Quantum Zeno approach with maximum stabilizer Hamiltonians for molecular energies

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We consider the adiabatic and the simulated-annealing framework for the quantum chemistry of small molecules. The initial Hamiltonian is taken to be the maximum stabilizer Hamiltonian constructed from the final Hamiltonian for molecules in the Pauli basis. We compare two variants, with the second variant being the main contribution of this work. The first method is simply to use the adiabatic evolution on the obtained time- or path-dependent Hamiltonian with the initial state as the ground state of the maximum stabilizer Hamiltonian. However, this does suffer from the usual problems of adiabatic quantum computation due to the degeneracy and energy-level crossing in the path-dependent Hamiltonian. This problem is solved by a Zeno method, i.e., via the eigenstate projection used in the quantum simulated annealing, with the path-dependent Hamiltonian augmented by the sum of Pauli $X$ terms whose contribution vanishes at the beginning and the end. In addition to the ground state, the low lying excited states can also be obtained using this quantum Zeno approach by varying initial states, whose accuracy is independent of the ground state.

I. INTRODUCTION

Quantum chemistry concerns the application of quantum mechanics to chemical properties of molecules, including their electronic structure, spectroscopy, and dynamics\textsuperscript{1,2}. Its impact goes beyond chemistry itself, ranging from material design to drug development. Many classical approaches have been developed and employed, such as the ab initio, density functional, molecular dynamics, Monte Carlo, and DMRG methods\textsuperscript{3–7}. The computational complexity scales substantially with the number of orbitals and electrons and has thus limited the real-life application to small molecules.

Recently it was suggested that quantum chemistry problem is one of the promising applications that quantum computation\textsuperscript{8} may be used to outperform classical algorithms. Among the earliest proposals, Lidar and Wang considered the use of quantum computing for calculating the thermal rate constant\textsuperscript{9}. Apsuru-Guzik et al. proposed to apply quantum computing to molecular energies\textsuperscript{10}, which was later implemented with a photonic system by Lanyon et al. for the hydrogen molecule\textsuperscript{11}, as well as with a liquid NMR system using an adiabatic state preparation\textsuperscript{12}. These prompted a surge of interest and subsequent works on quantum chemistry via quantum computers. The variational quantum eigensolver (VQE) was later proposed and implemented in the photonic system\textsuperscript{13}, which is suitable for noisy intermediate scale quantum processors. The performance of the VQE was later compared to that of the Quantum Phase Estimation in a study\textsuperscript{14} and the former was shown to be a better approach for ground states of molecules. The VQE has since become the standard approach for quantum chemistry\textsuperscript{15}, and extension such as excited states\textsuperscript{16,17} and an adaptive version\textsuperscript{18} have also been made.

Here, we present a study of an adiabatic framework that can be used to obtain eigenstates of small molecules in two different ways. Both variants are based on a path-dependent Hamiltonian as used in the adiabatic quantum computation\textsuperscript{19}, which, in particular, takes the initial Hamiltonian to be the one obtained from the maximum stabilizer method, i.e., it consists of a maximal set of commuting Pauli terms, to be described below. The first variant, which we will refer to as the maximum-stabilizer adiabatic approach (MSA), is the usual adiabatic quantum computation with such maximum stabilizer Hamiltonian as the initial Hamiltonian. The MSA method yields good results of molecular ground-state energy around the equilibrium position or shorter molecular distances, but not at larger distances, which is due to degeneracy and energy-level crossing. These problems arise because at large molecular separation, there are many closely spaced levels and possibly degeneracy. In an attempt to ameliorate these issues in obtaining the ground state, we add to the Hamiltonian a possible degeneracy breaking term whose strength is proportional to $(1-t/T)t/T$, so that its contribution vanishes at the initial and final times\textsuperscript{20}. Even though the resultant path-dependent Hamiltonian does not necessarily yield better results under the adiabatic evolution, its use in the setting of the quantum simulated annealing\textsuperscript{21} does improve the obtained ground-state energy. This second variant, which we will refer to as the maximum-stabilizer projection method (MSP), with the augmented path-dependent Hamiltonian, can mitigate the drawbacks of the adiabatic evolution by driving the computation via the Zeno-like projection to eigenstates of the instantaneous Hamiltonian along the path at discretized time steps\textsuperscript{21,22}. By starting with the initial states to be the ground state or lowest few excited states of the maximum stabilizer Hamiltonian, the ground state and the
lowest few excited states of the final Hamiltonian can be obtained for several small molecules that we consider, including LiH, BeH₂, CH₂, and H₂O. We also compare our results with those from the VQE. Our numerical simulations show that the MSP method performs the best among the three methods.

