Predicting excited states from ground state wavefunction by supervised quantum machine learning

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Abstract. Excited states of molecules lie in the heart of photochemistry and chemical reactions. The recent development in quantum computational chemistry leads to inventions of a variety of algorithms that calculate the excited states of molecules on near-term quantum computers, but they require more computational burdens than the algorithms for calculating the ground states. In this study, we propose a scheme of supervised quantum machine learning which predicts the excited-state properties of molecules only from their ground state wavefunction resulting in reducing the computational cost for calculating the excited states. Our model is comprised of a quantum reservoir and a classical machine learning unit which processes the measurement results of single-qubit Pauli operators with the output state from the reservoir. The quantum reservoir effectively transforms the single-qubit operators into complicated multi-qubit ones which contain essential information of the system, so that the classical machine learning unit may decode them appropriately. The number of runs for quantum computers is saved by training only the classical machine learning unit, and the whole model requires modest resources of quantum hardware that may be implemented in current experiments. We illustrate the predictive ability of our model by numerical simulations for small molecules with and without noise inevitable in near-term quantum computers. The results show that our scheme well reproduces the first and second excitation energies as well as the transition dipole moment between the ground states and excited states only from the ground state as an input. We expect our contribution will enhance the applications of quantum computers in the study of quantum chemistry and quantum materials.
1. Introduction

The rapid growth of the machine learning technology in the last decade has revealed its potential to be utilized in various engineering fields such as image recognition, natural language processing, and outlier detection [1, 2]. Its applications to scientific fields have also attracted numerous attentions recently as well as those to engineering. One of the most active research areas is physical science [3], especially studies of quantum many-body systems including condensed matter physics and quantum chemistry. For example, one can classify a phase of matter from its wavefunction [4, 5] or predict the atomization energy of molecules [6, 7, 8] from their molecular structures with sophisticated machine learning techniques.

Most of those researches employ classical machine learning, with which classical data are processed by classical algorithms and computers. On the other hand, machine learning algorithms on a quantum processor have been developed since the invention of Harrow-Hassidim-Lloyd (HHL) algorithm, and they are dubbed as “quantum machine learning” [9, 10, 11, 12, 13, 14, 15, 16]. In the last few years, there has been surging interest in quantum machine learning leveraging the variational method [17, 18, 19, 20, 21, 22] because a primitive type of quantum computers is about to be realized in the near future, and such machines may have the potentials to outperform classical computers [23, 24]. Those near-term quantum computers are called noisy intermediate-scale quantum (NISQ) devices [25] and consist of hundreds to thousands of physical, non-fault-tolerant qubits.

So far, quantum machine learning has been mostly applied to classical computing tasks with classical data such as pattern recognition of images [18, 19, 22]. In those studies, the classical data must be encoded in quantum states to be processed by quantum computers, but the encoding is generally inefficient unless the data have some special structure [26, 27, 28].

Therefore, it is natural to think of performing tasks with quantum nature. In this study, we consider the following task: predicting excited-state properties of a given molecular system from its ground state wavefunction. Specifically, we are interested in the Hamiltonian for the electronic states of molecules. The question we raise and want to solve leveraging quantum machine learning is whether it is possible to predict properties of the excited states from the ground state wavefunction $|\psi_0\rangle$. According to the celebrated Hohenberg-Kohn theorem [29], one can determine an external potential for electrons and thereby the whole original electron Hamiltonian from its ground state electron density $\rho_0(r) = \langle \psi_0|\hat{r}|\psi_0\rangle$ up to constant, where $\hat{r}$ is the position operator. Hence, it should be also possible to predict the excited states from the ground state in principle.

The task we propose here has various practical and conceptual attractions from the viewpoint of quantum machine learning and the studies of quantum many-body systems. First, practically, computing excited states of a given Hamiltonian needs significantly larger computational cost and is more difficult than computing the ground state [30, 31].
Since the excited-state properties are essential for thermodynamics of the system and non-equilibrium dynamics such as chemical reactions, a large benefit to the studies of quantum chemistry and quantum materials is expected if one may predict the excited states only from the ground state. We note that applying classical machine learning to predict excited states of molecules from classical data (molecular structure, coulomb matrix, etc.) has been widely explored in the literature [32, 33, 34, 35, 36]. Second, the problem of encoding data to quantum computers mentioned above can be circumvented in this setup; as we will see later, it is possible to input wavefunctions into quantum registers directly from outputs of another quantum algorithm which yields a ground state wavefunction, such as the variational quantum eigensolver (VQE), which is one of the most promising applications of the NISQ devices [37]. Third, from a conceptual point of view, the original “data” of quantum systems are wavefunctions, which are quantum in nature, so quantum machine learning dealing with quantum data as they are will take advantage of the whole information contained in the wavefunctions and potentially has stronger predictability than the classical counterparts which process only classical features of quantum data in a pure classical way [38, 39].

