Exploring Molecular Energy Landscapes of Hardware-Efficient Ansatze in Quantum Computing for Carbon Capture

Gopal Ramesh Dahale[1], Tom Magorsch[2] Amey Bhatuse[3]

[1] dahalegopal27@gmail.com,
[2] tommagorsch@gmail.com,
[3] ameybhatuse315@gmail.com

Abstract. One of the frontiers for the Noisy Intermediate-Scale Quantum (NISQ) era's practical uses of quantum computers is quantum chemistry. By employing Hybrid Quantum Classical Optimisation we aim to investigate the minimum of the Ground Potential Energy Surface (PES) of the BeH_2 molecule. Furthermore, we develop an algorithm that efficiently calculates the minimum of the PES for systems related to CO_2 capture using MOFs. We use a Variational Quantum Eigensolver (VQE) and focus on exploring the power of hardware-efficient ansatzes to improve the convergence of finding the ground state energy of the molecules. We study the latest paper published in this domain where the authors propose a simple deparameterisation procedure that reduces the number of trainable parameters while retaining high accuracy for the global minimum, simplifying the energy landscape, and hence speeding up optimization.

Keywords: VQE · BeH_2 · Carbon Capture · MOFs · Mn(II) · Cu(I) · Hardware-Efficient Ansatz · Deparameterisation

1 Introduction

Variational Quantum Eigensolver (VQE) is one of the successful quantum algorithm for calculating the ground state energy of molecules. However, the choice of the ansatz used to approximate the ground state is important in determining a close upper bound to the actual energy. There exists problem inspired ansatzes like UCCSD that utilizes the excitations present within the electronic structure of the molecules. As we know, these problem inspired ansatzes use multi-qubit gates and are high depth circuits. These are not suitable for the quantum hardware and infeasible due to limitations of NISQ devices.

With a focus on hardware-efficient ansatzes, we aim to improve the convergence of the VQE algorithm and make it feasible with current NISQ devices. We employ the methods presented in [Cho23] and extend them to carbon-dioxide capture with Metal Organic Frameworks (MOFs).

2 Direct Air Capture

Fig. 1 describes the process of direct air capture in a nutshell.

The technology's energy requirement is one of the biggest obstacles to overcome. Firstly, the atmosphere of the earth contains extremely diluted CO_2. As a result, a lot of air must pass through the filter in order to effectively capture CO_2. The ratio of the capture time to release time, which occurs throughout the two phases of CO_2 collection and release,

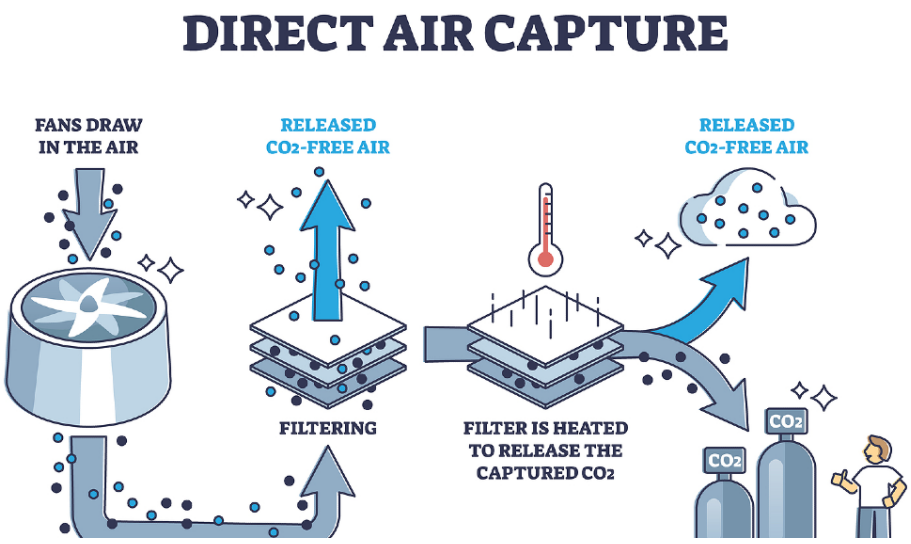

Figure 1: Direct Air Capture [pro]

directly relates to the filter's capacity. As a result, filters with a high capacity for CO_2 adsorption are generally desired.