The paper is organized as follows: in Sec. II we introduce the concept of the Maximum Stabilizer and numerically show that a greedy algorithm can efficiently well approximate Maximum Stabilizer. In Sec. III we use the adiabatic quantum computation (AQC) to drive the system to the ground state of molecules and numerically show that it works well in most cases. In Sec. IV we propose to use a spectral projection method for improving the results of the AQC with the path-dependent Hamiltonian augmented by a Pauli X term. This also allows us to obtain the excited states without further complexity. In Sec. V we discuss an alternative way to construct the path-dependent Hamiltonian, using the Hartree-Fock Hamiltonian as the initial Hamiltonian. In Sec. VI we make some concluding remarks.

II. MAXIMUM STABILIZER AND GREEDY APPROXIMATION

The coefficients in the Hamiltonians for the molecules, LiH, BeH₂, H₂O, and CH₂ that we consider in this work are computed in the Slater-type orbital (STO)-3G basis (see e.g. [2]). We shall set the X axis as the inter-atomic axis for the LiH, BeH₂, (see e.g. [1]). We shall set the X axis as the inter-atomic axis for the LiH, BeH₂, CH₂, and H₂O between A and B type atoms (or the angle of H-O-H and other molecules) and only consider the orbitals 1s for each H atom, 1s, 2s, and 2pₓ for the Li atom, and orbitals 1s, 2s, 2pₓ, 2pᵧ, and 2p₂ for Be, C and O atoms. We assume that the 2pᵧ and 2p₂ orbitals do not interact with the orbitals in LiH, so these orbitals are excluded in Hamiltionians for LiH, but they are included in BeH₂, CH₂, and H₂O. (It is also possible ignore them in BeH₂.) Our goal is to find the eigenstates and eigenenergies of a molecule’s Hamiltonian, including the ground state |ψ⟩ with

\[ H |ψ⟩ = E_G |ψ⟩ , \]

and a few low lying states. In the spin-orbital language, the Hamiltonian can be written in the second quantization form

\[ H = H_1 + H_2 = \sum_{\alpha,\beta} t_{\alpha\beta} a_\alpha^\dagger a_\beta + \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} u_{\alpha\beta\gamma\delta} a_\alpha^\dagger a_\gamma^\dagger a_\delta a_\beta , \]

where the coefficients in the one-body and two-body terms are given below, respectively,

\[ t_{\alpha\beta} = \int dx_1 \Psi_\alpha(x_1) - \frac{\nabla^2}{2} + \sum_i Z_i \right| \Psi_\beta(x_1) \]

\[ u_{\alpha\beta\gamma\delta} = \int dx_1 dx_2 \Psi_\alpha^*(x_1) \Psi_\beta(x_1) \frac{1}{|\Psi_{12}|} \Psi_\gamma^*(x_2) \Psi_\delta(x_2) . \]

These coefficients are calculated using the standard quantum chemistry package, such as PySCF [24], which is a collection of electronic structure programs powered by Python. We also assume that all 1s orbitals of Li, Be, C, and O atoms are filled. With such assumptions some of the one-body integrals will become constant and only brings a shift to the total energy and some two-body integrals reduce to one-body terms.

A. Maximum Stabilizer

As the quantum computers use qubits or equivalently spin-1/2 entities as the building blocks for computation, we needs to convert the above fermionic Hamiltonian to one composed of qubits. There have been a few methods or transformations, including the Jordan-Wigner, par-ity, Bravyi-Kitaev, superfast Bravyi-Kitaev transformation [25, 26]. By using any of these methods, we can transform the fermion operators into Pauli operators,

\[ H = \sum_i h_i P_i \]

where Pᵢ’s are n–qubit Pauli operators. For the conversion below, we use the ‘parity’ method. The VQE aims at approximating its ground state by a quantum simulator with certain kinds of ansatz wave function via quantum circuits and a classical optimizer to search for optimal parameters in the ansatz that minimize the energy expectation [13, 15]. The quality of the VQE results depends on the variational ansatz used and the convergence depends also on the classical optimizer.

