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1 Executive Summary

Here we present the quantum computing computational package for quantum chemistry. It contains the implementation of the variational Hamiltonian ansatz state preparation for chemical systems. Equipped with the variational algorithms for imaginary- and real-time evolution, the package can optimize and propagate in time wave functions for chemical systems. As the Pre-Born-Oppenheimer molecular structure is implemented, one can describe nuclear quantum effects. We show the use cases for the developed methods on small chemical systems such as lithium hydride and hydrogen molecules. Specifically, the real- and imaginary-time evolutions have been proven to work correctly and efficiently. The Pre-Born-Oppenheimer scheme delivers results in agreement with the reference. Furthermore, it is shown that the variational Hamiltonian ansatz may approximate wave functions more efficiently than traditional variational ansatzes.

2 Introduction

Among all possible applications for quantum computing, the simulation of quantum systems in the last decades achieved huge successes. Having at hand a decent number of long-term stable logical qubits in a universal quantum computer, one can solve, in polynomial time, problems in quantum chemistry intractable for a classical computer. Quantum chemistry gives access to information about the properties of molecular systems before their synthesis. This is a great advantage as otherwise a purely combinatorial experimental approach is unavoidable for finding molecules with desired properties.

The Noisy Intermediate-Scale Quantum (NISQ) devices have a limited number of qubits. Thus one needs a compact wavefunction parameterization giving a reasonable accuracy for molecular energies. Provided such a parameterization, it is of extreme interest to develop methods exploring chemical dynamics and reactivity on NISQ computers.

2.1 Repository

The Github repository collects Python scripts and Jupyter notebooks that allow the user to test different variational algorithms. It contains our custom functions (e.g. VHA ansatz, PBO Hamiltonian) that are built upon Qiskit libraries (Qiskit, 2021):

- qiskit-terra 0.19.0
- qiskit-nature 0.2.0
- qiskit-aer 0.8.2

In order to be able to run the example scripts, a custom environment is also provided. It automatically installs all the necessary libraries in a Conda environment that can be used across different machines.

3 Theory

3.1 Variational Hamiltonian ansatz

The Variational Hamiltonian Ansatz (VHA) (Wecker et al., 2015) have been implemented and adapted specifically for the application on a quantum chemical system. Inspired by a Trotterized adiabatic evolution

$$\hat{\mathrm{T}}_{\mathrm{ad}} = \prod_{k=1}^{n} \prod_{\alpha=1}^{N} e^{-\mathbf{i}\frac{\tau}{n}\hat{\mathrm{H}}_0} e^{-\mathbf{i}\frac{\tau}{n}\frac{k}{n}\hat{\mathrm{V}}}, \tag{3.1}$$

the VHA reduces the number of parameters used by grouping similar terms in Hamiltonian together under the same variational parameter

$$\hat{\mathrm{H}} = \sum_{\alpha=1}^{N} \hat{\mathrm{H}}_\alpha, \tag{3.2}$$

$$\hat{\mathrm{T}}(\boldsymbol{\theta}) = \prod_{k=1}^{n} \prod_{\alpha=1}^{N} e^{-\mathbf{i}\theta_{\alpha,k}\hat{\mathrm{H}}_\alpha}. \tag{3.3}$$

One of the ways to split terms in the electronic Hamiltonian is as follows

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_{\mathrm{diag}} + \hat{\mathrm{H}}_{\mathrm{hop}} + \hat{\mathrm{H}}_{\mathrm{ex}}. \tag{3.4}$$

Expressing the right-hand side of Eq. (3.4) with the creation, $\hat{\mathrm{a}}_p^\dagger$, and the annihilation, $\hat{\mathrm{a}}_q$, operators the diagonal term reads

$$\hat{\mathrm{H}}_{\mathrm{diag}} = \sum_p h_{pp}\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_p + \sum_{p,q} h_{pqpq}\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_p\hat{\mathrm{a}}_q^\dagger\hat{\mathrm{a}}_q. \tag{3.5}$$