In this study, we propose a simple quantum machine learning scheme to predict the excited-state properties of the Hamiltonian of a given molecule from its ground state wavefunction. Our simulations demonstrate the potential that one can implement our model in the real NISQ devices being robust to the inevitable noise of outputs on such devices. In particular, we employ and generalize the quantum reservoir computing [40] and quantum reservoir processing [41] techniques. We first mix the input wavefunctions with a quantum reservoir, or the time evolution of some random Hamiltonian, and measure the expectation values of simple one-qubit operators afterwards. The measurement results are post-processed by a classical machine learning unit, and we train only the classical unit to predict the target properties of the system by supervised learning so that the overall number of runs of quantum computers is small. In the Heisenberg picture, the quantum reservoir effectively transforms the one-qubit operators into complicated multi-qubit ones which contain essential information of the system, and the classical machine learning will decode them appropriately. We numerically demonstrate the predictive power of our scheme by taking three small molecules as examples. Our model can predict the excitation energies and the transition dipole moment between the ground state and the excited state properly only from the ground state wavefunction.

The rest of the paper is organized as follows. In Sec. 2, we explain our setup in detail and propose a model for quantum machine learning of excited states, besides presenting the way to train the model. In Sec. 3, we show the result of numerical simulations of our scheme predicting the excited-state properties of small molecules as examples. Section 4 is dedicated for the discussion of our result. We conclude the study in Sec. 5.
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2. Method

In this section, we propose a model for quantum machine learning and explain its training process. The schematic diagram of our model is described in Figure 1.

2.1. Model description

Let us consider an $N$-qubit system and a wavefunction $|\psi\rangle \in \mathbb{C}^{2^N}$ on it. Our learning model proceeds as follows. First, an input $N$-qubit state $|\psi\rangle$, which is assumed to be the ground state of a given Hamiltonian here, is prepared on a quantum computer and fed into a quantum circuit which is denoted as $U_{\text{ent}}$ in Figure 1. We call this circuit a quantum entangler or a quantum reservoir for its role of mixing quantum information of the input state $|\psi\rangle$ and encoding it to the output state $U_{\text{ent}}|\psi\rangle$. $U_{\text{ent}}$ is chosen to create enough entanglement in the wavefunction and fixed for each learning task (or an experiment). The details of $U_{\text{ent}}$ are not so important for the quality of learning as illustrated by an exactly-solvable model in Sec. 4, so one can use a quantum circuit easy to be realized on real quantum devices. After applying $U_{\text{ent}}$, we measure the expectation values of local Pauli operators $\{X_0, Y_0, Z_0, \ldots, X_{N-1}, Y_{N-1}, Z_{N-1}\}$, where $X_i, Y_i,$ and $Z_i$ represent a Pauli $X, Y, Z$ operator acting on the site $i$, respectively. Although the total number of operators is $3N$, we can measure the operators $X_0, \ldots, X_{N-1}$ simultaneously.
since they commute with each other, so can we for the cases of \( Y_0, \ldots, Y_{N-1} \) and \( Z_0, \ldots, Z_{N-1} \). Hence, one can measure all operators with only three different circuits, i.e., the number of shots of the measurement does not scale with the number of qubit \( N \). After the measurements, we obtain a \( 3N \)-dimensional real-valued classical vector:

\[
\mathbf{x}_{|\psi\rangle} = (\langle X_0 \rangle, \ldots, \langle Z_{N-1} \rangle)^T = \left( \langle \psi| U_{\text{ent}} X_0 U_{\text{ent}} |\psi\rangle, \ldots, \langle \psi| U_{\text{ent}} Z_{N-1} U_{\text{ent}} |\psi\rangle \right)^T.
\]  

Finally, the classical data \( \mathbf{x}_{|\psi\rangle} \) is fed into a classical machine learning unit with learnable parameters \( W \), such as a linear regression model or a neural network, and the prediction \( f_W(\mathbf{x}_{|\psi\rangle}) \) is obtained.