Here, we will focus on the adiabatic-based framework and first introduce a special initial Hamiltonian called the Maximum Stabilizer (MS). It will be demonstrated below that the ground state can be found in the adiabatic approach by connecting this initial MS Hamiltonian to the final Hamiltonian of the molecule.

First, we define the stabilizer S as a set of Pauli product operators that commute with each other,

\[ S = \{ P_1, P_2, ..., P_k \mid \forall i, j \in \{1, ..., k\}, [P_i, P_j] = 0 \} . \]

A maximum stabilizer is such a stabilizer operator set S that maximizes the weight

\[ h(S) = \sum_{i, P_i \in S} |h_i| \]

among all possible stabilizers. Here we present a simple example to illustrate the picture of the Maximum Stabilizer. For a Hamiltonian consists of Pauli operators,

\[ H = 2II + 3IX - 4IZ + 5ZI , \]

we assign every Pauli operator Pᵢ in H to a vertex, and associate with it a weight |hᵢ| and every pair of two commuting Pauli operators to an edge. The Hamiltonian is thus represented by a weighted graph, as illustrated in
the same molecule, the set of Pauli terms differ by only coefficients even as the molecular distance varies, so once we find an instance of the MS set at a particular distance, we can use it for other distances. In our experience, those terms in the MS set are of the form of product of Pauli Z and identity operators, such as $I \otimes \sigma^z \otimes \sigma^z \otimes \cdots$. In general, one can re-compute this MS set for each molecular distance as we will do below.

III. ADIABATIC APPROACH

A. Adiabatic evolution

To drive the system from the Maximum stabilizer to the desired Hamiltonian, a natural way is to use the idea of adiabatic evolution [19]. For the maximum stabilizer $S$, we take the partial Hamiltonian $H_i$ as the initial Hamiltonian

$$H_i = \sum_{i,p \in S} h_i P_i$$

whose ground state is easy to find, and take the target Hamiltonian $H_p$ as the problem Hamiltonian.

$$H_p = \sum_{i} h_i P_i$$

Naively, we can set the initial state $|\psi(0)\rangle$ to the ground state of $H_i$ and let the system evolves according to the Hamiltonian

$$H(t) = (1 - \frac{t}{T})H_i + \frac{t}{T}H_p = \sum_{i,p \in S} h_i P_i + \frac{t}{T} \sum_{i,p \notin S} h_i P_i.$$  

(10)

According to the adiabatic theorem [27], if the system evolves slowly enough, i.e. $T$ is large enough, then the evolving state $|\psi(t)\rangle$ will stay at the ground state of $H(t)$. Roughly speaking, $T$ should scale inversely proportional to the inverse of the minimal gap along the path. In such a large $T$ limit, when the system evolves form $t = 0$ to $t = T$, we will, up to a small error, arrive at our desired state—the ground state of $H_p$. We call this procedure the Maximum Stabilizer Adiabatic algorithm (MSA). If the first term of $H(t)$ includes large coefficients, which is true in most cases we consider, the second term in Eq. (10) can be regarded as a perturbation. In principle the minimum energy gap $\Delta$ (see e.g. Fig. 2) between the ground state and first excited state of the path-dependent Hamiltonian determines the evolution time $T$ (which is roughly $1/\Delta^2$) in order to achieve adiabaticity.

B. Ground state energy results

We apply our MSA approach to four different molecules LiH, BeH$_2$, H$_2$O, and present the results in
FIG. 2: The lowest few energy levels of $H_\alpha(s = t/T)$ of Eq. (12), which reduces to $H(s = t/T) = (1 - s) H_i + s H_p$ of Eq. (10) when $\alpha = 0$, for (a) $\text{H}_2\text{O}$ at the equilibrium position $d = 0.958\,\text{Å}$ between the O and an H atom with $\alpha = 0$, (b) $\text{H}_2\text{O}$ at equilibrium position $d = 0.958\,\text{Å}$ with $\alpha = 1$, (c) $\text{H}_2\text{O}$ at a position $d = 1.958\,\text{Å}$ with $\alpha = 0$, (d) $\text{H}_2\text{O}$ at a position $d = 1.958\,\text{Å}$ with $\alpha = 1$.

