Research Article

Ali Abu-Nada*

Quantum computing simulation of the hydrogen molecular ground-state energies with limited resources

<https://doi.org/10.1515/phys-2021-0071>

received May 27, 2021; accepted September 29, 2021

Abstract: In this article, the hydrogen molecular ground-state energies using our algorithm based on quantum variational principle are calculated. They are calculated through a simulator since the system of the present study (*i.e.*, the hydrogen molecule) is relatively small and hence the ground-state energies for this molecule are efficiently classically simulable using a simulator. Complete details of this algorithm are elucidated. For this, a full description on the fermions–qubits and the molecular Hamiltonian–qubit Hamiltonian transformations, is given. The authors search for qubit system parameters (θ_0 and θ_1) that yield the minimum energies for the system and also study the ground state energies as a function of the molecular bond length. Proposed circuit is humble and does not include many parameters compared with that of Kandala *et al.*, the authors control only two parameters (θ_0 and θ_1).

Keywords: quantum simulation, variational quantum eigensolver, quantum computing

1 Introduction

Feynman emphasized that simulating quantum systems on a computer that uses quantum bits (qubits) is very efficient [1]. Several algorithms have been produced after Feynman observation and all those algorithms confirm that it is noticeable and concrete [2–4]. Although the classical simulations of chemical systems have greatly helped us in understanding the structural, physical, and chemical

characteristics of these molecules, the resources necessary for a full simulation for the time-independent Schrödinger equation (1) scale exponentially with the number of atoms in a molecule [5] and hence with size of the H matrix in Eq. (1). Therefore, the exact solution of Eq. (1) is inadequate for large systems and it requires a lot of computational resources:

$$H|\Psi\rangle = E|\Psi\rangle. \quad (1)$$

Computational quantum chemistry relies on approximate methods that often succeed in predicting chemical characteristics of larger systems, and each approximation has different levels of accuracy according to the system complexity [6,7]. A quantum algorithm and a quantum computer could possibly beat all computational quantum chemistry approximations. Accomplishing such a high level of accuracy depends on the effectiveness of the quantum algorithms [5,8].

The dominant objective in the computational chemistry is to find the ground-state energies of many body-interacting fermionic Hamiltonians. Therefore, several algorithms have been developed to calculate ground-state energies for chemical systems. Some of these algorithms require many quantum overhead resources and exceed the limits of the available noisy intermediate-scale quantum (NISQ) such as the quantum phase estimation (QPE) algorithm [8]. Accordingly, Peruzzo *et al.* [9] developed the variational quantum eigensolver (VQE) to calculate the ground-state energies of a molecular system using quantum circuits with less overhead resources.

In this article, we calculate the hydrogen molecular ground-state energies using our algorithm based on quantum variational principle (QVP). We provide full details of this algorithm by, first, describing the fermionics–qubit transformation, and then, the molecular Hamiltonian–qubit Hamiltonian transformation as well. To find the ground-state energies of the hydrogen molecule, we follow the VQE to simulate the hydrogen molecule H_2 , but we do not implement our simulation on the noisy quantum processor and also we do not use the classical optimizer to update the quantum

* Corresponding author: Ali Abu-Nada, Faculty of Engineering Technology and Science, Higher Colleges of Technology, Abu Dhabi, UAE, e-mail: aabunada79@gmail.com

circuit parameters. For more details on VQE, we recommend the reader here to read Refs. [9,10]. VQE is a quantum/classical hybrid algorithm that can be used to find eigenvalues of a (often large) matrix H .

Our algorithm contains the following major phases: (1) we convert the fermion system to qubit system, furthermore, we also convert the molecular Hamiltonian into qubit Hamiltonian using the known binary-tree transformation and this also includes the fermionic–qubit operators transformation [11,12]; (2) we prepare the quantum state $|\Psi(\theta)\rangle$, normally called *ansatz* (we describe all elements of $|\Psi(\theta_i)\rangle$ in Section 3); (3) we measure the expectation value $\langle\Psi(\theta_i)|H|\Psi(\theta_i)\rangle$; and (4) we search for θ_i that makes $\langle\Psi(\theta_i)|H|\Psi(\theta_i)\rangle$ the minimum. This is often the same as for the VQE algorithm. However, VQE uses a classic optimizer (i.e., COBYLA and SPSA [13]) to find the updated *ansatz* parameters (θ_i) that reduce the expectation value of H as follows:

$$\frac{|\langle\Psi_{\min}(\theta)|H|\Psi_{\min}(\theta)\rangle|}{|\langle\Psi_{\min}(\theta)|\Psi_{\min}(\theta)\rangle|} \geq E_{\min}, \quad (2)$$

where $E_{\min}$ is the minimum energy eigenvalue.

