



# Quantum Computing

## Quantum Chemistry - Finding the minimum energy of molecules

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January 2023

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## Abstract

The variational quantum eigensolver (VQE) is explored to determine the minimum state energy of three molecules:  $H_2$ , NaH and  $BeH_2$ . For this, two different ansatzes were explored: UCCSD with a Hartree Fock initialisation and the hardware-efficient EfficientSU2, with the accompanying optimisers SPSA and SLSQP respectively. This method proved possible the computation of the minimum state energy of molecules, obtaining only a 4.38% error, in comparison to classical methods, in real hardware.

**Keywords:** *Quantum Computing; Chemistry; Molecule; Variational Quantum Eigensolver; Simulation*

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## 1 Introduction

Even though quantum mechanics was borne in the early 20<sup>th</sup> century with the ideas of well-known physicists such as Planck and Heisenberg, the concept of quantum computation only appeared in the 1980s with Richard Feynman [1]. After Richard Feynman proposed to use quantum mechanics phenomena, like superposition and entanglement, to perform computation, various researchers developed the theoretical foundations of quantum computation, quantum hardware, and software.

The basic unit of classical computers is a bit, a bit can be 0 or 1, i.e. bits only have two states. In contrast, the basic unit of quantum computers - qubit - can be in any superposition of the  $|0\rangle$  and  $|1\rangle$  states. This fact, allied with other quantum physics phenomena, makes quantum computers solve certain problems must faster than classical ones, such as factoring large numbers. In fact, even though without a practical utility, the first algorithm to show this quantum advantage was Deutsch-Jozsa one in 1992 [2]. Furthermore, while on classical computers, the logic gates are the basic operating unit on quantum devices the basic units are quantum (logic) gates. Quantum gates can be of one or two qubits and are unitary operators and so can be represented as unitary matrices, such as Pauli's matrices or controlled nots (cnot).

The promise that quantum computers could outperform classical ones and the vast amount of consequences that this brings, like easily breaking classical cryptography, led to massive financial and scientific investments in this area. As a consequence, currently, there are the so-called noise intermediate-scale quantum (NISQ) devices. These are near-term devices with a limited number of qubits that are not yet advanced enough for fault tolerance or large enough to achieve quantum supremacy. Even so, it has already been shown that these devices can outperform the traditional ones in some problems [3]. Attending to the characteristics of these computers, the algorithms running in real quantum hardware should require a small number of qubits, be resilient to noise, and consequently, have a moderate number of operations and quantum gates.

Despite these challenges and limitations, research in this area is still ongoing and considerable progress is being made. The research on quantum computation applications covers an extensive area that includes cryptography [4], machine learning [5], physics [6], biology [7], chemistry, and so on. This particular report focuses on quantum chemistry, more precisely finding the minimum energy of molecules.

One of the branches of chemistry is computational chemistry, where computer simulations and models are used to study chemical systems with aim of predicting their properties and behaviours. This has a significant impact on the development of new materials, drugs, and any kind of chemical process. Consequently, it is an area that has the attention of the scientific and industrial community. Even though there are a lot of classical methods to approximate the properties of chemical systems, for large systems, very accurate calculations are costly and require large amounts of computational power. One of the main reasons for this obstacle is that the correlations between the constituent electrons of molecular systems demand methods that scale exponentially with the size of the systems. This problem, jointly with the fact that molecular systems are ruled by quantum laws and that quantum systems exponentially increase with the size of the systems, was the motivation for investigating quantum algorithms and methods to solve and simulate chemical problems.

Therefore, some quantum algorithms and sub-routines that brought advantages to computational chemistry appeared. These include quantum phase estimation (QPE) - used to estimate the eigenvalues of a unitary operator, which can be used to determine the energy levels of a molecule -, variational quantum eigensolver (VQE) - uses a combination of quantum and classical computing to find the lowest-energy state of a molecule, by applying a sequence of unitary transformations to a trial wave function -, quantum approximate optimisation algorithm (QAOA) - also uses a combination of quantum and classical computing to find approximate solutions to optimisation problems -, quantum Monte Carlo (QMC) - simulate the behaviour of electrons in a molecule, and can be used to calculate properties such as the electronic structure -, etc.

In this report, the variational quantum eigensolver (VQE) is explored to determine the lowest-energy eigenstate of three molecules,  $H_2$ ,  $NaH$  and  $BeH_2$ . Finding the lowest-energy eigenstate of systems can not be easy and requires sophisticated techniques, but knowing it can be critical because it often corresponds to the most stable and long-lived state of a system. Particularly, the properties of a material, such as its conductivity or magnetism, are closely related to the electronic structure of this state. In addition, in condensed matter physics, the ground state of a system is the starting point for understanding its behaviour at low temperatures and phenomena such as superconductivity and quantum magnetism.