Figs. 3, 4, 5, and 6. In these simulations we set $T = 10$ and use discrete-time slices to approximate the continuous time evolution,

$$|\psi(T)\rangle \approx e^{-iH(T)\Delta T} e^{-iH(T-\Delta T)\Delta T} \cdots e^{-iH(\Delta T)\Delta T} |\psi(0)\rangle.$$  

(11)

We choose a constant increment $\Delta T = 0.5$ in the simulations, as we do not and cannot rely on the knowledge of the gap, which may close (e.g. see Fig. 2). Our results from this MSA method are compared to those from the VQE with the UCCSD variational form and the COBYLA optimizer, which begins with the Hartree-Fock state and runs with iteration steps up to 200 for short molecular distances and 1000 for large molecular distances in order to optimize the variational parameters used in the circuit. The exact solutions we compare to are obtained from directly diagonalizing the qubit Hamiltonian in Eq. (9).

1. LiH molecule

For LiH, the results of the adiabatic approach are slightly worse than those of the VQE, as seen in Fig. 3. This is mostly due to the small number in the discrete-time steps, and the accuracy can be improved using smaller $\Delta T$ and hence more segments along the Hamiltonian path, as seen in the bottom panel of Fig. 3. In this calculation, 4 qubits are needed to represent the Hamiltonian. We note that the simulation of an iterative quantum phase estimation for the ground-state energy of LiH was done in Ref. [10] and the implementation of the VQE on quantum computers was presented in Ref. [15].

2. BeH$_2$ molecule

For BeH$_2$, the results, shown in Fig. 4, are mostly better than those of the VQE, and agree very well with the exact solutions at smaller distances and around the equilibrium position but become worse at large distance, in particular greater than $d > 2.4\,\text{Å}$. It is due to the degeneracy of ground states in the initial Hamiltonian. (We note that this issue can be ameliorated by employing the projection method below.) In this calculation, 10 qubits are needed to represent the Hamiltonian. If we remove the $2p_y$ and $2p_z$ orbitals, then the number of qubits can be reduced to 6. The implementation of the six-qubit VQE on quantum computers was presented in Ref. [15].

3. CH$_2$ molecule

For CH$_2$ molecule, the results are shown in Fig. 5. In this case, the MSA performs better than the VQE. How-
FIG. 3: The ground state energy of LiH with different approaches—(a) top panel: results using $T = 20$ and $\Delta T = 0.5$, (b) bottom panel: results using $T = 40$ and $\Delta T = 0.5$. The result of MSA is slightly worse than that of the VQE because of the small size of the 4-qubit Hamiltonian, but can be improved using longer time or equivalently more segments.

FIG. 4: The ground state energy of BeH$_2$ vs. the distance $d$ between the Be and one H atoms, with different approaches at the equilibrium angle 180°. The results of last 6 points of MSA are not so good as other points due to the appearance of degeneracy in initial ground states.

ever, the MSA has the similar issue of degeneracy and level crossing at large molecular distances $d$ between C and H atoms, in particular, greater than $d \gtrsim 2.1$ Å. In this calculation, 10 qubits are needed to represent the Hamiltonian. One of the earlier results simulating the molecular energy of CH$_2$ via quantum algorithm was presented in Ref. 28 using an iterative quantum phase estimation.

FIG. 5: The ground state energy of CH$_2$ as a function of the distance $d$ between the C and an H atom at the equilibrium angle $\theta \approx 101.89^\circ$.

FIG. 6: The ground state energy of H$_2$O (a) as a function of the distance $d$ between the O and an H atom at the equilibrium angle $\theta \approx 104.45^\circ$ and (b) a function of the H-O-H angle $\theta$ at the equilibrium position $d = 0.958$ Å. The result of MSA at $d \approx 1.76$ Å is not so good because of the appearance of degeneracy in initial ground states.

4. H$_2$O molecule

For H$_2$O, the MSA approach in the rough approximation in Eq. (11) already brings reasonably accurate results for ground state energy and the ground state itself compared to those of the VQE, as shown in Fig. 6. However, there is the issue of degeneracy around $d \approx 1.76$ Å. Despite this deviation, the ground-state energy versus the angle $\theta$ at the equilibrium distance by the MSA is very accurate. In this calculation, 10 qubits are needed to
represent the Hamiltonian. We note that the simulation of an iterative quantum phase estimation for the ground-state energy of H$_2$O was presented in Ref. [10] and the first singlet excited state in Ref. [29], as well as the more recent implementation of the VQE and the equation-of-motion approach for excited states in Ref. [17].