The article is organized as follows, in Section 2, we clarify the fermion–qubit transformation. In Section 3, we discuss the algorithm and the simulation details, while in Section 4, we present the results. Finally, we conclude in Section 5.

2 Fermion–qubit transformation

Abrams and Lloyd suggested a simulation pattern for fermions hooping on a lattice [3]. Subsequently, Somma *et al.* [14] used the Jordan–Wigner transformation to simplify the simulation pattern suggested by Abrams and Lloyd [3]. The fermion–qubit transformation is accomplished in two steps: (1) we convert the occupation number basis vectors of the fermion to qubit states; and (2) we express the fermionic creation and annihilation operators in terms of Pauli operators acting on qubits so that maintain the fermionic anti-commutation relations (Eq. (3)) [12].

$$\{a_j, a_k\} = \{a_j^\dagger, a_k^\dagger\} = 0, \{a_j, a_k^\dagger\} = \delta_{jk}1, \quad (3)$$

where a_j and $a_j^\dagger$ are the creation and annihilation operators for a mode j . The first quantized formulation equation of the molecular Hamiltonian H_{molec} can be written as:

$$H_{\text{molec}} = -\sum_i \frac{\nabla_{R_i}^2}{2M_i} - \sum_i \frac{\nabla_{r_i}^2}{2} - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j>i} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i,j>i} \frac{1}{|r_i - r_j|}, \quad (4)$$

where R_i , M_i , Z_i are the positions, masses, and charges of the nuclei, respectively, and r_i are the positions of the electrons. It is well known that the nuclei are much heavier than the electrons, so they do not move freely and at the same times scale as the electrons. Here we use the Born–Oppenheimer approximation such that the performance of the nuclei and electrons can be isolated and the first term in Eq. (4) will be cancelled.

To transform the molecular Hamiltonian H_{molec} Eq. (4) to the second quantized formulation, we deal with the nuclei as immovable classical point charges. We choose a basis ψ_i to represent the wave function and use the antisymmetry with the fermions creation and annihilation operators $a_i^\dagger$ and a_j and obtain

$$H_{\text{elec}} = \sum_{pq=1}^M h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs=1}^M h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s, \quad (5)$$

where M is the number of fermi modes. We define the one-body integrals

$$h_{pq} = \int dr \psi_p^*(r) \left(-\frac{1}{2} \nabla^2 - \sum_i \frac{Z_i}{|R_i - r_j|} \right) \psi_q(r) \quad (6)$$

and two-body integrals

$$h_{pqrs} = \iint dr_1 dr_2 \frac{\psi_p^*(r_1) \psi_q^*(r_2) \psi_r(r_2) \psi_s(r_1)}{|r_1 - r_2|}. \quad (7)$$

The molecular orbitals (ϕ_i) can be either occupied or unoccupied. The capacity of each molecular orbital is two electrons. However, we actually work with spin-orbitals which are associated with a spin up (α) and spin down (β) electrons. Thus, spin orbitals can contain one electron or be unoccupied as in Figure 1.

Finally, the second quantized molecular Hamiltonian must be converted to qubit Hamiltonian. The hydrogen molecule Hamiltonian is mapped first onto four qubits using a binary-tree transformation [11,12]. We display the

Figure 1: Two s orbitals on hydrogen atoms, each orbital filled with either spin-up or spin-down electrons and thus the total number of spin orbitals is 4. The two shared electrons in the hydrogen molecule will have opposite spins.