The hopping term

$$\hat{\mathrm{H}}_{\mathrm{hop}} = \sum_{pq} h_{pq}\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_q + \sum_{p,r,q} h_{prrq}\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_q\hat{\mathrm{a}}_r^\dagger\hat{\mathrm{a}}_r \tag{3.6}$$

contains normal and correlated components, while

$$\hat{\mathrm{H}}_{\mathrm{ex}} = \sum_{<p,q,r,s>} h_{pqrs}\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_q^\dagger\hat{\mathrm{a}}_r\hat{\mathrm{a}}_s \tag{3.7}$$

has all other exchange terms with indexes $< p, q, r, s >$ being distinct.

3.2 Variational time evolution

Approaching chemical dynamics with quantum computing methods is challenging, as one faces the limitations of NISQ devices. The recently appeared variational time evolution algorithms (Yuan et al., 2019) have modest requirements on decoherence time and noise. That motivated us to base our chemical dynamics methods on variational evolution techniques.

3.2.1 Real-time evolution

To evolve in time the closed quantum system represented by the trial state $\Psi(\boldsymbol{C}[t])$ with parameters $\boldsymbol{C}[t]$,

$$e^{-\mathbf{i}\delta t\hat{\mathrm{H}}}\,|\Psi(\boldsymbol{C}[t])\rangle \quad \Rightarrow \quad |\Psi(\boldsymbol{C}[t+\delta t])\rangle$$

one considers time-dependent Schrödinger equation

$$\frac{\partial}{\partial t}\,|\Psi(\boldsymbol{C}[t])\rangle = -\mathbf{i}\hat{\mathrm{H}}\,|\Psi(\boldsymbol{C}[t])\rangle\,.$$

Then applying the McLachlan variational principle (Yuan et al., 2019)

$$\delta|| \left(\partial/\partial t + \mathbf{i}\hat{\mathrm{H}}\right) |\Psi(\boldsymbol{C}[t])\rangle \, || = 0.$$

and following the steps in Ref. (Yuan et al., 2019) it is possible to derive the equation for the Variational Real-Time Evolution (VRTE)

$$\sum_j A^{\Re}_{ij} \dot{C}_j = G^{\Im}_i,$$

where the metric tensor, A_{ij}, and derivative term, G_i, have following form

$$\begin{aligned} A_{ij} &= \left(\frac{\partial \langle \Psi(\boldsymbol{C}[t])|}{\partial C_i} \frac{\partial |\Psi(\boldsymbol{C}[t])\rangle}{\partial C_j} \right), \\ G_i &= \left(\langle \Psi(\boldsymbol{C}[t])| \, \hat{\mathrm{H}} \frac{|\Psi(\boldsymbol{C}[t])\rangle}{\partial C_i} \right). \end{aligned} \tag{3.8}$$

Evaluating $A^{\Re}_{ij}$ and $G^{\Im}_i$ on quantum machine, one can update wave function parameters $\boldsymbol{C}[t]$ on the classical machine according to the following rule

$$\boldsymbol{C}[t+\delta t] = \boldsymbol{C}[t] + \delta t \left(A^{\Re}\right)^{-1} G^{\Im}.$$

3.2.2 Imaginary-time evolution

Alternatively, replacing real time with imaginary time $\tau = it$ and imposing constraints on the wavefunction norm, one can consider Wick rotated Schrödinger equation

$$\frac{\partial}{\partial \tau} |\Psi(\boldsymbol{C}[\tau])\rangle = \left[E(\tau) - \hat{\mathrm{H}}\right] |\Psi(\boldsymbol{C}[\tau])\rangle,$$

whereas the McLachlan variational principle has following form

$$\delta|| \left(\partial/\partial \tau + \hat{\mathrm{H}} - E_\tau\right) |\Psi(\boldsymbol{C}[\tau])\rangle \, || = 0.$$