We have several comments in order. First, the process to obtain \( \mathbf{x}_{|\psi\rangle} \) from \(|\psi\rangle\) can be viewed as compressing the data of \( 2^N \)-dimensional complex-valued vector \(|\psi\rangle\) into \( 3N \)-dimensional real-valued data. Although the way of compression is quite complicated due to the entangler \( U_{\text{ent}} \), the classical machine learning unit can decode the information in \( \mathbf{x}_{|\psi\rangle} \) and use it to predict the properties of the excited states of the Hamiltonian. Second, the model is identical to quantum reservoir computing proposed in Ref. [40] and quantum reservoir processing proposed in Ref. [41] if we choose the linear regression as the classical machine learning unit in the model. One may also consider using general classical models such as the neural network, the Gaussian process regression, etc. Even though the numerical simulations we carried out in this study leverage only a linear model, which actually gives sufficiently accurate predictions at least for the molecules we consider here, nonlinearity in the classical machine learning unit may be necessary to predict the excited states for certain tasks as discussed in Sec 4 using an exactly-solvable toy model for the hydrogen molecule. Third, as mentioned in the previous section, we stress that this scheme is very suitable to be combined with the VQE. The VQE finds a quantum circuit that produces an approximate ground state of a given Hamiltonian by using the variational principle and has been extended to obtain the excited states recently [42, 43, 44, 45, 46, 47, 48, 49]. Since it can handle Hamiltonians of large systems that are intractable by classical computers, the VQE is considered as one of the best approaches to utilize the NISQ devices for real-world problems. In our quantum machine learning model, one can use the quantum circuit obtained by the VQE to make an input state (approximate ground state wavefunction) for the training and the prediction of our model. There is no overhead cost at all to feed target data to the learning model in this case (see also Ref. [50]).

### 2.2. Supervised learning of the model

Next, we explain the procedure for supervised learning of our model. First, we define the training set \( \mathcal{R} \) whose elements \( r \in \mathcal{R} \) are a set of characteristics of a molecule (e.g., name of a molecule and its atomic configuration), and we prepare the data \( \{ |\psi_0(r)\rangle, y(r) \}_{r \in \mathcal{R}} \) for training. In the case of predicting excited states of a given Hamiltonian from its ground state, \(|\psi_0(r)\rangle\) is the ground state of the molecular Hamiltonian \( H(r) \) and \( y(r) \) contains the target properties of the excited states of \( H(r) \), such as excitation energies.
Next, by using the training set, the classical machine learning unit $f_W$ is trained to predict $\{y(r)\}_{r \in \mathbb{R}}$ from the classical vectors $\{x_{\psi_0(r)}\}_{r \in \mathbb{R}}$ which are calculated in the way described in the previous subsection. A typical training algorithm for the supervised learning is to minimize a cost function defined to measure the deviations of the prediction $\{f_W(x_{\psi_0(r)})\}_{r \in \mathbb{R}}$ from the training data $\{y(r)\}_{r \in \mathbb{R}}$ by tuning $W$.

We note that our model is easier to be trained and less costly in terms of the number of runs of quantum computers compared with the so-called “quantum circuit learning” where parameters of the quantum circuit are optimized [20, 21, 18, 19] since once the classical representation of the quantum state $\{x_{\psi_0(r)}\}_{r \in \mathbb{R}}$ is obtained, there is no need to run the quantum device afterwards for training the model.

3. Numerical demonstration for small molecules

In this section, we numerically demonstrate the ability of our model to reproduce excited-state properties from the ground state wavefunctions by taking small molecules as examples. We consider three types of molecules: LiH molecule, $H_4$ molecule whose hydrogen atoms are aligned linearly with equal spacing, and $H_4$ molecules whose hydrogen atoms are placed in a rectangle shape. We call them as LiH, $H_4$ (line), $H_4$ (rectangle), respectively. We evaluate our model in two situations, in one of which ideal outputs of the quantum circuits are available (noiseless), and inevitable noise in the real NISQ devices is considered in the other (noisy). The electronic ground states of those molecules with various atomic geometries are prepared by diagonalizing the Hamiltonian for the noiseless simulation and by numerically simulating the VQE for the noisy simulation. Then, we train our model with the linear regression as its classical machine learning unit to predict the first and second excitation energies and the transition dipole moment among them whose values are obtained by exactly solving the Hamiltonian. Numerical results show that our model can properly reproduce the excited states and illustrate the predictive power of our model.