L spin orbitals by registering the first $L/2$ spin-up ones and then the $L/2$ spin-down ones. When using the binary-tree transformation, this creates a qubit Hamiltonian diagonal in the second and fourth qubit, which has the total particle and spin Z_2 symmetries encoded in those qubits [15], we recommend the readers to go through Appendix A for more details of removing those two electrons.

The final qubit Hamiltonian contains four terms, each term contains a tensor product of two Pauli operators acted on two-qubits for the hydrogen molecule. In ref. [11], it was witnessed that two-qubits could be detached after the binary tree transformation and hence we end up with two-qubits. Thus, the final shape of qubit Hamiltonian of the hydrogen molecule will be written as follows:

$$H_{\text{qubit}} = \alpha \mathbb{I}_1 \otimes \mathbb{I}_2 + \beta Z_1 \otimes \mathbb{I}_2 + \gamma \mathbb{I}_1 \otimes Z_2 + \delta Z_1 \otimes Z_2 + \zeta X_1 \otimes X_2, \quad (8)$$

where $\alpha, \beta, \gamma, \delta$, and ζ are real numbers and their values to be governed based on the value of the molecular distance of the hydrogen molecule. Moreover, $\mathbb{I}_i, X_i$, and Z_i represent the Pauli operators acting on the i th qubit.

3 Overview of the algorithm and simulation details

The primary concern of this article is to calculate the ground-state energies of the hydrogen molecule and also to study how the difference of the molecular bond length affects these energies with limited resources. So, our circuit we use in this article is humble and does not include many parameters compared with ref. [16].

The eigenstate (*ansatz*) $|\Psi_{\min}(\theta_i)\rangle$ which has been mentioned in Eq. (2) is built by applying the parameterized circuit (Figure 2) characterized by $U_i(\theta_i)$ to vacuum state $|00\rangle$ and generate $U(\theta_i)|00\rangle = |\Psi(\theta)\rangle$ as follows:

$$|\Psi(\theta)\rangle = \left[\prod_{q=1}^2 U_1(\theta_1) \times \text{CNOT} \right]_{\text{layer 1}} \times \left[\prod_{q=1}^2 U_1(\theta_1) \times \text{CNOT} \right]_{\text{layer 2}} \times \left[\prod_{q=1}^2 U_0(\theta_0) \right] |00\rangle. \quad (9)$$

The estimation of the ground-state energy is iteratively optimized by a classical controller changing the parameters (θ_1 and θ_0) we just control two parameters (θ_0 and θ_1).

We describe the fermionic systems using the formalism of second quantization, where n single-particle states can be either empty $|0\rangle$ or occupied $|1\rangle$ by a spinless fermionic particle. In the circumstances of quantum chemistry, these n states represent spin orbitals, so one-electron energy eigenfunctions and often molecular orbitals found by the Hartree–Fock (HF) method [12,17]. We start our study by creating the Hamiltonian of the hydrogen molecule using QISKIT [13] at different bond lengths. The molecular Hamiltonian of the hydrogen molecule (Eq. (4)) assumed in this article are calculated in the STO-3G basis, using QISKIT software free package [13]. QISKIT is interfaced with different classical codes which are able to find the H–F solutions. Interfacing between QISKIT and a PySCF driver is already available for the hydrogen molecule at equilibrium bond length (0.735 Å) and in the singlet state and with no charge. This determines the number of particles, number of orbitals-spin orbitals, and the one- and two-electron integrals. The molecular Hamiltonian is then written in terms of fermionic operators (Eq. (5)).

The molecular Hamiltonian is then encoded into the qubit Hamiltonian using the binary tree transformation [11], which allows us to remove two-qubits by symmetry considerations and thus only two-qubits are needed as shown in Eq. (8). Subsequently, we construct the system qubits state $|\Psi(\theta_i)\rangle$, also known as the *ansatz*. Figure 2 represents the *ansatz* used for this study, and the two-qubit system are prepared in the $|00\rangle$ state. The two-qubit system is given initial rotations the unitary gates U_0 followed by the entangler, where the entangler contains CNOT and gates U_1 (each CNOT and U_1 gates represent one layer for the entangler). The unitary gates U_i are of the form $\text{Ry}(\theta_i) \text{Rz}(\theta_i)$. For simplicity, we assign θ_0 for the two-qubits in the initial rotations and θ_1 for each of the layers in the entangler to minimize number of the parameters.