Similarly to the previous case the equation for the Variational Imaginary-Time Evolution (VITE) is derived

$$\sum_j A^{\Re}_{ij} \dot{C}_j = -G^{\Re}_i,$$

where $A^{\Re}_{ij}$ and $G^{\Re}_i$ are evaluated on quantum devices, while $\boldsymbol{C}[\tau]$ is update on the classical machine accordingly

$$e^{-\delta\tau\hat{\mathrm{H}}} |\Psi(\boldsymbol{C}[\tau])\rangle \quad \Rightarrow \quad \boldsymbol{C}[\tau+\delta\tau] = \boldsymbol{C}[\tau] - \delta\tau \left(A^{\Re}\right)^{-1} G^{\Re}.$$

The VITE can be viewed as an alternative to the traditional wavefunction optimization methods, providing advantages for certain cases (McArdle et al., 2019).

3.3 Pre-Born-Oppenheimer molecular structure theory

In solving the Schrödinger equation for chemical systems, one usually considers nuclear and electronic parts separately, reasoning by the large mass difference between nuclei and electrons. Such an assumption, the so-called Born-Oppenheimer (BO) approximation, considerably simplifies the solution of the Schrödinger equation and leads to coupled electronic and nuclear equations. Generally, BO approximation fails when potential energy surfaces for electronic states are too close. Thus it is hard to study such phenomena as the excited-state dynamics, photochemistry, charge transfer, nuclear tunneling, excited vibrational-electronic states *etc.*. We establish our work on the Pre-Born-Oppenheimer (PBO) molecular structure theory (Muolo et al., 2020; Veis et al., 2016; Webb S. P., 2002)

$$\left[-\sum_i^N \frac{1}{2}\nabla_i^2 - \sum_A^M \frac{1}{2M_A}\nabla_A^2 - \sum_{i,A}^{M,N} \frac{Z_A}{r_{iA}} + \sum_{i<j}^N \frac{1}{r_{ij}} + \sum_{A<B}^M \frac{Z_A Z_B}{R_{AB}} \right] \Psi(\boldsymbol{r}, \boldsymbol{R}) = E\Psi(\boldsymbol{r}, \boldsymbol{R}),$$

as nuclear quantum effects are incorporated in the calculation without any additional corrections. Although, one has to mention that the *a posteriori* corrections from the non-adiabatic coupling theory (Ollitrault et al., 2020) are available and might deliver acceptable results.

The PBO Hamiltonian in second quantization formalism was implemented based on the electronic Hamiltonian. Specifically, the nuclear kinetic, nuclear-nuclear, as well as nuclear-electronic Coulomb interaction terms have been added, resulting in the following Hamiltonian

$$
\begin{aligned}
\hat{\mathrm{H}} = & -\sum_{ij} \overset{\text{el. kinetic}}{\left[\int \phi_i(r)\frac{1}{2}\nabla^2\phi_j(r)dr\right]} \hat{\mathrm{a}}_i^\dagger \hat{\mathrm{a}}_j - \sum_{MN} \overset{\text{nuc. kinetic}}{\left[\int \phi_p(M)\frac{1}{2M}\nabla^2\phi_N(R)dR\right]} \hat{\mathrm{a}}_M^\dagger \hat{\mathrm{a}}_N \\
& + \frac{1}{2}\sum_{ijkl} \overset{\text{el.-el. Coulomb}}{\left[\int \phi_i(r_1)\phi_k(r_2)\frac{1}{|r_1 - r_2|}\phi_l(r_2)\phi_j(r_1)dr_1 dr_2\right]} \hat{\mathrm{a}}_i^\dagger \hat{\mathrm{a}}_k^\dagger \hat{\mathrm{a}}_l \hat{\mathrm{a}}_j \\
& + \frac{1}{2}\sum_{MNPQ} \overset{\text{nuc.-nuc. Coulomb}}{\left[\int \psi_M(R_1)\psi_P(R_2)\frac{Z_1 Z_2}{|R_1 - R_2|}\psi_Q(R_2)\psi_N(R_1)dR_1 dR_2\right]} \hat{\mathrm{a}}_M^\dagger \hat{\mathrm{a}}_P^\dagger \hat{\mathrm{a}}_Q \hat{\mathrm{a}}_N \\
& - \sum_{ijPQ} \overset{\text{el.-nuc. Coulomb}}{\left[\int \phi_i(r)\psi_P(R)\frac{Z}{|R - r|}\psi_Q(R)\phi_j(r_1)drdR\right]} \hat{\mathrm{a}}_i^\dagger \hat{\mathrm{a}}_P^\dagger \hat{\mathrm{a}}_Q \hat{\mathrm{a}}_j,
\end{aligned}
$$