3.1. Dataset

To prepare a dataset for the simulations, we consider the electronic Hamiltonians of the following configurations. For LiH molecule and $H_4$ (line), the atomic distances are in the range of $[0.5\text{Å}, 3.3\text{Å}]$. For $H_4$ (rectangle), we choose the two spacing of atoms (lengths of two edges) in $[0.5\text{Å}, 2.0\text{Å}] \times [0.5\text{Å}, 2.0\text{Å}]$. We perform the standard Hartree-Fock calculation by employing the STO-3G minimal basis and construct the fermionic second-quantized Hamiltonian for all of the molecules and configurations [51, 52] with open-source libraries PySCF [53] and OpenFermion [54]. Two Hartree-Fock orbitals with the highest and the second-highest energies of LiH molecule are removed by assuming they are vacant. Then the Hamiltonian is mapped to the sum of the Pauli operators by the Jordan-Wigner transformation [55] which we denote $H(r)$. Then, the electric Hamiltonians for all of the molecules turn into 8-qubit Hamiltonians.
The training and test datasets for the simulations are prepared for each Hamiltonian \( H(r) \) in the following way. First, in the case of the noiseless simulation, the ground state of \( H(r) \) is prepared by the exact diagonalization. In the case of the noisy simulation, the VQE algorithm is applied to \( H(r) \), and the approximate ground state is obtained as \( |\tilde{\psi}_0(r)\rangle = U(\tilde{\theta}) |0\rangle \). Here \( U(\tilde{\theta}) \) is a variational quantum circuit (ansatz) with classical parameters \( \tilde{\theta} \) and \( |0\rangle \) is a reference state. We adapt the unitary coupled-cluster singles and doubles ansatz [56] as \( U(\tilde{\theta}) \). Next, we compute the quantities of the excited-state properties to be predicted,

\[
y(r) = (\Delta E_1(r), \Delta E_2(r), \|\mu_{eg}(r)\|)^T,
\]

where \( \Delta E_{1(2)}(r) = E_{1(2)}(r) - E_0(r) \) is the first (second) excitation energy of \( H(r) \) in the sector of neutral charge, where \( E_{0,1,2}(r) \) are three lowest eigenenergies of \( H(r) \) in the same sector ignoring degeneracy. For our choice of the molecules and configurations, \( E_0(r) \) is the energy of the spin-singlet ground state \( S_0 \), and \( E_1(r) \) is the energy of the spin-triplet excited state \( T_1 \). \( E_2(r) \) is the energy of the spin-singlet excited state \( S_1 \) or the spin-triplet excited state \( T_2 \) depending on the configurations of the molecule. The transition dipole moment between the ground state and the excited state \( \mu_{eg}(r) \) is defined as

\[
\mu_{eg}(r) = \langle \psi_0(r)|\mu|\psi_{ex}(r)\rangle,
\]

where \( |\psi_0(r)\rangle \) is the exact ground state of \( H(r) \) (the singlet state \( S_0 \)), \( |\psi_{ex}(r)\rangle \) is the exact excited state of \( H(r) \) which has the lowest energy among those having a non-zero transition dipole moment from the ground state (typically \( S_1 \) state), and \( \mu = \mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z} \) is the dipole moment operator with electronic charge \( e \). In this study, we use its L2-norm \( \|\mu_{eg}(r)\| \) for the learning tasks. The calculation of each value of \( y(r) \) is performed by the exact diagonalization of \( H(r) \) for both of the noiseless and noisy simulations. We normalize those calculated values to fit them into the \([-1, 1]\) range.

In the learning process, we randomly split those obtained data \( \{|\tilde{\psi}_0(r)\rangle, y(r)\}_r \) into a training set and a test set for the evaluation of the model. We used 30 training data points and 50 test points, respectively for the tasks of LiH and \( H_4 \) (linear) molecules, and 250 training data points and 1250 test data points for \( H_4 \) (rectangle) molecules.

### 3.2. Model for the simulations

The entangler \( U_{ent} \) in the model is chosen to be the time-evolution operator \( e^{-i H_{\text{TFIM}} T} \) under the random transverse-field Ising model (TFIM),

\[
H_{\text{TFIM}} = \sum_{i,j=0}^{N-1} J_{ij} Z_i Z_j + \sum_{i=0}^{N-1} h_i X_i,
\]

where \( X_i \) and \( Z_j \) are Pauli operators acting on the site \( i,j \)-th qubit, coefficients \( h_i \) and \( J_{ij} \) are sampled from the Gaussian distributions \( N(1, 0.1) \) and \( N(0.75, 0.1) \), respectively, and we set \( T = 10 \). These coefficients are fixed during each of the numerical simulations.
This type of the entangler can be implemented on various types of the NISQ devices; for example, in the case of superconducting qubits, it can be realized by a sequence of the cross resonance gates \[57, 58\] or simply tuning the resonance frequency of the qubits \[18\]. We note that a similar kind of the quantum reservoir has recently been implemented on a real NISQ device \[59\].

For the classical machine learning unit for the numerical demonstration, we employ the linear regression (LR) \[60\]. Although the LR does not have nonlinearity which is in principle necessary to compute the excited-state properties (see Sec. 4), it performs well enough for the molecular Hamiltonians we consider for the simulations as shown in Sec. 3.4, so it serves as a nice demonstrative model to evaluate the concept of our model.