This report is divided into 6 sections, in this one, an introduction and motivation to the problem were made. In the second one, the mathematical, chemistry, and physics principles are exposed, the algorithm is presented and some important considerations are pointed out. Next, in the third one, the implementation used is discussed. In the fifth one, the results are discussed, the conclusions are made and future work is exposed. The last is simply the acknowledgements.

## 2 Methods

In order to solve the problem of finding the minimum energy of a molecule, or system, it's convenient to start by refreshing the relevant ideas of the Hamiltonian of molecular systems and to know to map it into quantum circuits, [subsection 2.1](#). It's also needful to understand how the chosen hybrid algorithm works and its mathematical foundations, [subsection 2.2](#).

## 2.1 Molecular Systems

As already referred, it's desired to find the minimum energy of a molecular system, so in some way, the Hamiltonian representative of the system must be obtained. Although along this report the Hamiltonian of the molecules and its representation in terms of qubit operators was obtained through the use of functions already implemented on the module *Qiskit Nature*, for a reader more comfortable with mapping molecular dynamics into second quantization operators, this process can be made in a classical way (by hand) and the same point should be reached.

The molecular Hamiltonian is given by

$$H = -\sum_I \frac{\nabla_{R_I}^2}{M_I} - \sum_i \frac{\nabla_{r_i}^2}{m_e} - \sum_I \sum_i \frac{Z_I e^2}{|R_I - r_i|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} + \sum_I \sum_{J>I} \frac{Z_I Z_J e^2}{|R_I - R_J|}, \quad (1)$$

where the upper letters stand for the nucleus and lower cases for electrons,  $M_I$  is the mass of nucleus I,  $Z_I$  is the atomic number of nucleus I, and  $m_e$  is the mass of the electron. As you may already know, the Laplace operator of particle i is

$$\nabla_{r_i}^2 \equiv \nabla_{r_i} \cdot \nabla_{r_i} = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}. \quad (2)$$

Using the Born-Oppenheimer approximation, i.e. the behaviour of nuclei and electrons can be decoupled, since nuclei are much heavier than electrons, and so they do not move on the same time scale, the Hamiltonian with nucleus coordinators only as parameters is

$$H_{el} = -\sum_i \frac{\nabla_{r_i}^2}{m_e} - \sum_I \sum_i \frac{Z_I e^2}{|R_I - r_i|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|}. \quad (3)$$

Solving the non-relativistic time independent Schrödinger equation  $H_{el} |\Psi_n\rangle = E_n |\Psi_n\rangle$ , the ground state energy (minimum energy) is given by

$$E_0 = \frac{\langle \Psi_0 | H_{el} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}. \quad (4)$$

To solve this problem in a quantum computer the Hamiltonian in [Equation 3](#), should be rewritten in terms of second quantization operators, this is

$$\hat{H}_{elec} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s. \quad (5)$$

Above  $\hat{a}_p$  is an electron annihilation operator that removes an electron from an orbital with label p and, similarly,  $\hat{a}_p^\dagger$  is the creation operator that creates an electron on an orbital with label p. The weights of the operators are given by the molecular integrals below. In [Equation 6](#) and [Equation 7](#), there are the 1-body integrals and 2-body integrals, respectively.

$$h_{pq} = \int \phi_p^*(x) \left( -\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|R_I - r|} \right) \phi_q(x) dx \quad (6)$$

$$h_{pqrs} = \int \frac{\phi_p^*(x_1) \phi_q^*(x_2) \phi_r(x_2) \phi_s(x_1)}{|r_1 - r_2|} dx_1 dx_2 \quad (7)$$

The molecular orbitals ( $\phi_u$ ) can be occupied or virtual (unoccupied). In the above equations  $x_i$  denotes the spatial and spin coordinates, i.e.  $x_i = (r_i, \sigma_i)$ .

The Hamiltonian in [Equation 5](#) is written in terms of creation and annihilation operators (fermionic). These operators should be mapped into spin operators in order to encode the problem into states of quantum computers. There are different mappers to do this such as the Jordan-Wigner, the Bravyi-Kitaev and the Parity mapper. In this report, it was chosen to use the latter.