We can use Metal-Organic Frameworks (MOFs) as filters for CO_2. To reduce the problem's complexity we focus on only the active binding site of the MOF i.e. the metal ion. Our objective is to use VQE for finding the minimum of the PES of a CO_2 with 2 metal ions $Mn(II)$ and $Cu(I)$ (separately). We run the algorithm on simulators and use the deparametrisation technique to make it suitable for running on noisy simulators and real hardware.

We consider only one metal ion at a time with fixed orientation and compute the minimum of the PES for a fixed distance between CO_2 and the metal ion. There also exist fragmentation strategies based on Density Matrix Embedding Theory as applied by [Gre22], but we will keep it simple here. Fig. 2 shows that the molecules (CO_2 with $Mn(II)$ and $Cu(I)$) lie on a single axis.

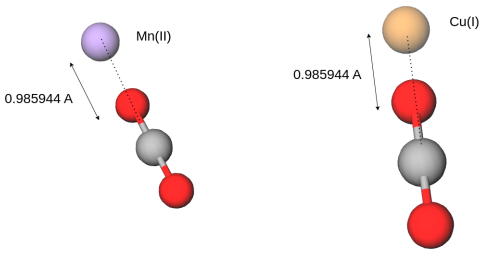

Figure 2: CO_2 with $Mn(II)$ and $Cu(I)$

3 Methodology

Assume we have the molecular hamiltonian constructed H. We use a hardware efficient ansatz for L layers as shown in the Fig. 3 below.

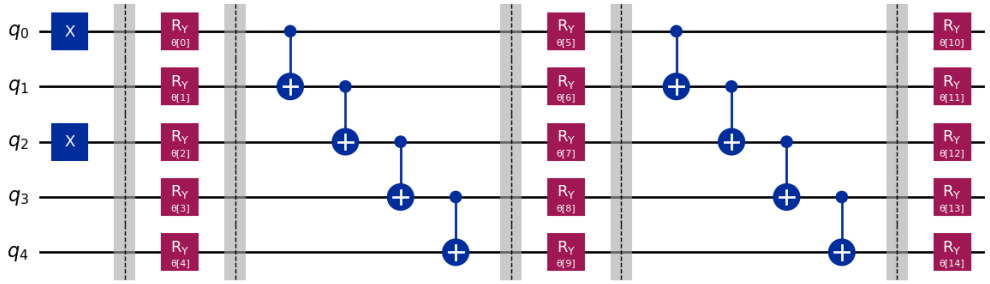

Figure 3: Hardware-efficient ansatz with 2 layers and initial Hartree-Fock state

[Cho23] formulates that for a given convergence criterion, as the number of layers of the hardware-efficient ansatz increases, it is expected that the increase in parametric expression and entangling power would allow for a better approximation of the ground state energy E_0 up to a certain minimum circuit layer depth L_{min}.

3.1 Deparameterisation

[Cho23] suggests that in some situations, when Hamiltonian is sufficiently sparse, producing a global minimum with an exact energy does not need full parametrisation of all R_y gates in a ansatz with depth L_{min} (or greater). Thus, a heuristic deparameterisation approach can be used to further minimise the number of parameter. The easiest implementation is the one described below.

A parametrised R_y gate is initially chosen and frozen by giving it a set rotation value. The preferred rotation amplitude is zero, however other standardised values, such as $\pm\pi/2$ or $\pm\pi$, can also be utilised. The former option is preferred for a number of reasons, including

- The ability to transform the R_y gate into a virtual identity gate that does not require actual implementation, which eliminates any related quantum gate noise.
- The computational cost of improving the parameter linked to that gate is likewise reduced in terms of software.
- Last but not least, we can build quantum circuits with more degrees of freedom for circuit translation by searching for as many virtual identity gates as possible. This may enable more effective mapping of the quantum circuit onto real quantum hardware and hence reduce its effective depth.

4 Results for Beryllium Di-hydride

BeH_2 is an alkaline earth hydride with 6 electrons. A full simulation of this molecule for finding the ground state energy will require 14 qubits. We will limit ourselves with 4 active electrons and 4 spatial orbitals and freeze the core. We first try to see which fermionic to qubit mapping has the lowest number of hamiltonian terms and uses the least number of qubits.

