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。因此，爲了最佳化利用計算資源，多種基底集 (basis set) 的應用成爲了分析小分子電子結構問題 (molecular electronic structure problem) 的重要手段。然而，當前的 basis set 大多是以 Variational Quantum Eigensolver 的形式引入量子電路中，僅能在結構相對簡單的分子上得到具有化學準度 (Chemical Accuracy) 的相關性質 (基態能量、鍵長鍵角、振動頻率)。因此，本研究引入深度學習中的神經網路 (Neural Networks) 模型，同時搭配數個指標性的 basis set function 應用於 quantum computational chemistry 中，預期生成的模型準確率、量子電路大小與深度、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，將深度學習運用於分析 Daubechies wavelet molecular Hamiltonian 也是前所未有的嘗試，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 ready for rigorous implementation. To get the best performance out of limited computational resources, a plethora of basis sets for encoding molecular Hamiltonian in electronic structure problem has become a crucial step. However, most basis sets are implemented by UCCSD-VQE method into quantum circuits to-date, and are accomplishing chemical accuracy only on relatively simple-structure-molecules. (e.g. ground state energy, bond length and angle, molecular vibration frequency). Hence, we introduce the neural network method while adopting the top pioneering basis sets (Daubechies wavelet) within this research. It is expected that the results of this work would be comparable with or better than that 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, various algorithms in quantum computational chemistry are ready for rigorous implementation. Among them a plethora of basis sets for encoding molecular Hamiltonian has played a key

role in electronic structure problem.

One of the promising algorithm for near-term quantum hardware is the VQE (Variational Quantum Eigensolver) [1][2], it uses the quantum computer for a state preparation and measurement subroutine, and it uses 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.

However, the aforementioned VQE method predicts electronic properties via various ways of encoding molecular Hamiltonian through basis functions within chemical accuracy only on a small portion of relatively simple molecules (e.g. H_2, LiH) to-date. There is still space for improvement on efficiently harvesting the power of resource-saving basis function (i.e. Daubechies wavelet).

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 network to the quantum circuit with chosen basis sets [3]. With the help of unsupervised learning on NN, some characteristics that are not considered by previous 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 [3]. The "potential energy surface" problem can be described as the following:

Input: The bond lengths of the considered molecules. The cost function 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 network with the j^{th} bond length as input, with H_j being the corresponding Hamiltonian.

Output: A sequence of "potential energy surface" that plot 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 lab 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 model generation are also crucial indicators. Note that there exists a trade-off among each indicator.

(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 [4][5]:

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

, 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 molecular orbitals (DW)

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 [6][7][8]. 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 Circuit (PQC)

A parameterized quantum circuit is a quantum circuit consisting of parameterized gates with fixed depth. In general, an n-qubit PQC can be written as

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

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

(2) Constructions of the Quantum Layer

The quantum layer consists of two parts: the variational encoding part and PQC part. One can use the variational encoding [9] to decrease the depth of the quantum circuit so that it can be implemented on NISQ devices.

The input state is initialized 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.

The quantum computation part is to use a simple PQC consisting of R_y and CNOT gates, which can be written as

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

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

, 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.

(3) **The Nonlinear Layer**
The classical layer is enabled by expectation values of the 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.