The parity encoding or parity mapper [\[8\]](#) encodes information about the parity of the orbitals occupied up to the  $j^{\text{th}}$  qubit in this qubit. If the number of orbitals up to the  $j^{\text{th}}$  qubit (inclusive) is even the spin state is  $|0\rangle$  and if it is odd  $|1\rangle$ .

Attending at this definition, given a certain fermionic state  $|v_0v_1...v_n\rangle$  it's possible to traduce it to a spin state  $|p_0p_1...p_n\rangle$  trough:

$$p_i = \sum_{j \leq i} v_j \bmod 2 = \sum_j [\pi_n]_{ij} v_j \bmod 2. \quad (8)$$

In the above expression, the operator  $\pi_n$  is a  $n \times n$  matrix as defined below.

$$\pi_n = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 1 & 1 & \dots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & 1 & 1 \end{pmatrix} \quad (9)$$

Interpreting this definition, if the parity change in the  $j^{\text{th}}$  qubit means that the  $j^{\text{th}}$  orbital is occupied. Contrarily, if the parity doesn't change means that the orbital is unoccupied.

Knowing that the fermionic operators give a minus sign when there is the state  $|1\rangle_{j-1}$  and a plus when there is  $|0\rangle_{j-1}$  and that changing the occupation of an orbital changes the parity of the following qubits, the parity transformation is given by

$$\begin{aligned} \hat{a}_j^\dagger &\rightarrow \frac{Z_{j-1} \otimes X_j - iY_j}{2} \otimes X_{j+1} \otimes \dots \otimes X_{n-1} \\ \hat{a}_j &\rightarrow \frac{Z_{j-1} \otimes X_j + iY_j}{2} \otimes X_{j+1} \otimes \dots \otimes X_{n-1} \end{aligned} \quad (10)$$

Even though the predefined functions deal with this calculation and transformations, it's obligatory to define some properties and approximations to obtain the representative Hamiltonian, just as made when calculating it classically (by hand). The information and definitions needed are:

- **Molecule geometry** : It's necessary to give the atoms of the molecule and their respective positions (relative positions);
- **Multiplicity and charge** : It's necessary to give the charge of the molecule and respective multiplicity (charge \* 2 + 1);
- **Basis** : The basis set is used to encode and approximate the orbitals. In this report it was used the STO-3G basis set;
- **Problem** : It's necessary to define the problem to solve. In this, just as presented in this section the problem is Electronic Structure Problem;
- **Approximations** : To solve this problem more efficiently it's possible to use the freeze core transformer to "remove" the core orbitals and only account for valence ones. Further, it's possible to remove some of the valence orbitals but it's necessary to a priori know that they are unoccupied (or not relevant);
- **Mapper** : As explained in this section there are different mappers, consequently, it's necessary to define which mapper to use. As referred it was used the Parity mapper.

## 2.2 VQE

The Variational Quantum Eigensolver (VQE) was first proposed in 2014 by a team of scientists at Google and NASA, and it has since become a popular method for solving quantum chemistry problems. It's a hybrid quantum-classical algorithm for finding the ground state energy (or lowest-energy state) of a given quantum system, such as a molecule, which is often a difficult problem to solve, as already mentioned. It uses a quantum computer to prepare trial states and a classical computer to optimise the parameters of those states, and the idea is to use a parameterised quantum circuit to prepare a state that approximates the ground state of the system and then use classical optimisation techniques to find the best set of parameters that minimise the energy of the state.

Historically, finding the ground state energy of a molecule was a difficult task that required a significant amount of computational resources. Traditional quantum chemistry methods such as the

Hartree-Fock method and density functional theory are accurate but computationally expensive, making them infeasible for large systems. VQE was developed as a way to find the ground state energy of a molecule (or system) using a quantum computer, which has the potential to perform certain calculations exponentially faster than classical computers and is expected to be a key component of the future of quantum computing.

The main steps of this algorithm can be summarised as follows:

1. **State preparation** : A parameterised quantum state ( $|\Psi(\vec{\theta})\rangle$ ) is prepared through the application of a parameterised unitary  $U(\vec{\theta})$  to an initial state  $|\Psi_0\rangle$ . The initial state can be a state of the computational basis. The parameterised unitary is determined by the choice of the ansatz;
2. **Energy estimation** : The expectation value of the energy is determined through the Hamiltonian averaging process ( $\langle\Psi(\vec{\theta})|H|\Psi(\vec{\theta})\rangle$ ). Except for the *statevector simulator*, this involves taking the expectation value of the tensor products of the unitary (Pauli) terms presents in the qubit representation of H;
3. **Classical optimisation** : A classical optimiser is used to adjust the parameters ( $\vec{\theta}$ ) of the unitary operations to minimise the expectation value of the energy;
4. **Repetition** : The above steps are repeated until the energy converges to the ground state energy of the molecule or the defined maximum number of iterations is reached.