The output function of the LR is

\[
f^{(k)}(x|\psi) = w^{(k)}_{\text{out}} \cdot x|\psi\rangle,
\]

where \(w^{(k)}_{\text{out}}\) is a \(3N\)-dimensional vector, or parameters of the model, to be optimized, and \(k = 0, 1, 2\) corresponds to the component of the prediction for \(y = (y^{(0)}, y^{(1)}, y^{(2)})^T\). The model is trained to minimize the mean squared error (MSE) cost function

\[
L_{LR}(\{w^{(k)}_{\text{out}}\}) = \frac{1}{|R|} \sum_{r \in R} |w^{(k)}_{\text{out}} \cdot x_{|\psi_0(r)\rangle} - y^{(k)}(r)|^2,
\]

where \(R\) represents the training dataset, respectively for each target property. The exact optimum of the cost function can be obtained as

\[
w^{(k)\ast}_{\text{out}} = (V^T V)^{-1} V^T Y^{(k)},
\]

where \(V\) is a \(|R| \times 3N\) dimensional matrix whose \(i\)-th row is \(x_{|\psi_0(r_i)\rangle}^T\), and \(Y^{(k)}\) is a \(|R|\) dimensional column vector whose \(i\)-th component is \(y^{(k)}(r_i)\), where \(r_i\) is the \(i\)-th element of \(R\). The whole classical process requires the computational complexity of \(O(N^3 + N^2|R|)\).

### 3.3. Simulation of quantum circuits

To check the practical advantage of our model with the NISQ devices, we numerically simulate quantum circuits of the model considering the noiseless and noisy situations (including preparation of the ground state wavefunctions by the VQE for the noisy case). The latter reflects a more realistic situation of experiments on a real NISQ device, but we stress that the former still serves as a reference point to judge whether the model has the capability of performing the learning task or not.

In the noiseless simulation, the expectation value of the Pauli operator \(\langle \psi | P_i | \psi \rangle\), where the \(|\psi\rangle\) is a quantum state and \(P_i\) is the Pauli operator acting on \(i\)-th qubit, is estimated exactly by calculating the inner product. In the noisy simulation, we consider two error sources which make estimations of those expectation values deviate from the exact ones. One of them is a sequence of the depolarizing noise channels \[61\] that transform the quantum state \(\rho = U_{\text{ent}} |\psi\rangle \langle \psi| U_{\text{ent}}^\dagger\) from the reservoir into \(\rho' = \)
Table 1. The MAEs evaluated with the test set for the trained models in the noiseless situation with and without the entangler. The output values and the excited-state properties are rescaled in the $[-1,1]$ range. The MAEs for the random guess are also presented as a reference.

|                      | LiH     | H4 (line) | H4 (rectangle) |
|----------------------|---------|-----------|----------------|
| Test MAE with entangler $U_{ent}$ | 0.0181  | 0.0203    | 0.0836         |
| Test MAE without entangler $U_{ent}$ | 0.172   | 0.324     | 0.300          |
| Random Guess         | 0.673   | 0.544     | 0.444          |

$\mathcal{E}_{N-1} \circ \ldots \circ \mathcal{E}_0(\rho)$, where $\mathcal{E}_i$ is the depolarizing channel that acts on $i$-th qubit as $\mathcal{E}_i(\sigma) = (1-p)\sigma + \frac{p}{3}(X_i\sigma X_i + Y_i\sigma Y_i + Z_i\sigma Z_i)$. We take $p = 0.01$ in the simulations. The other source is the so-called shot noise that stems from the finite number of shots for the projective measurements of the Pauli operator $P_i$. Each measurement returns $\pm 1$ according to the probability distribution determined by the exact values of $\text{Tr}(\rho P_i)$. We sample $10^6$ shots of measurements for each Pauli operator, which is still a feasible number in experiments [57].

3.4. Results

The model described in the previous subsections is trained by the training dataset and evaluated by the test set. The evaluation is performed based on the mean absolute error (MAE) for the test set $\mathcal{T}$,

$$C_T = \frac{1}{3|\mathcal{T}|} \sum_{r \in \mathcal{T}} \sum_{k=0}^{2} |f_W(x_{|\psi_0(r)\rangle}) - y(r)^{(k)}|,$$

where $f_W(x)$ is the output of the model considered as a vector. We train and evaluate the model for each molecule separately.

3.4.1. Noiseless simulation

The prediction results by the trained model in the noiseless numerical simulation are shown in Figures 2 and 3. Our model obviously reproduces the exact values of the excited-state properties $y(r)$ for all of the three molecule types. Also, we investigate the necessity of the entangler $U_{ent}$ by comparing the values of the MAE for the test set (Eq. (8)) after the training. The evaluations of the learners with and without the entangler are summarized in Table 1, indicating that the entangler significantly enhances the predictive power of the model. In Sec. 4, another supporting result for the necessity of the entangler is presented by using an exactly solvable model for the hydrogen molecule.