The expectation value the qubit Hamiltonian Eq. (8) is measured by measuring individual term in the equation one after another using at the end of the circuit in Figure 2.

$$\langle H_{\text{qubit}} \rangle = \alpha \langle \mathbb{I}_1 \otimes \mathbb{I}_2 \rangle + \beta \langle Z_1 \otimes \mathbb{I}_2 \rangle + \gamma \langle \mathbb{I}_1 \otimes Z_2 \rangle + \delta \langle Z_1 \otimes Z_2 \rangle + \zeta \langle X_1 \otimes X_2 \rangle. \quad (10)$$

For $\langle \mathbb{I} \otimes Z \rangle$, $\langle Z \otimes \mathbb{I} \rangle$, and $\langle Z \otimes Z \rangle$, we use the same circuit in Figure 2. However, for the $\langle X \otimes X \rangle$ term, we apply final Hadamard H rotation gate before we implement the measurements and this is due to the fact that QISKIT performs the measurement only in the standard basis of Z gate, or simply, Z basis ($|0\rangle$ and $|1\rangle$). So, we use the Hadamard gate to transform the X gate to Z gate. The Hadamard gate can be thought as a unitary transformation

Figure 2: The quantum circuit (ansatz) $|\Psi(\theta)\rangle$ for the hydrogen molecule.

Figure 3: The quantum circuit (ansatz) $|\Psi'(\theta)\rangle = H|\Psi(\theta)\rangle$ for the hydrogen molecule.

that maps qubit operations in x -basis (i.e., $|-\rangle$ and $|+\rangle$) to the z -basis (i.e., $|0\rangle$ $|1\rangle$) and *vice versa*. For example, $HZH = X$ and $HXH = Z$. Therefore, $\langle X_1 \otimes X_2 \rangle = \langle \Psi | XX | \Psi \rangle$ can be written as follows:

$$\langle \Psi | XX | \Psi \rangle = \langle \Psi | HZH HZH | \Psi \rangle. \quad (11)$$

Here, we use $HH = \mathbb{I}$, then Eq. (11) becomes:

$$\langle \Psi' | ZZ | \Psi' \rangle, \quad (12)$$

where $|\Psi'\rangle = H|\Psi\rangle$. Figure 2 represents the circuit of $|\Psi'\rangle$.

Then, we vary θ_0 and θ_1 randomly from -3 rad. to 3 rad. until we achieve the values that give us the minimum energy for the equilibrium bond length ($0.735 \text{ \AA}$). Finally, we fix the values of θ_0 and θ_1 that achieve the minimum energy and we change the bond length.

4 Results

After computing the expectation value of the qubit Hamiltonian Eq. (9), we search for the parameters (θ_0 and θ_1) that produce the lowest energy. Figure 4 represents the hydrogen molecular energies at the equilibrium bond length ($0.735 \text{ \AA}$) as a function of angles (ansatz parameters) θ_0 and θ_1 displayed in Figures 2 and 3. We note that the lowest (minimum) energy is almost equal to -1.1373053 Hartree and it occurs each and every time when θ_0 and θ_1 values are -1 rad. and 1 rad., respectively, and it is nearly equal to the standard value -1.13730604 Hartree,

obtained using QISKIT software in the full Hilbert space [13,18].

We fix θ_0 and θ_1 to be -1 and 1 rad., respectively, so that the minimum energy takes place and then we change the atomic distance of the two hydrogen atoms, we do this, to elucidate the effect of this distance on the binding energies and compare with the exact binding energies for the hydrogen molecule.

Figure 4 shows the experimental results of the ground-state energies of the hydrogen molecule, and these results are compared with the exact ground-state energies attained using the exact diagonalization of the molecular Hamiltonian. The black points in Figure 4 are computed using

Figure 4: Binding energy of the hydrogen molecule as a function of θ_0 and θ_1 .