C. Degeneracy and energy level crossing

Degeneracy and energy crossing are two main factors that AQC may fail. If the $H_i$ contains an accidental symmetry and has degenerate ground states, and we arbitrarily choose one of the states as the initial state, the outputs can be a superposition of any states connected to these initial degenerate states and thus the final state after the evolution is not necessarily an eigenstate. If there exists an energy crossing during the evolution, the state may evolve to the excited state rather than stay in the ground state. These two cases can occur in simulations for real molecules. In our simulations, the energy level crossing only occurs when the molecular distances are large, for example, in Fig. 2c. We have indeed seen that the results from the MSA match the exact results very well for smaller molecular distances, including near the equilibrium position, except for the CH$_2$ molecule.

We initially suspected that such issues might be improved by adding in Eq. (10) another term, which is of the form $H_X \equiv \sum_q \sigma^x_q$ with a strength $\alpha$ and which does not commute with Pauli Z terms (occurring in $H_i$),

$$H_\alpha(t) = \left(1 - \frac{t}{T}\right)H_i + \frac{t}{T}H_p + \alpha \left(1 - \frac{t}{T}\right)\frac{t}{T}H_X,$$  \hspace{1cm} (12)

where the summation in $H_X$ is over all qubits labeled by $q$'s and $\alpha$ is an adjustable factor. The $H_X$ term does not change the evolution in the beginning and at the end, but can break up the degeneracy and eliminate some energy crossings in the middle of the evolution. However, as infinitesimal gaps will exist when the degeneracy are broken, this modification cannot necessarily ensure the adiabatic evolution to find the exact ground state. In our simulations, we do see some minor improvement via the MSA method using small $\alpha$ (e.g. 0.1), but the results become worse for large $\alpha$ (e.g. 0.5). Despite this, we will demonstrate below that the augmented Hamiltonian (12) can produce much improved outcomes by a spectral projection method, discussed next.

IV. SPECTRAL PROJECTION METHOD FOR GROUND AND EXCITED STATES

From the previous discussions, we see that the MSA method does not always bring forth good results for ground states due to the limitation of the adiabatic approach that we explain above. For excited states, energy crossing and degenerate initial eigenstates are more likely to appear during the evolution. In these cases, the MSA becomes insufficient and its outputs may contain superposition of eigenstates. Therefore, we propose a different approach by using measurement instead of evolution according to the path-dependent Hamiltonian $H_i$. This method was introduced in Ref. [21], called the quantum simulated annealing in the context of optimizing a classical function. The standard quantum phase estimation [8] can be used to achieve this, but it is not yet suitable for current noisy quantum computers. Other ways of spectral projection have been proposed, including the quantum-walk based algorithm [22], and a Hadamard-test spectral projection method by measuring an ancilla iteratively [23]. These different methods also allow extraction of the corresponding eigenenergy. Such a Zeno-like measurement projects an arbitrary initial state to an eigenstate according to the Born’s Rule. In our work here, we do not specify which particular algorithms to realize the projection, but assume the projection can be performed and the eigenenergy can be extracted.

FIG. 7: The statistics of how each initial eigenstate will result in after 20 steps of successive eigenstate projections via the MSP method with $\alpha = 0$ for (a) H$_2$O at the equilibrium position $d = 0.958\text{A}$. (b) BeH$_2$ at the equilibrium position $d = 1.33\text{A}$. Different colors and their labels 1i, 2i,...,8i denote the 8 lowest initial eigenstates. The labels in the horizontal axis 1f, 2f,..., etc. denote the obtained eigenstates according to the final Hamiltonian and the vertical axis shows the accumulated distribution (summing those probabilities at a particular final state). The statistics is gathered from simulating the projection process 1000 times.
FIG. 8: The statistics of how each initial eigenstate will result in after 20 steps of successive eigenstate projections for H\textsubscript{2}O at the position \textit{d} = 1.958\text{Å} with (a) \(\alpha = 0\), (b) \(\alpha = 0.1\), (c) \(\alpha = 0.5\) and (d) \(\alpha = 1\). Different colors and the corresponding labels \(1i, 2i, 3i, \text{and } 4i\) denote the lowest four initial eigenstates. The labels in the horizontal axis \(1f, 2f, \ldots\) etc. denotes the obtained eigenstates of final Hamiltonian and the vertical axis shows the accumulated distribution (summing those probabilities at a particular final state from different initial states). Statistics is obtained from simulating the procedure 1000 times.