The described pipeline, or illustration of the algorithm, can be visualised in [Figure 1](#).

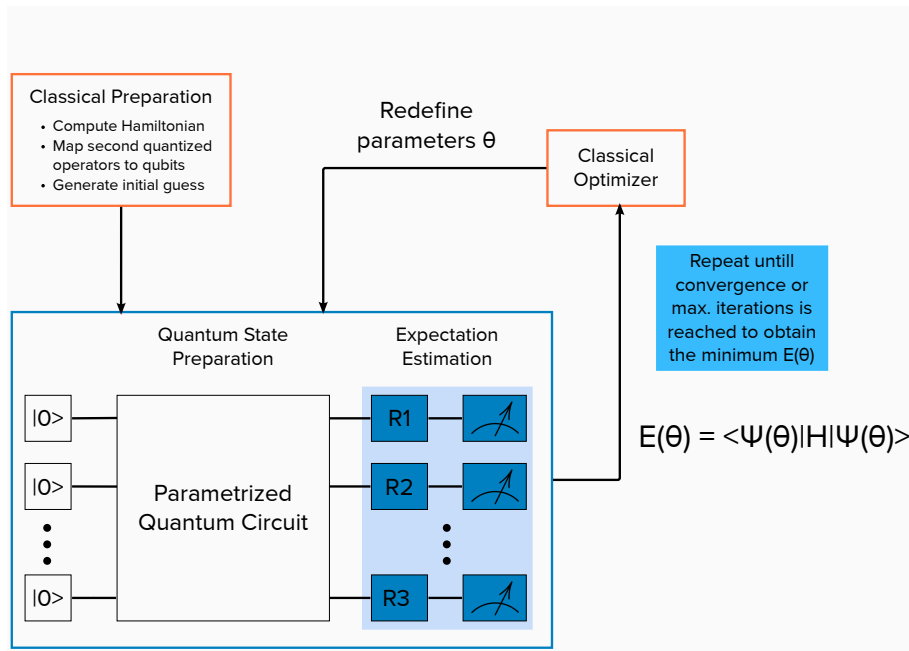


Figure 1: Variational Quantum Eigensolver Pipeline.

After giving the big picture of the VQE algorithm, in the following subsections some details and mathematical principles of the ansatz ([subsection 2.2.1](#)) and the classical optimiser ([subsection 2.2.2](#)) will be explored.

### 2.2.1 Ansatz

As already mentioned, the parameterised quantum state or trial wavefunction is constructed by the application of a parameterised unitary to the initial basis state  $|\Psi_0\rangle$ . The parameterised unitary is determined by the selected ansatz and there are two main different groups of anstazs. These are the Coupled Cluster (CC) Ansatz and the Heuristic Ansatz.

The Qiskit’s function that implements the Heuristic Ansatz is the *EfficientSU2*. The circuit of this kind of unitary consists of layers of  $SU(2)$ <sup>1</sup> followed by entanglement layers (cnot), just as in [Figure 7](#). As the name points out, this kind of Ansatz is known for having worse performance in simulation (ideal scenario) but they use fewer gates which is advantageous for real devices.

In UCCSD Ansatz, the state vector is parameterised as follows:

$$|\Psi(\vec{\theta})\rangle = e^{T(\vec{\theta}) - T^\dagger(\vec{\theta})} |\Psi_0\rangle \quad (11)$$

Consequently, the unitary is  $e^{\hat{T}(\vec{\theta}) - \hat{T}^\dagger(\vec{\theta})}$  where  $\hat{T}(\vec{\theta}) = \hat{T}_1(\vec{\theta}) + \hat{T}_2(\vec{\theta}) + \dots + \hat{T}_n(\vec{\theta})$ . The Qiskit’s function that implements this one is UCCSD (UCC single double), and so  $\hat{T}$  is restricted to the first two terms. Mathematically, these two terms are

$$\begin{aligned} \hat{T}_1(\vec{\theta}) &= \sum_{i,m} \theta_i^m \hat{a}_m^\dagger \hat{a}_i, \\ \hat{T}_2(\vec{\theta}) &= \sum_{i,j,m,n} \theta_{i,j}^{m,n} \hat{a}_n^\dagger \hat{a}_m^\dagger \hat{a}_j \hat{a}_i. \end{aligned} \quad (12)$$

Please note that  $\vec{\theta} = \{\{\theta_i^m\}, \{\theta_{i,j}^{m,n}\}\}$ . In circuit representation, this ansatz is exemplified in [Figure 6](#).