Mapper	with reduction		without reduction	
	#H	#qubits	#H	#qubits
Parity	135	6	119	5
Jordan Wigner	149	8	119	5
Bravyi Kitaev	149	8	119	5

As we can see that without any z2 symmetry reduction, ParityMapper has the lowest number of hamiltonian terms (135) and also the least number of qubits used (6). Upon using the z2 symmetry reduction, all the mappers have the same number of terms in their hamiltonian (119) and the same number of qubits (5). Without loss of generality, we use the ParityMapper with z2 symmetry reduction for our computations.

We select STO-3G basis for our analysis. We use NIST [Com] to obtain optimal structure of BeH_2 which has the bond length of 1.329 Å. The resulting energies are given below

```
=== GROUND STATE ENERGY ===
* Electronic ground state energy (Hartree): -18.949323143851
  - computed part:      -3.917749148316
  - ActiveSpaceTransformer extracted energy part: -15.031573995535
~ Nuclear repulsion energy (Hartree): 3.383298951396
> Total ground state energy (Hartree): -15.566024192455
```

The VQE only has to reach the computed part energy. The initial Hartree-fock state is $|10100\rangle$. We used the L_BFGS_B optimizer for maximum 30 iterations. For $L = 1$ layer circuit, The ideal simulation reaches the desired energy. The relative error is within 10^{-2} Hartree. We increase the layers from $L = 1$ to $L = 6$ and calculate the relative error in each case. Fig 4 shows the analysis of the result.

4.1 Inference

Increasing the number of layers resulted in a decrease in the relative error. The relative error 7.3×10^{-5} being the lowest at $L = 6$. With $L = 5$, we are within 10^{-3} relative error. Although, increasing the layers reduces the relative error, the optimizer time and the circuit depth increases drastically. Although we have the lowest relative error with $L = 6$ circuit, the number of gates grows up to 51 which comes with a cost of high noise.

For further analysis, we stick with the $L = 5$ layer circuit.

4.2 Deparameterisation of Layer 5 circuit

For the $L = 5$ circuit, we iteratively freeze the parameters. Moreover, we observe that several parameters in the global minima tend to have the standardised values of 0, $\pm\pi/2$ or $\pm\pi$. 4. We specifically froze parameter 12, 17, and 23 while keeping all other parameters active for the first run of the deparameterization method. The technique was then repeated until the maximum decrease of active parameters from 30 to 11 was achieved. With 11 parameters, we did not find any standardised values and hence we stop.

Initially, the relative error for $L = 5$ circuit was 0.00064 and the runtime was 24.7 seconds. After deparameterisation, the relative error increase to 0.00066. A 2.82 percent increase to be precise. However, the optimizer runtime reduces by 60.8 percent.

The time required for optimization is significantly impacted by the deparameterization procedure's significant simplification of the $L = 5$ circuit ansatz energy landscape and the decrease in computing cost brought on by optimising fewer parameters.