Figure 5: Experimental results (black circles) when $\theta_0 = 1$ rad. and $\theta_1 = -1$ rad. vs exact energy surfaces (curve line) for different bond length values of the hydrogen molecule.

10,000 numerical optimizations at different inter-atomic distances (Figure 5).

5 Conclusion

The ground-state energies of the hydrogen molecule using our algorithm based on the QVP, are calculated and only through a simulator since the presented study system (i.e., hydrogen molecule) is relatively small and hence the ground state energies of this molecule are efficiently classically simulable using a simulator. Full details of this algorithm are explained. For this, complete descriptions of fermions–qubits and the molecular transformations of the Hamiltonian–qubit Hamiltonian, are given. The authors search for the parameters of the qubit system (θ_0 and θ_1) that yield the minimum energies of the system and also study the ground state energies as a function of the molecular bond length. In the future, the authors will go through more completed chemical structure to be simulated using the real noisy quantum processors along with the error mitigation.

Acknowledgements: The authors would like to express their sincerest thanks to the reviewers for their valuable suggestions and comments.

Funding information: The authors state no funding involved.

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.

Conflict of interest: The authors state no conflict of interest.

References

- [1] Feynman RP. Simulating physics with computers. *J Theor Phys.* 1982;21:467–88.
- [2] Lloyd S. Universal quantum simulators. *Science.* 1996;273:1073–8.
- [3] Abrams DS, Lloyd S. Simulation of many-body Fermi systems on a universal quantum computer. *Phys Rev Lett.* 1997;79:2586.
- [4] Cleve R, Ekert A, Macchiavello C, Mosca M. Quantum algorithms revisited. *Proc Roy Soc London Sect A.* 1998;454:339–54.
- [5] Aspuru-Guzik A, Dutoi AD, Love PJ, Head-Gordon M. Simulated quantum computation of molecular energies. *Science.* 2005;309:1704–7.
- [6] Helgaker T, Jorgensen P, Olsen J. *Molecular electronic-structure theory.* USA: John Wiley and Sons; 2002.
- [7] Veis L, Pittner J. Quantum computing applied to calculations of molecular energies: CH_2 benchmark. *J Chem Phys.* 2010;133:194106.
- [8] Grimsley HR, Economou SE, Barnes E, Mayhall NJ. An adaptive variational algorithm for exact molecular simulations on a quantum computer. *Nature Commun.* 2019;10:1–9.
- [9] Peruzzo A, McClean J, Shadbolt P, Yung MH, Zhou XQ, Love PJ, et al. A variational eigenvalue solver on a photonic quantum processor. *Nature Commun.* 2014;5(1):1–7.
- [10] McClean JR, Romero J, Babbush R, Aspuru-Guzik A. The theory of variational hybrid quantum-classical algorithms. *New J Phys.* 2014;18:4023023.
- [11] Bravyi S, Gambetta JM, Mezzacapo A, Temme K.. Tapering off qubits to simulate fermionic Hamiltonians. *arXiv:https://arXiv.org/abs/arXiv:1701.08213*, 2017.
- [12] Seeley JT, Richard MJ, Love PJ. The Bravyi-Kitaev transformation for quantum computation of electronic structure. *J Chem Phys.* 1982;137:224109.
- [13] QISKIT, www.qiskit.org.
- [14] Somma R, Ortiz G, Gubernatis JE, Knill E, Laflamme R. Simulating physical phenomena by quantum networks. *Phys Rev A.* 2002;65:42323.
- [15] Bravyi S, Gambetta JM, Mezzacapo A, Temme K. Tapering off qubits to simulate fermionic Hamiltonians. *arXiv:https://arXiv.org/abs/arXiv:1701.08213*, 2017.
- [16] Kandala A, Mezzacapo A, Temme K, Takita M, Brink M, Chow JM, et al. Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets. *Nature.* 2017;549(7671):242–6.
- [17] McWeeny R. *Methods of molecular quantum mechanics.* 2nd ed. United States: Academic Press; 1992.
- [18] Self C, Khosla K, Smith A, Sauvage F, Haynes P, Knolle J, et al. Variational quantum algorithm with information sharing. *NPJ Quantum Inform.* 2021;7:116.
- [19] Moll N, Fuhrer A, Staar P, Tavernelli I. Optimizing qubit resources for quantum chemistry simulations in second quantization on a quantum computer. *J Phys A.* 2016;49:295301.
- [20] Szabo A, Ostlund N. *Modern quantum chemistry: introduction to advanced electronic structure theory.* Courier Corporation. Revised edition. United States: McGraw-Hill; 1989.