This ansatz can achieve better results than the other but requires a larger number of gates which is problematic in NISQ-era devices [\[9\]](#).

Concluding, the UCCSD usually yields better results when compared to its counterpart but due to the effects of noise increase as the number of two-qubit gates circuit depth increases, the heuristic variational and hardware efficient form *EfficientSU2* was seen as a good alternative to its shallower circuits and substantially fewer two-qubit gates.

### 2.2.2 Classical Optimiser

Attending to the finality of the application an appropriate classical optimiser should be chosen. Sometimes the choice of the correct optimiser is not a straight path because quantum hardware is affected by different types of noise that have implications on the cost function, etc. In the work developed, there are essentially two different situations: noise is present or it isn’t.

When noise isn’t present in the cost function evaluation (state vector simulation), various classical optimisers can be used. One of the appropriated optimizers presented in Qiskit nature is the Sequential Least Squares Programming optimiser (SLSQP).

On the other hand, an appropriate optimizer to optimize the parameters of a circuit is the Simultaneous Perturbation Stochastic Approximation optimizer (SPSA). This method approximates the gradient of the objective function using only two measurements, by concurrently perturbing all parameters randomly, as opposed to gradient descent which perturbs each parameter independently.

## 3 Implementation

The goal of this report is to find the lowest-energy state of a molecule. Since the energy of a molecule depends on the distance between its atoms, it is necessary to compute the ground-state energy of the molecule, for different distances between its atoms to find the distance that minimises the energy. The process starts by defining the molecule this is, its geometry (where the atoms are placed, multiplicity and molecule charge), electronic structure (we’re taking advantage of *PySCF* driver and representing the molecule in the *sto3g* basis), properties (e.g the number of particles and number of spin orbitals) and an electronic structure problem given the freeze core approximation (fixed nucleus - only valence orbitals matter for the interaction, as mentioned in [subsection 2.1](#)). After all of this, it’s possible to obtain the Hamiltonian described in terms of its second quantization, and by converting it into a qubit operator and applying the two-qubit

<sup>1</sup> $SU(2)$  is the special unitary group of degree 2. Its elements are unitary and have determinant 1. This group includes the Pauli rotation gates.

reduction<sup>2</sup> when possible the final qubit operator is obtained. These operators will be used to obtain the eigenvector of the Hamiltonian.

The Hamiltonian lowest-energy eigenvector for each distance will be obtained by the VQE algorithm, and, in this work, different approaches will be explored. The first step is initialisation which embeds the trial wave function through a parameterised unitary. For this, two different methods were explored, [subsubsection 2.2.1](#): Unitary Coupled-Cluster Single and Double (UCCSD) with a Hartree Fock initialisation and the hardware efficient SU(2) 2-local (EfficientSU2). This serves as the ansatz for the VQE which will be optimised, [subsubsection 2.2.2](#), by a Sequential Least Squares Programming (SLSQP) or by a Simultaneous Perturbation Stochastic Approximation (SPSA) optimizer.

Note that when the UCCSD ansatz was used it was also used Hartree Fock initialisation. In few words, the Hartree-Fock method assumes that the exact N-body wave function of a system can be approximated by a single Slater determinant (for fermions). Hence the trial wave function is assumed to be a single Slater determinant, which is a product of one-electron wave functions.

To evaluate the circuits, it is used three different backends (devices):

- **Statevector simulator** : To simulate the perfect scenario was used this simulator since it is the one that gives the results most efficiently. This happens because the expectation value of the energy is directly obtained by matrix products when there is access to the statevector. Contrarily, in the cases below, where the output is simply probabilities, it's necessary to measure the circuit on various basis to obtain the energy.
- **Noisy simulator** : When the number of qubits permits, it is also used a more realistic simulator, i.e a simulator that mimics the behaviour of a real device. The chosen real device was *ibm\_lagos*. Its calibration data can be found in [Appendix B](#).
- **Real quantum computer** : Just as in the previous point, when the number of qubits permits, it was used a real device to execute the circuits. The device used was *ibm\_lagos*.