where the regular and capital letters were used as indices for electrons and nuclei correspondingly.

4 Discussions and Conclusions

To benchmark the VRTE, VITE, and PBO Hamiltonian implementations, the H_2 molecule at equilibrium distance, 0.735 Å, was chosen as a test system. The TwoLocal hardware efficient ansatz (Kandala et al., 2017) was chosen for all calculations using an ideal state-vector simulation with the Jordan-Wigner transformation for fermionic Hamiltonians. The full entangling pattern for Cz gates was interleaved by Ry and Rz gates, repeated 3 times. The setups for calculations similar to those mentioned in Subsection 4.1 and 4.2 are available in the neoh2vqe.py, h2evo.py, neoh2evo.py python scripts.

4.1 Pre-Born-Oppenheimer molecular structure

The PBO Hamiltonian implementation has been tested in the Variational Quantum Eigensolver (VQE) calculation. For the reference we performed the Nuclear Electronic Orbitals Complete Active Space Correlation Interaction (NEOCASCI) (Webb S. P., 2002) calculation in 6-31G for electrons and DZSNB (Webb S. P., 2002) for nuclei basis sets. To limit the number of utilized qubits, the active space was composed of 2 electrons on 2 orbitals and 2 orbitals for 2 hydrogen nuclei (8 spin orbitals in total). The corresponding integrals for nuclei and electrons were utilized in the VQE calculation. In table 1 one can find the results of VQE energy minimizations employing solely PBO Hamiltonian as well as those with constraints on the number of particles, $\hat{\mathrm{N}}$, and the spin projection, $\hat{\mathrm{S}}_z$.

Table 1: *The energies of H_2 molecule employing solely PBO Hamiltonian as well as with constraints on number of particles, $\hat{N}$, and spin projection, $\hat{S}_z$.*

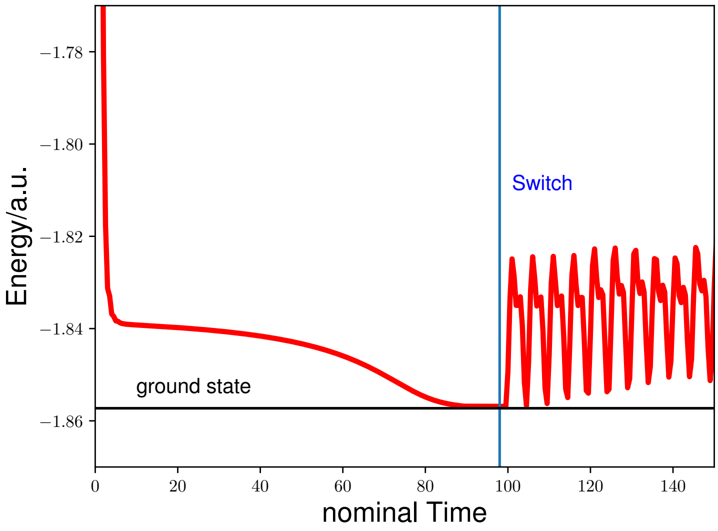
method	constraints	Energy/a.u.
Reference	-	-1.0537650432
TwoLocal	-	-1.0537606126
TwoLocal	$\hat{\mathrm{N}}$	-1.0537647634
TwoLocal	$\hat{\mathrm{N}}$, $\hat{\mathrm{S}}_z$	-1.0537650258