Appendix A

In several specific examples, such as the hydrogen molecule and the Fermi–Hubbard model it has been observed that some qubits can definitely be removed from the simulation without loss of information [19]. Significantly, the elimination of qubits in these examples conserves a simple structure of the encoded Hamiltonian enabling efficient simulations with less qubits. This inspires the question of how to generalize these approaches and how to remove unwaged qubits in a computationally efficient manner for larger systems [11]. We generalize the methodology and consider a system of M fermi modes and assume that our target Hilbert space is the full Fock space $\mathcal{F}_M$. We consider encodings $\mathcal{E}$ such that:

$$\mathcal{E}|x\rangle = |Ax\rangle, \quad (\text{A.1})$$

where A is some $M \times M$ invertible binary matrix and Ax stands for the matrix–vector multiplication modulo two. Consider the Hamiltonian in Eq. (5) that describes a molecule with M spin orbitals. Consequently, each fermi mode, for example, p includes the spatial orbitals $i = 1, 2, \dots, M/2$, and the spin orientation $s = \uparrow$ or $\downarrow$. It is well known that molecular Hamiltonians based on the non-relativistic Schrodinger equation conserve the number of particles with a fixed spin orientation [20]. We order the M modes such that the first (the last) $M/2$ modes describe orbitals with spin up (spin down). Then

$$[H_{\text{molec}}, N^\uparrow] = [H_{\text{molec}}, N^\downarrow] = 0, \quad (\text{A.2})$$

where

$$N^\uparrow = \sum_{p=1}^{M/2} \alpha_p^\dagger \alpha_p \quad \text{and} \quad N^\downarrow = \sum_{p=M/2+1}^M \alpha_p^\dagger \alpha_p \quad (\text{A.3})$$

are the particle number operators for spin-up and spin-down modes. We assume that the symmetry in Eq. (14)

can be engaged to eliminate just two-qubits from the simulator Hamiltonian gained *via* the binary tree encoding that we use in this article. For a special case when $M = 4$, H_{elec} describes the hydrogen molecule. Let A be the matrix defined by Eq. (13). We note that the M th row of A has a form 1^M (the all-ones string). Moreover, the row $M/2$ has a form $1^{M/2}0^{M/2}$ as follows:

$$A = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix}. \quad (\text{A.4})$$

Also,

$$(Ax)_M = \sum_{p=1}^M x_p \quad (\text{mode } 2) \quad (\text{A.5})$$

and

$$(Ax)_{M/2} = \sum_{p=1}^{M/2} x_p \quad (\text{mode } 2). \quad (\text{A.6})$$

Comparing Eqs. (14), (17), and (18) one concludes that

$$\mathcal{E}(-1)^{N^\uparrow} \mathcal{E}^\dagger = Z_{M/2} \quad \text{and} \quad \mathcal{E}(-1)^{N^\uparrow + N^\downarrow} \mathcal{E}^\dagger = Z_M. \quad (\text{A.7})$$

From Eqs. (14) and (19) one infers that the simulator Hamiltonian $H_{\text{qubit}} = \mathcal{E}H_{\text{molecule}}\mathcal{E}$ commutes with Z_M and $Z_{M/2}$. This means that eigenvectors of H_{qubit} can be selected as eigenvectors of Z_M and $Z_{M/2}$. Therefore, when looking for the ground energy of H_{molec} in a variational approach one can replace Pauli operators Z_M and $Z_{M/2}$ by their eigenvalues ± 1 and remove qubits M and $M/2$ from the simulator system. Significantly, this elimination does not affect locality properties of the binary tree encoding, that is, the final Hamiltonian H_{qubit} acting on $M - 2$ qubits is a linear combination of Pauli-like operators with weight $O \log(M)$.