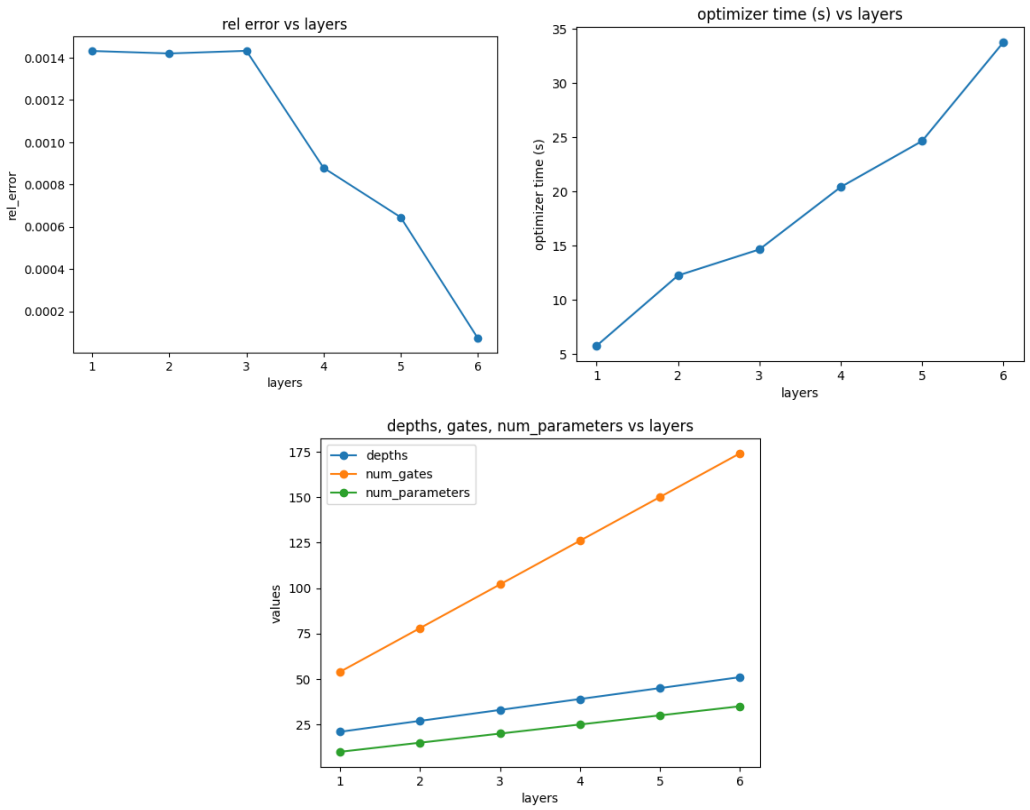

Figure 4: Results with L = 1 for BeH2

4.3 Results with BraketLocal Backend

We used BraketLocalBackend provided by the qiskit-braket-provider [com] to test our deparameterised circuit. The simulator is ideal. The results, as expected are close to the exact energy. The relative error being 0.00144, within 10^{-2} Hartree. The runtime was unexpectedly high 948 seconds i.e. ~16 minutes.

The qiskit-braket-provider is still in an early phase and requires more development on the side of simulators.

4.4 Results with Noisy Backend

We tested the reduced parameter circuit with the noisy sim as backend. Specifically, we used the FakeNairobi backend for local simulations. We used Qiskit's Backend Estimator Primitive [qisa] for this purpose. We tried different error mitigation schemes which is controlled by the parameter resilience level:

- 0: No mitigation
- 1: Twirled Readout Error eXtinction (TREX)
- 2: Zero Noise Extrapolation (ZNE)
- 3: Probabilistic Error Cancellation (PEC)

More details can be found here [qisb].