With the aim of achieving better results, in the presence of noise, it was applied error mitigation techniques through the definition of the quantum instance<sup>3</sup>. The technique used is *CompleteMeasFitter*, where it is used a measurement calibration matrix to correct the circuit measurements. This matrix essentially encodes the probabilities of occurring bit flips for the initialisation in the different base states.

As a benchmark, the energy was also calculated using classical methods (Exact Energy), namely using the *GroundStateEigensolver* and *NumPyMinimumEigensolverFactory* functions.

## 4 Simulation & Exact Results

In this section, the ground state energy of different molecules will be computed by exact methods and by simulating quantum hardware with or without a noise model mimicking real devices. The ground state energy was calculated for the distances range [0.5, 3] Angstrom with a step size of 0.2 Angstrom. This range was chosen because the expected values were known a priori. To clarify the terms used exact results (energy), with notation abuse, stands for the ones found with the classical methods.

Accordingly to the [Computational Chemistry Comparison and Benchmark DataBase](#), the distance between atoms that minimises the lowest-state energy for each molecule and respective energy is in [Table 1](#).

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<sup>2</sup>The qubit reduction eliminates the central and last qubit in a list of Pauli that has diagonal operators (Z,I) at those positions. The chemical meaning of this approximation is beyond the scope of this report, although it is associated with the molecule's symmetries.

<sup>3</sup>The quantum instance holds a backend as well as the configurations for the circuit transpilation and execution.



Molecule	Minimum energy (Hartree)	Atoms' distance (Angstrom)
H <sub>2</sub>	-1.117506	0.712
NaH	-160.315703	1.654
BeH	-15.561353	1.291

Table 1: Expected minimum energy and respective inter-atomic distance for each molecule accordingly to the [Computational Chemistry Comparison and Benchmark DataBase](#). This values were obtained through the Hartree-Fock method.

The three molecules used are H<sub>2</sub>, NaH and BeH<sub>2</sub>. The latter is a triatomic molecule but has a linear configuration, consequently, it's only needed to compute the distance Be - H. Furthermore, the circuits for the first two molecules required 8 qubits, and since we only have access to devices with up to 7 qubits only the circuit for the latter could be executed in a real device.

Note that in the following sections, the VQE optimiser used a total of 100 iterations.

#### 4.1 H<sub>2</sub> Molecule

The ground state of the H<sub>2</sub> molecule was computed by using a noiseless and noisy simulation and real device ([subsection 4.4](#)). The first two were performed by the statevector and AerSimulator with the noise model from the real quantum hardware (*ibm\_lagos*), respectively. Has shown in [Figure 2](#), the methodologies used for the noiseless results were using the UCCSD ansatz with the SLSQP optimiser, and for the noisy results, it was chosen the Efficient SU(2) ansatz combined with the SPSA optimiser, as inferred in [section 3](#).

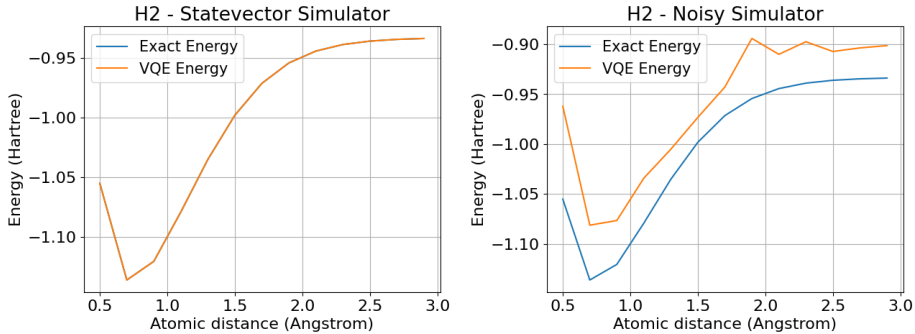


Figure 2: Simulation and exact results for the H<sub>2</sub> molecule.

The noiseless simulation obtains the minimum energy of  $-1.1361$  Hartree which is precisely the exact energy, and the noisy simulation gives  $-1.0581$  Hartree, which corresponds to a relative error of  $-6.87\%$ , both for a distance of  $0.7$  Angstrom.

#### 4.2 NaH Molecule

Following the same procedure as the previous section, the ground state energy of the *NaH* molecule was computed. Since the authors have limited access to IBM's Quantum API, the noisy simulation is missing due to a lack of access to quantum computers that possess 8 qubits - which was required for this particular molecule.