These results from the noiseless simulations illustrate the predictive power of our model for the difficult task to predict the excited-state properties only from the ground state.
3.4.2. Noisy simulation  

In order to evaluate our scheme in a realistic situation with a quantum device, we add two noise sources to the simulation as described in Sec. 3.3. In this case, to enhance the noise robustness, we make two modifications to the noiseless case as follows. First, after obtaining the classical vectors \( \{ x_{\psi_0(r)} \} \) by processing the training dataset with the noisy quantum circuit, we make 100 copies of every vector \( x_{\psi_0(r)} \) on a classical computer, and add a gaussian noise \( N(0, 2 \times 10^{-3}) \) to each component of it. We stack these vectors, and now we have a new \( 100 |\mathcal{R}| \times 3N \) dimensional matrix \( V' \). The vector \( Y^{(k)} \) is also duplicated 100 times to match up with \( V' \) (let us call this new vector \( Y'^{(k)} \) for later use). Notice that this modification does
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Figure 3. The same figures as Figure 2 for H₄ (rectangle). x and y denote the two atomic spacings of the rectangular geometry.

not affect the required number of measurements of the quantum circuit. Second, we add the L2 regularization term into the cost function of the LR, particularly saying the cost function becomes

\[ L_{LR}'(\{w_{out}^{(k)}\}) = L_{LR}(\{w_{out}^{(k)}\}) + \alpha \|w_{out}^{(k)}\|^2, \]  

where we used \( \alpha = 10^{-3} \) in the simulations. We may obtain the exact optimum by computing

\[ w_{out}^{(k)*} = (V'TV' + \alpha I)^{-1} V'TY^{(k)}, \]  

where \( I \) is an identity matrix of \( 3N \times 3N \) dimensions. Both of these two modifications work as regularizations preventing the model from overfitting due to the outliers with large noises.

The prediction results are presented in Figures 4 and 5. We see that the model still predicts \( y(r) \) well even in this noisy case.

4. Discussion

4.1. Necessity of the entangler \( U_{ent} \) and the nonlinearity of \( f_W \)

Here we discuss the necessity of the entangler \( U_{ent} \) and the nonlinearity in the classical machine learning unit \( f_W \) by considering an exactly solvable model of fermions, namely, the 2-site fermion Hubbard model at half-filling [62].

The 2-site Hubbard model is defined as

\[ H_{Hub}(U) = - \sum_{\sigma = \uparrow, \downarrow} \left( c_{0,\sigma}^{\dagger} c_{1,\sigma} + h.c. \right) + U \sum_{i=0,1} n_{i,\uparrow} n_{i,\downarrow} \]  

where \( c_{i,\sigma}, c_{i,\sigma}^{\dagger} \) are fermionic creation and annihilation operators acting on an electron with spin \( \sigma = \uparrow, \downarrow \) located at \( i \)-th site (\( i = 0, 1 \)), and \( n_{i,\sigma} = c_{i,\sigma}^{\dagger} c_{i,\sigma} \) is the number operator of an electron with spin \( \sigma \) at \( i \)-th site. The parameter \( U > 0 \) determines the strength of electron repulsion. This system can be considered as a simplified model of a hydrogen molecule whereas it also serves as a prototype of strongly-correlated materials. When
we restrict ourselves into the sector where the number of electrons is two, i.e. the neutral hydrogen states, the first, second excitation energies and the transition dipole moment.
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Figure 5. The same figures as Figure 4 for $H_4$ (rectangle). $x$ and $y$ denote two atomic spacings of the rectangular geometry.

are

$$\Delta E_1 = \frac{U}{2} \left( -1 + \sqrt{1 + \frac{16}{U^2}} \right),$$  \hspace{1cm} (12)$$

$$\Delta E_2 = \frac{U}{2} \left( 1 + \sqrt{1 + \frac{16}{U^2}} \right),$$  \hspace{1cm} (13)$$

$$\|\mu_{eg}\| = \sqrt{\frac{1 - (1 + 16/U^2)^{-1/2}}{2}},$$  \hspace{1cm} (14)$$

respectively. We note that the dipole moment operator is defined as $\mu = \frac{1}{2}(n_{1,\uparrow} + n_{1,\downarrow} - n_{0,\uparrow} - n_{0,\downarrow})$.