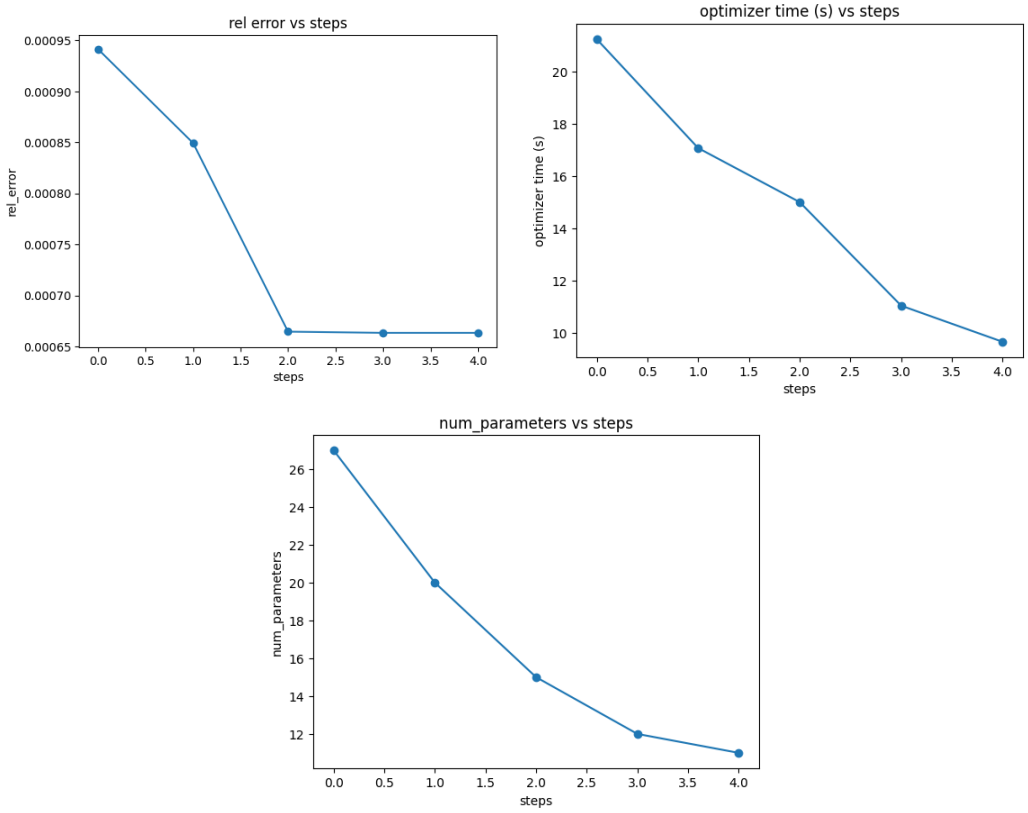

Figure 5: Deparameterisation of L = 5 circuit for BeH2

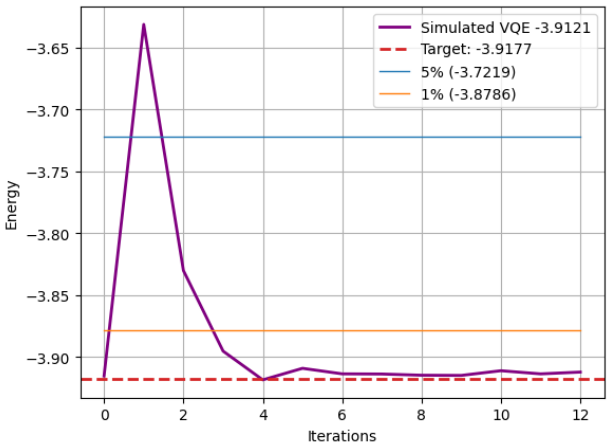

Figure 6: Convergence with Braket Local Backend (deparameterised circuit)

The relative error decreases as we increase the resilience level. We did not report the result with resilience level = 3 as it was not time effective. The least relative error is 0.068 with level = 2 which is within 6.7 percent the actual value. A more interesting result is that the runtime with level = 2 is the least of all the other levels. We need to perform further experiments on this topic.

The results are not within 1 percent due to high noise of the device and large number

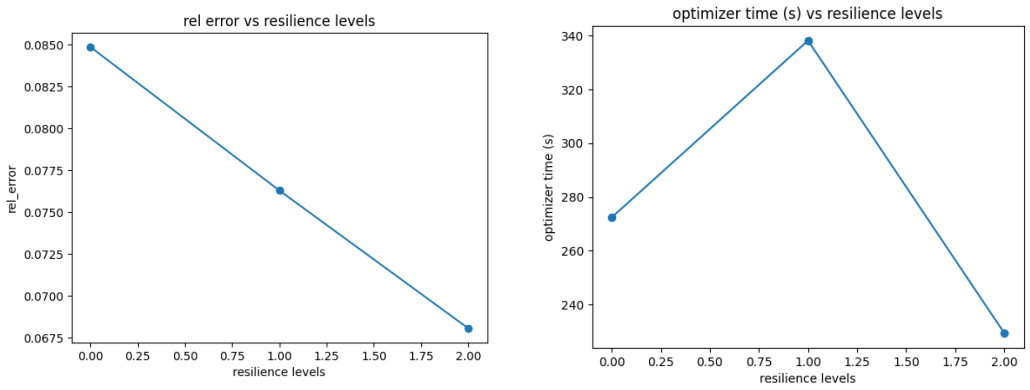

Figure 7: Results with deparameterised L=5 circuit on noisy simulator

of 2 qubit gates (20 CNOT gates).

5 Results for CO2 @ Mn (II) (Simulation)

For finding the reference energy of the system of molecules we use Quantistry [tea]. We get the Hartree-fock energy, Second-order Møller–Plesset perturbation theory (MP2 energy) and Coupled Cluster Singles and Doubles (CCSD energy) as reference.

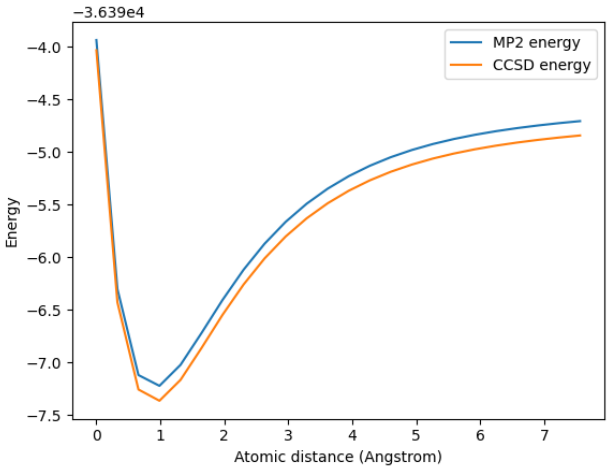

Figure 8: Reference solution for CO2 @ Mn (II)

For our analysis, we take the minimum CCSD energy and use the corresponding root mean square deviation (in Å). From the plot below, we chose the 0.986 Åas the distance between the $Mn(II)$ metal ion and CO_2 oxygen atom. The corresponding CCSD energy is -36397.363860 eV.