4.2 Variational time evolution

We tested the variational evolution methods on the electronic Hamiltonian with integrals taken from a Hartree-Fock calculation with STO-3G basis set. Initially, the VITE simulation started with the time step equal to 0.1 (the imaginary and real time are given in a.u. here). After 80 iterations, the total energy decreased to the ground state energy, see Figure 1, and at iteration 100, the simulation was switched to VRTE with the time step equal to 0.05. One can immediately see at that point the start of the energy oscillation. It is worth noting that until the end of VITE the norm of the update vector was constantly decreasing to zero. Contrary, for VRTE the norm becomes reasonably large and keeps its value between 2.5 and 3.3 during the simulation.

The oscillation has the same repetitive pattern slightly changing at the end due to numerical noise. One can consider that as excited states exploration in the vicinity of the ground state. Currently, we are working on performing the same experiment but on the PBO Hamiltonian and introducing orbital relaxation upon changing atomic orbitals centers.

***Figure 1**: The variational imaginary-time and real-time evolution on H_2 at equilibrium distance.*



4.3 Variational Hamiltonian ansatz

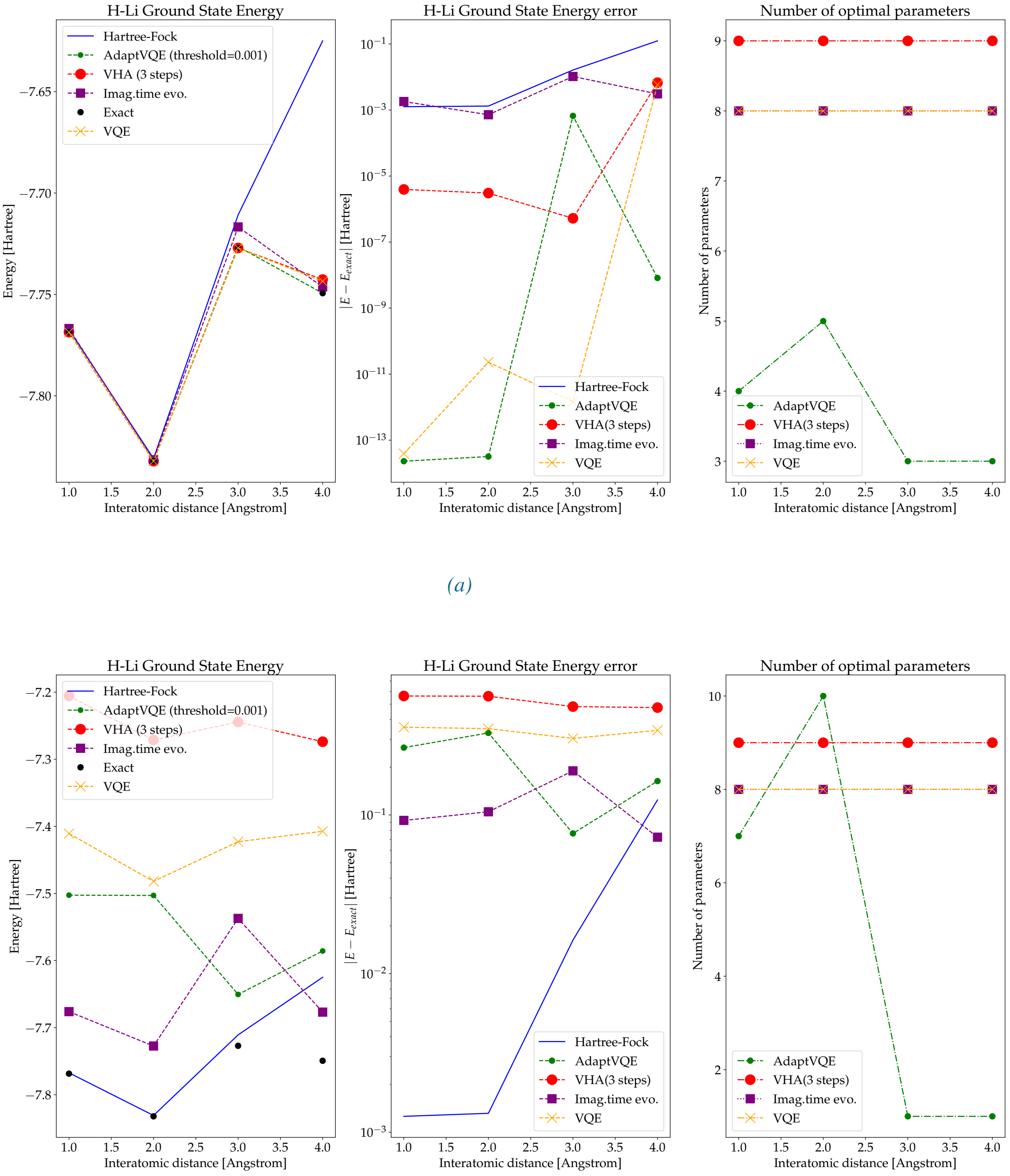
One can also benchmark the capabilities of various variational algorithms on the determination of the ground state and energy for the Li-H molecule. We provide jupyter notebooks that encompass 4 different methods to find the ground state:

