input with error mitigation techniques applied to the output.

(6) Conduct experiments and get the potential energy surface of various small molecules to evaluate the accuracy and efficiency of our method and compare with previous works.

(7) Fine-tune our works and conduct academic paper writing.

(五) 預期結果

1. **Performance**

   As mentioned in (二), there are several crucial indicators to evaluate the work, including the deviation between the generated ground state energy surface and the experimental results, the circuit size, the runtime and qubit used during model generation and simulation calculations.

   For chemical accuracy, since the Daubechies wavelet basis orbitals possess advantageous features over those of other basis sets (e.g. STO-3G or 6-31G), the self-consistent field calculations based on a Daubechies wavelet basis set can prepare a better set of molecular orbitals, which in turn results in a better many-body Hamiltonian. Thus it is expected that the accuracy of our model will be comparable with or even better than previous works.

   For circuit size, since we will conduct tests on a variety of quantum neural network architecture in this research, it is expected to result in a resource-efficient and short-depth circuit while maintaining the desired chemical accuracy.

2. **Novelty**

   Though several previous researches in quantum computational chemistry areas which took neural-network-based approaches had overcame some bottlenecks of the corresponding VQE algorithm flows [20, 21] for calculating molecular potential energy

surfaces, it's unprecedented to apply quantum machine learning methods into quantum computational chemistry with molecular Hamiltonian generated by Daubechies wavelet orbital basis. It is thus expected that this work could break the bottleneck of finding more accurate molecular properties and would even develop a new series of systematical methods in relevant research areas.

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(七) 需要指導教授指導內容

1. **Discussion about the direction of the research:** It's my first time engaging in such an academic research, so I'm not familiar with the whole process of conducting a research. Through regular meeting with Prof. Goan, I can avoid getting lost during the research.
2. **Clarification of the Daubechies wavelet method and quantum neural network architecture:** Prof. Goan is an expert in quantum computing and possesses extensive research experiences about the topics of quantum computational chemistry and quantum machine learning. The methods in this work could be justified with the help of Prof. Goan.
3. **Usage of relevant software packages (e.g. IBM Qiskit, OpenFermion):** This research is based on the quantum machine simulator IBM qiskit package, which Prof. Goan possess extensive experience manipulating with.