The results obtained from quantistry are with the ccpvdz basis, so we use it here. We consider all the electrons in system and try to find the number of spatial orbitals with which we can efficiently calculate the ground state energy.

We iterate over the num_spatial_orbitals from 3 till 10. Beyond 10, it was not feasible to proceed with the amount of time it takes to calculate the Hamiltonian.

5.1 Analysis with num_spatial_orbitals

We use Qiskit's NumPyMinimumEigensolver [qisc] to find the exact ground state energy of the system while varying the num_spatial_orbitals. Increasing the num_spatial_orbitals lead to increase the number of qubits needed to simulate the hamiltonian. The interesting part is the ground state energy which remains the same −36126.84103093809 eV. Only the absolute values of the computed energy and the ActiveSpaceTransformer extracted energy part changes.

The ground state energy as computed by the NumPyMinimumEigensolver is within 0.0074 relative error. Since the number of hamiltonian terms scales quickly with num_spatial_orbitals, we stick to num_spatial_orbitals = 3 for the analysis.

With 3 spatial orbitals, the goal is to use VQE to reach the computed part energy = −663.889337946369 Hartree. Note that Qiskit uses Hartree as the unit of energy. We need to multiply the result with '27.2114' to get result in eV. The resulting energies are given below

```
* Electronic ground state energy (Hartree): -1561.574491530425
  - computed part:      -663.889337946369
  - ActiveSpaceTransformer extracted energy part: -897.685153584056
~ Nuclear repulsion energy (Hartree): 233.938242350371
> Total ground state energy (Hartree): -1327.636249180054
```

With 3 spatial orbitals, we use SPSA optimizer for updating the parameters. Only a single layer of the Hardware-efficient ansatz is used (which still led to low relative error). Even after z2 symmetry reduction the number of hamiltonian terms are 100 and the number of qubits is 4. The computed Hartree-Fock state is $|1001\rangle$.

5.2 VQE Simulation Results

The algorithm sucessufully converges to the computed part energy in ~30 seconds with a relative error of 0.000014 that is within 10^{-4} Hartree. The relative error of VQE's ground state energy with the ground state energy of the NumPyMinimumEigensolver is calculated as follows:

- Total ground state energy by NumPyMinimumEigensolver (Hartree): −1327.63625
- Total ground state energy by VQE (Hartree) = VQE's computed part energy + ActiveSpaceTransformer extracted energy part + Nuclear repulsion energy = 1327.62723 Hartree

The relative error is 0.0000068 which is within 10^{-5} Hartree.

The relative error of VQE's ground state energy with the classical reference solution is calculated as follows:

- Convert Hartree to eV: $1327.62723 \times 27.2114 = -36126.59564$ eV
- Classical reference solution: −36397.36386 eV

The relative error is 0.0074 which is within 10^{-2} Hartree.

5.3 Deparameterisation of ansatz

We perfromed deparameterisation of the ansatz as we did previously with BeH_2. We observe that most of the parameters are in the vicinity of $-\pi/2$. We freeze these parameters and now we are left with only 3 parameters to optimize for. The optimization needed on 5

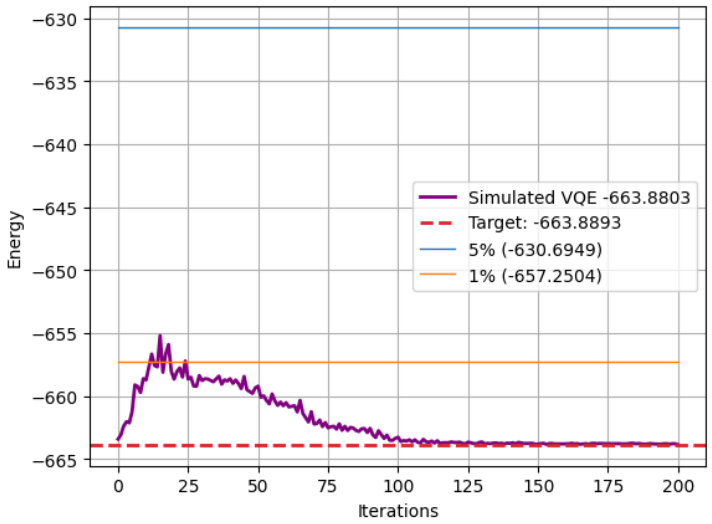

Figure 9: VQE Simulation for CO2 @ Mn (II)

iterations (~2 seconds, a 93.3 percent decrease in the runtime) with a relative errror of 0.0000094 (30 percent decrease).