Applying the Jordan-Wigner transformation [55] to the system (11), we obtain the 4-qubit Hamiltonian $H_{\text{qubit}}(U)$. We denote the ground state of $H_{\text{qubit}}(U)$ as $|\psi_0(U)\rangle$. When there is no entangler, the classical vector $x_{|\psi_0(U)\rangle}$ is trivial because

$$\langle X_j \rangle_{\text{GS}} = \langle Y_j \rangle_{\text{GS}} = \langle Z_j \rangle_{\text{GS}} = 0$$  \hspace{1cm} (15)$$

holds for all qubit sites $j = 0, 1, 2, 3$, where we define $\langle \ldots \rangle_{\text{GS}} = \langle \psi_0(U) | \ldots | \psi_0(U) \rangle$.

In contrast, when there is an entangler $U_{\text{ent}}$ in our model, it converts the Pauli operators $X_j, Y_j, Z_j$ into a sum of more complicated Pauli strings as $U_{\text{ent}}^\dagger Z_0 U_{\text{ent}} = Z_0 Z_1 + 0.2 Z_1 X_1 Z_2 Y_2 + \ldots$ in the Heisenberg picture. Then, the classical vector $x_{|\psi_0(U)\rangle}$ contains contributions from the terms like $\langle Z_0 Z_1 \rangle_{\text{GS}}$. It follows that

$$\langle Z_0 Z_1 \rangle_{\text{GS}} = - \left( 1 + \frac{16}{U^2} \right)^{-1/2},$$  \hspace{1cm} (16)$$
\[ \Delta E_1 = \frac{2(1 + \langle Z_0 Z_1 \rangle_{GS})}{\sqrt{1 - \langle Z_0 Z_1 \rangle_{GS}^2}}, \]  
\[ \Delta E_2 = \frac{2(1 - \langle Z_0 Z_1 \rangle_{GS})}{\sqrt{1 - \langle Z_0 Z_1 \rangle_{GS}^2}}, \]  
\[ \|\mu_{eg}\| = \sqrt{\frac{1 + \langle Z_0 Z_1 \rangle_{GS}}{2}}. \]  

These equations indicate that the excitation energies can be predicted by utilizing the values of \( \langle Z_0 Z_1 \rangle_{GS} \) appropriately. Therefore, one can see that it is possible to predict the excitation energies from the classical vector \( x_{|\psi_0(U)\rangle} \) if the ground state vector is processed by an entangler, and the classical machine learning unit \( f_W \) has enough nonlinearity. These equations also imply that the details of the entangler, which determine coefficients of the terms like \( \langle Z_0 Z_1 \rangle_{GS} \) in \( x_{|\psi_0(U)\rangle} \), is not so important for predictions; the classical machine learning unit can compensate the difference of such coefficients. In Appendix, we provide further analysis of the 2-site Hubbard model including the necessity of nonlinearity.

4.2. Generalizability

In the numerical simulations in Sec. 3, the models are trained and evaluated for each molecule separately. The generalizability of our model to predict the properties of various molecules simultaneously is one possibility of our model for future extensions.

To make our model more powerful and capable of taking various molecules as inputs, several modifications can be considered. First, including the ground state energy which can also be calculated by the VQE besides the ground state in the input of the classical machine learning unit \( f_W \) will be necessary since otherwise, one may not determine the energy scale of an input molecule. Second, replacing the entangler \( U_{\text{ent}} \) with a parametrized quantum circuit \( V(\theta) \) and optimizing the circuit parameters \( \theta \) along with the classical machine learning unit increase the degree of freedoms of the model and may result in a better predictive power, with a possible drawback that the number of required experiments on the NISQ devices would increase in the training step. Exploring these ideas is an interesting future direction of the work.

5. Conclusion

In this study, we introduce a new quantum machine learning framework for predicting the excited-state properties of a molecule from its ground state wavefunction. By employing the quantum reservoir and choosing simple one-qubit observables for measurements accompanied by post-processing with classical machine learning, one may process our framework easily on the NISQ devices requiring the realistic number of runs of them. The numerical simulations with and without the noise in outputs of quantum
circuits demonstrate that our model accurately predicts the excited states. Although our framework is tested only with small molecules to illustrate its potential in the numerical simulations, we expect that it will benefit the calculation of excited states of larger molecules by reducing the computational cost from calculating exact solutions. Our result opens up the further possibility to utilize the NISQ devices in the study of quantum chemistry and quantum material fields.

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Appendix: Nonlinearity of excited-state properies

In this Appendix, we present further analysis of the 2-site Hubbard model discussed in Sec. 4. The exact expressions of the excited-state properties of the Hubbard model in terms of the elements of the classical vector $\mathbf{x}_{|\psi_0(r)\rangle}$ present specific examples demonstrating that they may and may not be approximated with a linear model, given the classical vector.