We discretize the Hamiltonian \(\textbf{12}\) into sufficiently many discrete ones,

\[
H_k = H_\alpha \left( \frac{k}{N} T \right), \quad \text{with } k = 0, 1, \ldots, N, \quad (13)
\]

and perform the projections successively on eigenstates of these Hamiltonians \(H_k\) with \(k = 1, \ldots, N\). If the overlap of successive ground states is sufficiently close to unity, then by the quantum Zeno effect the resultant final state, after the whole sequence of measurement, will be very close to the ground state of the final Hamiltonian \[21\]. If there does not exist any ground-state degeneracy in the initial Hamiltonian, the projections will drive the initial ground state into the ground state of the final Hamiltonian with high probability. In the case of the initial degeneracy that is split later, then the projection method can yield one of the split eigenstates, in contrast to the adiabatic evolution which produces certain superposition. A few repetitions of this measurement procedure can result in multiply split eigenstates. To obtain the lowest \(k\) eigenstates, we prepare about \(k\) different lowest initial states and perform the maximum stabilizer projection (MSP) multiple times. With high probability, the outputs will contain the desired low lying eigenstates.

A. MSP procedure and numerical results

Let us list the procedure of our maximum stabilizer projection (MSP) method as follows.

1. Given a Hamiltonian of a molecule, transform the fermion operators to Pauli operators;
2. Find the (approximating) maximum stabilizer of the Pauli operators by greedy algorithm;
3. Discretize the time steps by \(t_k = \frac{k}{N} T\) and obtain a series of Hamiltonians \(H_k = H_\alpha(t_k)\);
4. Choose one of the maximum stabilizer’s eigenstate as the initial state, and perform the projections on \(H_k\) successively for \(k = 1, \ldots, N\), and we will obtain one eigenstate of the final Hamiltonian;
5. Repeat the above procedure multiple times and we will get a distribution of final eigenstates. We can pick the desired eigenstate from the distribution to perform further analysis.

As seen in Fig. \[3\] LiH is the simplest of all molecules
FIG. 9: The ground state energy of BeH$_2$ vs. the distance $d$ between the Be and one H atoms at the equilibrium angle, via the MSP approach with several choices of $\alpha$.

FIG. 10: The ground state energy of CH$_2$ vs. the distance $d$ between the C and one H atoms at the equilibrium angle, via the MSP approach with several choices of $\alpha$.

FIG. 11: The ground state energy of H$_2$O vs. the distance $d$ between the O and one H atoms at the equilibrium angle, via the MSP approach with several choices of $\alpha$.

considered in this paper, and the results from the three different methods work very well, including the MSP approach discussed in this section. This approach also works well for other molecules, as shown in Figs. 4, 5, and 6, and is the best among the three different methods. This can be understood from the large gap in the path-dependent Hamiltonian, as seen e.g. in Fig. 2 with $\alpha = 0$ and $\alpha = 1$. Moreover, we have performed simulations of the MSP using lowest few initial states and gather statistics of final eigenstates that are arrived at, as illustrated in Fig. 7 for H$_2$O and BeH$_2$ at their respective equilibrium position.

B. Improvement using nonzero $\alpha$

However, for distances larger than the equilibrium position, the results via using MSP with $\alpha = 0$ can deviate significantly from the exact ones. As explained earlier, this is due to many closely spaced energy levels at large distances that are degenerate in the infinite separation, illustrated in Fig. 2. Therefore, the interpolation used in Eq. 10 encounters level crossing and closely packed energies for $s$ close to unity. As we have indicated, this can be resolved by introducing a potentially degeneracy breaking term, as used in Eq. 12, and the overall constant $\alpha$. We thus compare the outcomes using nonzero $\alpha$ with those obtained using $\alpha = 0$ via the MSP method. As an illustration we compare the statistics of the final states from a few lowest initial states of the Maximum Stabilizer Hamiltonian with different values of $\alpha$, for H$_2$O molecule at $d = 1.958\text{Å}$, for which the deviation from the exact solution is visible in Fig. 6. As shown in Fig. 8, the statistics for the lowest few final states increases when $\alpha$ becomes nonzero and the probability of obtaining the final ground state by using the initial ground state of the Maximum Stabilizer Hamiltonian is enhanced.