- VQE (Peruzzo et al., 2014) with Unitary Coupled Clusters Singles and Doubles (UCCSD) ansatz (native to Qiskit)
- Adaptive Variational Quantum Eigensolver (AdaptVQE) (Grimsley et al., 2019) with UCCSD ansatz (native to Qiskit)
- VQE with VHA ansatz from Section 3.1
- VITE from Section 3.2.2 with TwoLocal ansatz

The methods are applied to the same molecule across a range of interatomic distances and the ground state energies are compared against the exact solution computed using NumpyMininumEigensolver. The number of optimal parameters used in the ansatz is also shown. In the prospect of running these algorithms on NISQ hardware, is important to keep the number of parameters as low as possible to ensure a shallow quantum circuit.

The result are shown in Fig. 2a using an ideal state-vector simulation. The VQE and AdaptVQE algorithms obtain the best result in terms of the energy of the ground state, with the latter having the lowest amount of optimal parameters used in the ansatz.

It is also possible to run the computation using a simple noise model from the IBM libraries to simulate a more realistic scenario on a quantum device. The results from a noisy simulation are in Fig. 2b. With noise, the situation changes and we can see that overall the imaginary time evolution is more robust to noise, with AdaptVQE offering the best performance for larger values of inter-atomic distance.



(a)

(b)

***Figure 2**: Comparison of the ground state energy calculation for the different variational algorithms and ansatzes using (a) state-vector simulation and (b) noisy simulation (FakeVigo from IBM).*

List of Acronyms

Term	Definition
VRTE	Variational Real-Time Evolution
VITE	Variational Imaginary-Time Evolution
NISQ	Noisy Intermediate-Scale Quantum
VHA	Variational Hamiltonian Ansatz
BO	Born-Oppenheimer
PBO	Pre-Born-Oppenheimer
VQE	Variational Quantum Eigensolver
AdaptVQE	Adaptive Variational Quantum Eigensolver
NEOCASCI	Nuclear Electronic Orbitals Complete Active Space Correlation Interaction
UCCSD	Unitary Coupled Clusters Singles and Doubles
STO-3G	minimal Slater-Type Orbital basis with 3 Gaussian primitives
6-31G	split-valence double-zeta basis set with 6 Gaussian primitives
DZSNB	Split-valence Double-Zeta Nuclear Basis set
Li-H	lithium hydride
H_2	hydrogen molecule

Table 2: Acronyms and Abbreviations

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