There are $4^4 = 256$ Pauli operators (from $I_0I_1I_2I_3$ to $Z_0Z_1Z_2Z_3$) which may act on the Hilbert space for the 2-site Hubbard model (11). Exhaustive search for all of these Pauli operators reveals that only two functions of $U$ appear as the ground state expectation values:

\[
 f_1(U) := \frac{1}{\sqrt{1 + \frac{16}{U^2}}} = -\langle Z_0Z_1 \rangle_{GS} = \langle Z_0Z_3 \rangle_{GS} = \langle Z_1Z_2 \rangle_{GS} = -\langle Z_2Z_3 \rangle_{GS} \tag{20}
\]

\[
 f_2(U) := \frac{1}{\sqrt{1 + \frac{U^2}{16}}} = \langle X_0X_1X_2X_3 \rangle_{GS} = \langle Y_0Z_1Y_2 \rangle_{GS} = \langle X_1Z_2X_3 \rangle_{GS} = \langle Y_1Z_2Y_3 \rangle_{GS} \tag{21}
\]

In other words, for any choice of the entangler $U_{ent}$, all components of the classical vector $\mathbf{x}_{|\psi_0(U)\rangle}$ = \left( \langle \psi_0(U)|U_{ent}^\dagger X_0U_{ent}|\psi_0(U)\rangle, \cdots, \langle \psi_0(U)|U_{ent}^\dagger Z_{N-1}U_{ent}|\psi_0(U)\rangle \right)^T will be written as a linear combination of $f_1(U)$ and $f_2(U)$.

Now, we can see that the nonlinearity in the classical unit is not necessary for a small value of $U$, but it is for a large $U$. For $0 < U \ll 1$, $f_1(U) \approx U/4$ and $f_2(U) \approx 1$, and the excited-state properties in terms of these functions are

\[
 \Delta E_1 \approx 2 - \frac{U}{2}, \quad \Delta E_2 \approx 2 + \frac{U}{2}, \quad \|\mathbf{\mu}_{eg}\| \approx \frac{1}{\sqrt{2}} - \frac{U}{8\sqrt{2}}. \tag{24}
\]
ignoring $O(U^2)$ terms. In this case, the excited-state properties can be expressed easily as the linear combination of $f_1(U)$ and $f_2(U)$. On the other hand, when $U$ is large, i.e. when $0 < 1/U \ll 1$, it follows that $f_1(U) \approx 1$ and $f_2(U) \approx 4/U$, and the excited state properties can be expressed as

$$\Delta E_1 \approx \frac{4}{U}, \quad \Delta E_2 \approx U, \quad \|\mu_{eg}\| \approx \frac{2}{U},$$

ignoring $O(1/U^2)$ terms. $\Delta E_2$ may not be expressed as a linear combination of $f_1$ and $f_2$.

To support the observation, we also perform a numerical simulation for the 2-site Hubbard model. We randomly sample 30 distinct values of $U$ for the training data and 50 distinct values of it for the test data in the range of $U \in [0.1, 6]$ (Case 1) and $U \in [0.1, 20]$ (Case 2). The ground state wavefunction of $H_{\text{Hub}}(U)$ is prepared by the exact diagonalization. Instead of using an entangler, here we define the classical vector $x_{\psi_0(U)}$ as $(\langle Z_0 Z_1 \rangle_{\text{GS}}, \langle X_0 Z_1 X_2 \rangle_{\text{GS}})^T$. The linear regression to learn the excited state properties $y = (\Delta E_1, \Delta E_2, \|\mu_{eg}\|)^T$ from $x_{\psi_0(U)}$ is performed both for Case 1 and Case 2. All values of $x_{\psi_0(U)}$ and $y$ are standardized by using the mean and the standard deviation of the training dataset respectively during the training process of the LR. The results are shown in Figure 6. The LR predicts the excites state properties almost perfectly for small values of $U$ as one may see in the results for Case 1, whereas it fails once one tries to learn and predict from the data with large $U$ values as shown in the results for Case 2, especially evident from the prediction of $\Delta E_2$. Those results support our expectation that a linear classical unit can sufficiently approximate the excited state properties in the case of small $U$, but it may not for a large $U$. We consider a similar mechanism applies to the numerical simulations of small molecules in Sec. 3, where atomic-spacings are not very small so that the Coulomb repulsion $U$ is not large.

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Figure 6. The prediction results by the trained model for the 2-site Hubbard model (11) with two datasets sampled from (Case 1) $U \in [0.1, 6]$ (left column) and (Case 2) $U \in [0.1, 20]$ (right column). Top, middle, and bottom panels display the first, second excitation energies and the transition amplitude, respectively. The blue circles indicate the training data points and the red crosses do the predictions. The exact values are displayed as the black line.
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