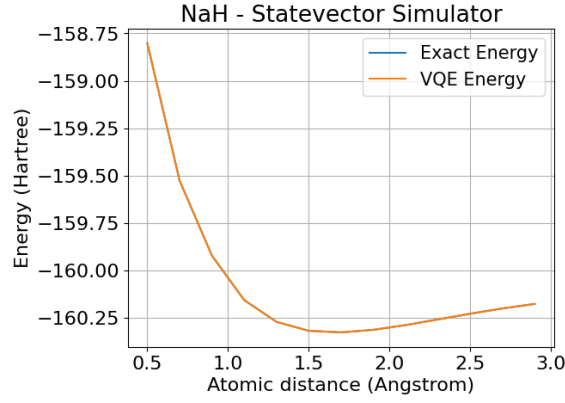


Figure 3: Results for the NaH molecule, using UCCSD ansatz and SLSQP optimiser.

By analysing Figure 3, the noiseless simulation obtains a ground state energy of  $-159.92214$  Hartree for a distance of 1.7 Angstrom, corresponding to the exact energy of the NaH molecules.

### 4.3 BeH<sub>2</sub> Molecule

Following the same procedure as the previous sections, the ground state energy of the BeH<sub>2</sub> molecule was computed.

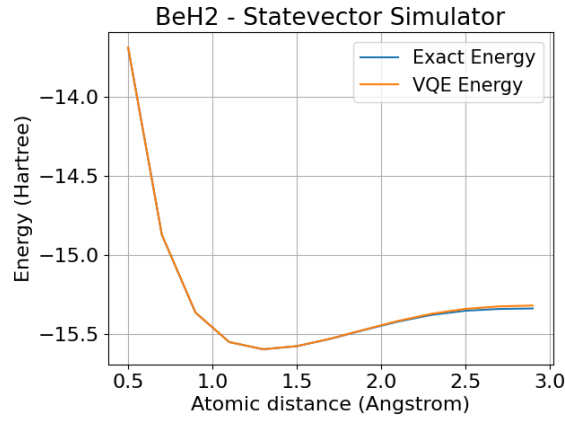


Figure 4: Results for the BeH<sub>2</sub> molecule, using UCCSD ansatz and SLSQP optimiser

By analysing Figure 4, the noiseless simulation obtains a ground state energy of  $-15.59436$  Hartree for a distance of 1.3 Angstrom, which is slightly different from the exact energy of  $-15.59471$  Hartree of the BeH<sub>2</sub> molecules, which represents an error of 0.002%.

### 4.4 Real Hardware Results - H<sub>2</sub> Molecule

For testing the feasibility of the methods discussed so far in real scenarios, the VQE algorithm using the EfficientSU2 ansatz and SPSA optimizer was run on real hardware. This differs from the methodology of the previous sections since it only uses 20 optimiser iterations instead of 100, due to limited access to real hardware.

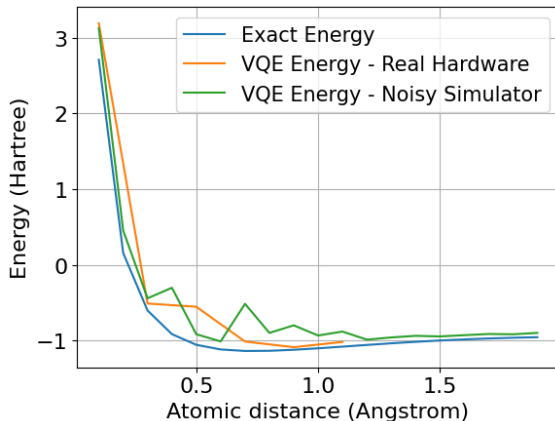


Figure 5:  $H_2$  results obtained using a VQE in *IBM Lagos* (See [Appendix B](#) for more information).

By analysis of [Figure 5](#), it's clear that even though real NISQ-era hardware presents itself as "noisy", the energy curve produced by the VQE when compared to the exact curve is very similar, effectively showing that it's possible to use quantum hardware to acquire the minimum state energy of a molecule.

In this case, the VQE on quantum hardware obtained a energy of  $-1.0864$  Hartree, for a distance of  $0.9$  Angstrom, which has a  $4.38\%$  error from the exact energy of  $-1.1361$  Hartree. Furthermore, the noisy simulator was run with the same number of optimiser iterations, which yielded energy of  $-1.01065387$  Hartree for a distance of  $0.6$  Angstrom, with a  $11.04\%$  error.

Rounding the expected distance to the first decimal case, [Table 1](#), only the results in this section don't correspond to the expected inter-atomic distance, this can be explained by the lack of iterations, since the noisy simulator with more iteration, [Figure 2](#), achieved the expected distance.