We thus see improvements in Figs. 9, 10, and 11, for the ground states; there, we only use initial ground states as inputs and repeat the procedure 40 times and select the lowest energy. Note that the MSA cannot be improved by repetition and adding the $\alpha$ term actually make the results worse. Moreover, the choice of the exact value of $\alpha$ does not seem to be important in the overall performance. If necessary, one may repeat the procedure with a few different values of $\alpha$. Thus, we conclude that the MSP method with nonzero $\alpha$ provides an alternative approach for studying molecular energies.

We demonstrate the utility of the MSP method (with $\alpha = 0.5$) for the H$_2$O molecule in Fig. 12. In order to get the lowest few eigenstate of a molecule, we can choose as initial states the lowest few eigenstates of the maximum stabilizer Hamiltonian (8). As all the operators in the maximum stabilizer commute with each other, it is easy to find those initial eigenstates. Specifically, for the molecular problem we consider here, these operators contain only product of Pauli Z operators (and identities); thus, the eigenstates belong to the computational basis states.

While the MSA method in Sec. III may result in superposition of final eigenstates, the projection method by design will always result in an eigenstate, despite that we cannot predict in advance which eigenstate will appear. The introduction of the $\alpha$ term in the Hamiltonian actually make the performance of the MSA method worse (results not shown). Regarding the excited, we note that their fidelity does not depend on the fidelity of the ground states, in contrast to the VQE approach with the equa-
FIG. 12: The energy of the ground state and first three excited states for H$_2$O calculated by the MSP with $\alpha = 0.5$. The inset shows the blow-up in the range $d \in [2.0, 3.0]\AA$. The lines indicate the exact solution. We use the lowest 4 eigenstates of Maximum Stabilizer as initial states, and repeat projection procedure 40 times and take the lowest 4 final eigenstates as results.

V. COMPARISON WITH HARTREE-FOCK INITIAL HAMILTONIAN

In the previous section, we use the maximum stabilizer Hamiltonian as the initial Hamiltonian. It seems more natural to use the Hartree-Fock Hamiltonian as the initial Hamiltonian $H_{HF}$ to implement the above Zeno approach. We thus numerically calculate the energy levels of $H(s) = (1 - \frac{s}{T})H_{HF} + \frac{s}{T}H_p$ for H$_2$O at the equilibrium position, see Fig. 13. The Hartree-Fock Hamiltonian is computed by the PySCF package [24] and transformed to Pauli operators by the Qiskit [30]. The transformation includes parity mapping and 1s orbital-freezing. For visual convenience we add an identity term to the Hartree-Fock Hamiltonian to force its ground state energy equal to the ground state energy of the final Hamiltonian. We find that the spectra along such interpolation are not favorable to the adiabatic nor the projection approach, as there are low-lying eigenstates with close energies and small gaps or level crossings, as well as degeneracy for certain range of $s$. Adding the $\alpha$ term would not improve these. This shows that using the maximum stabilizer works better than the Hartree-Fock Hamiltonian.

VI. CONCLUSION

We propose to use the adiabatic framework for the eigenstates and energies of molecules, and in particular we adopt the maximum stabilizer as the initial Hamiltonian, as opposed to the Hartree-Fock Hamiltonian. However, the issue of degeneracy can cause the results of the adiabatic quantum computation approach (i.e. the MSA) for the task of simulating molecular ground-state energies not to be accurate at large molecular distances. As we have examined, the alternative projection method, i.e., the Maximal Stabilizer Projection with additional Pauli $X$ terms resolves this issue and obtains very accurate results.

We demonstrate numerically that the MSP approach can output the ground state and low lying eigenstates with high probability. Compared to finding excited states via the VQE, our method does not rely on a precise ground state. At the moment, the MSP approach may not be readily implementable due to the drawback that
the multiple-qubit Pauli terms may not be directly available in current quantum computers and require decomposition into one- and two-qubit gates. However, there are a few proposals as to how to perform spectral projection [21,22], and it is an interesting future direction to consider how to make spectral projection for Hamiltonians with multiqubit Pauli terms suitable for near-term quantum computers. For example, one may optimize the specific proposal by using controlled evolution and ancilla measurement in Ref. [23] by optimizing the expansion of the controlled evolution in discrete one- and two-qubit quantum gates. How the number of gates scale requires further investigation. Moreover, ideas from the work by Wan and Kim on fast digital methods for adiabatic state preparation may be considered [31]. With future large-scale quantum computers and better multi-qubit gates, one may apply the Zeno-based approach to finding eigen-systems of large molecules.

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