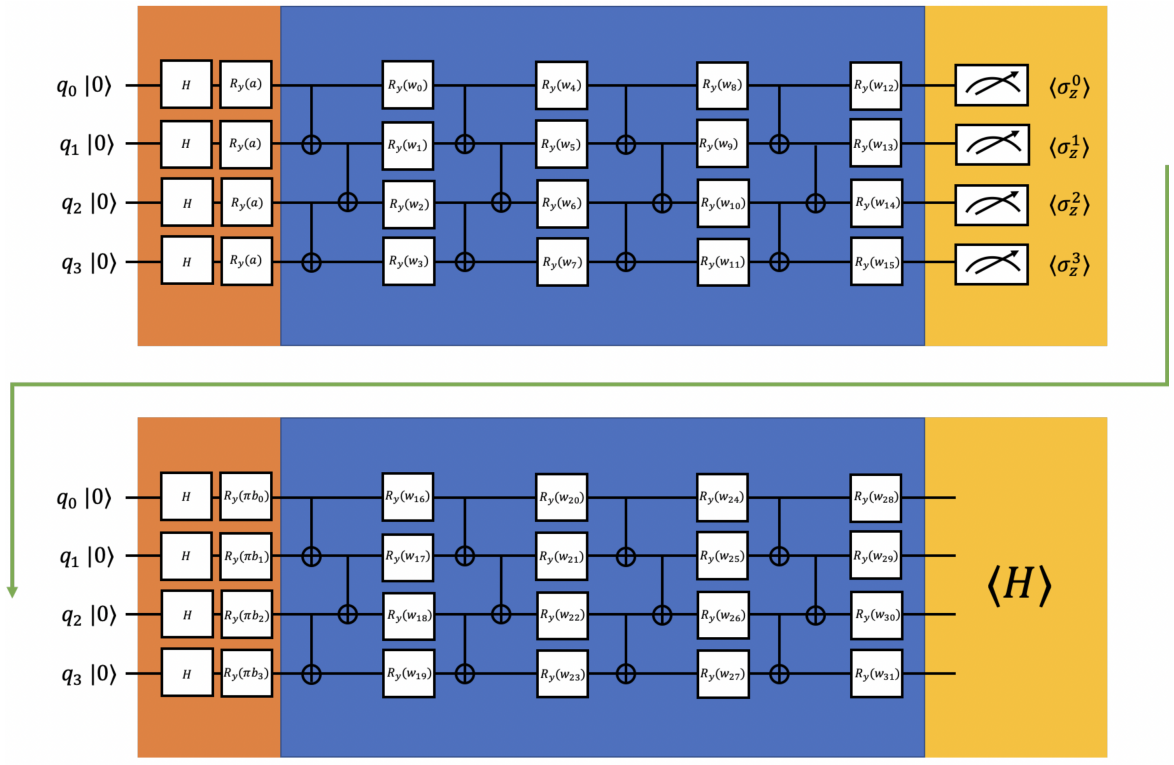

Figure 1: 4-qubit quantum-classical neural network. The orange parts are the data encoding, the blue parts are parameterized quantum circuits, and the yellow parts are measurements. Notice that the first measurements serve as nonlinear operations connecting two PQC. [3]

(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 with [10] as reference, with the follow up transformation to the qubit Hamiltonian utilizing the OpenFermion package [11].

(2) **Implementation of Neural Networks**
To train a NN model on a hybrid circuit, we need to define a reliable network architecture. Since increasing the number of layers of the parameterized quantum circuit (PQC) would reach saturation and may not improve the performance when the number of layers is large enough [12], 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, as plotted in Figure 2.

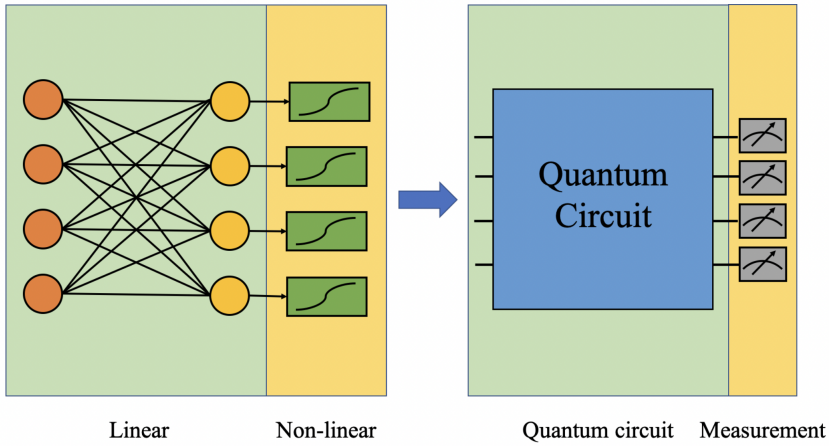

Figure 2: quantum-classical hybrid neural network, the linear part in the classical neural network is replaced by the quantum circuits and the nonlinear part is replaced by measurements.

(3) **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. [14][15][16]

2. **研究步驟**

(1) Review previous researches regarding molecular Hamiltonian encoding (especially 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 [7][17], 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 length.

(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 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 usage.

   For chemical accuracy, since the Daubechies wavelet method possess advantage against other method for establishing basis set (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 test on a variety of 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**
   It's unprecedented to apply machine learning methods into molecular Hamiltonian generated by Daubechies wavelet method. As several previous researches in quantum computational chemistry areas which took NN-based approaches and overcame the bottlenecks of the corresponding algorithm flows [18][19], it's expected that this work could break the bottleneck of molecular properties finding and even develop a new series of systematical method in relevant research area.

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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 DW method and quantum neural network architecture:** Prof. Goan 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.