## 5 Conclusion

With the aim of finding the lowest-energy state of molecules, i.e. finding the inter-atomic distance that minimises the energy of the fundamental state, the Hamiltonian of the system in terms of qubit operators was computed and the minimum energy for various distances was found using the VQE algorithm and this Hamiltonian. Thereby the distance that minimises the energy and the respective energy were found.

Numerically speaking, according to the referred chemistry database, it was expected to find an energy of  $-160.316$  Hartree (rounded) for a distance of  $1.654$  Angstrom for the  $NaH$  molecule. For both the classical method and VQE computation the energy found was  $-159.922$  for a distance of  $1.7$ . Attending the distance step used, it was possible to find the nearest distance possible to the expected one. The energy found was quite the same too, since the distance is not ideal and even on the chemistry database the energy slightly varies with the method used. As far as  $BeH_2$  is concerned, the justification is the same. In this case, it was expected  $-15.561$  Hartree for  $1.291$  Angstrom and it was found  $-15.594$  Hartree (using the VQE) for a distance of  $1.3$  Angstrom. Finally, for the  $H_2$ , it was expected  $-1.117$  Hartree for a distance of  $0.712$  Angstrom. With the state vector simulation, it was found  $-1.136$  Hartree for a distance of  $0.7$  Angstrom, the distance is the nearest to the expected one and the energy is not the same but is not out of the range of energies in the database (calculated by other methods). The noisy simulation with  $100$  iterations has more erratic behaviour, although the energy found was  $-1.058$  Hartree for the same distance, which can be considered within the expected. When running on a real device, the energy found for this molecule was  $-1.086$  for a distance of  $0.9$  Angstrom. This is not exactly the expected results but it's important to stand out that, due to quantum computer access limitations, it was only possible to do  $20$  maximum iterations for each point. For fairest comparison, the noisy simulation was executed with the same number of iterations, in this case the energy found was  $-1.011$  for  $0.6$  Angstrom. Again, the results are not exactly the expected ones, which reinforces the idea that with a larger number of iterations the real quantum computer would probably give better results.

To sum up, even though with slight differences, it's possible to say that, in a general way, the distances that minimise the energy and respective energies were successfully found, even on real devices. For constructing more efficient circuits and achieving even better results, as future work, it would be nice to execute on real devices with more iterations and explore ways to reduce the number of qubits such as removing valence orbitals that don't have a significant impact (this implies a deeper chemical knowledge).

## 6 Acknowledgements

We acknowledge the use of IBM Quantum services for this work. The views expressed are those of the authors, and do not reflect the official policy or position of IBM or the IBM Quantum team. [10]

## A Appendix - Circuit Examples

For demonstration purposes in this section of the Appendix, the circuits for the different methods for ansatz construction are shown for the particular case of the  $H_2$  molecule.

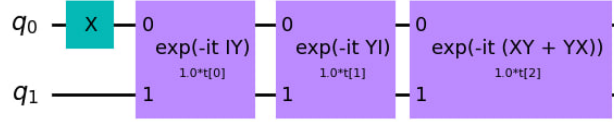


Figure 6: UCCSD ansatz.

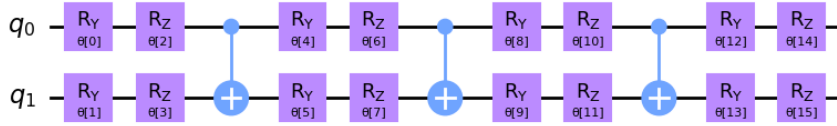


Figure 7: EfficientSU2 ansatz.

## B System properties

Throughout this work, *ibm\_lagos* quantum computer was used for real quantum hardware benchmarking. At the time of use, this was the latest available calibration data retrieved at 2023-01-14 05:44:19 UTC time.

Qubit	T1	T2	Frequency	Anharmonicity	Readout Error	Readout Length
0	130.981	44.223	5.235	-0.340	0.012	789.333
1	75.242	78.338	5.100	-0.343	0.021	789.333
2	132.230	164.934	5.188	-0.342	0.010	789.333
3	81.938	51.336	4.987	-0.345	0.015	789.333
4	156.550	30.965	5.285	-0.339	0.029	789.333
5	58.367	77.060	5.176	-0.341	0.039	789.333
6	187.291	45.064	5.064	-0.343	0.013	789.333

Table 2: Latest retrieved calibration data. The units for T1, T2 and Readout Length are *us*, for Frequency and Anharmonicity is *Ghz*.

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