The relative error of VQE's ground state energy with the classical reference solution is 0.00744 (a 0.0279 percent decrease).

5.4 Results on Noisy Backend

We tested the reduced parameter circuit with the noisy sim as backend. We try different error mitigation schemes which is controlled by the parameter resilience level.

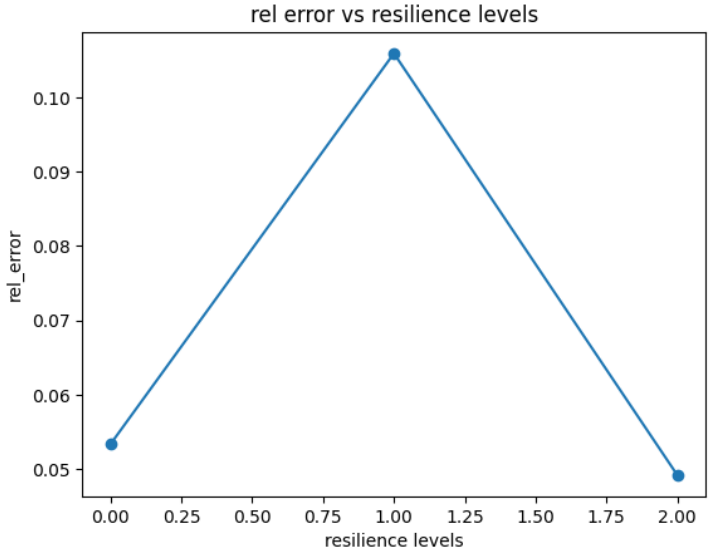

Figure 10: Results with deparameterised circuit on noisy simulator

The lowest relative error was achieved at resilience level = 3 with a value of 0.0492 which is within 5 percent the actual computed part energy. There is a rise in the relative

error with level=1 which is more than level=0 (no mitigation). The reason being that with no-mitigation, the result might have found a local minima by chance. We ran it few more times and verified it. We need to perform further experiments on this topic on noise mitigation.

6 Results for CO2 @ Cu (I) (Simulation)

We now aim to find the minimum of the PES of a CO_2 with $Cu(I)$. From the plot, we chose the 0.985944 Åas the distance between the $Cu(I)$ metal ion and CO_2 oxygen atom. The corresponding CCSD energy is -49727.23960 eV.

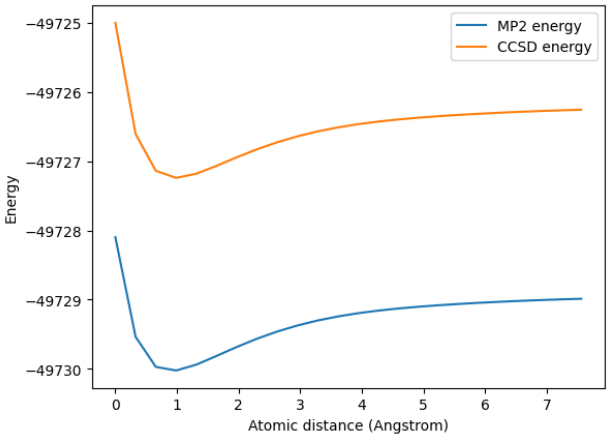

Figure 11: Reference solution for CO2 @ Cu (I)

We stick to num_spatial_orbitals = 4 spatial orbitals, we use the SPSA optimizer for updating the parameters. After z2 symmetry reduction the number of hamiltonian terms are 155 and the number of qubits is 5. The computed Hartree-Fock state is $|10101\rangle$. The resulting energies are given below

```
=== GROUND STATE ENERGY ===

* Electronic ground state energy (Hartree): -2086.990348710701
  - computed part:      -1029.241990884978
  - ActiveSpaceTransformer extracted energy part: -1057.748357825723
~ Nuclear repulsion energy (Hartree): 262.099737482148
> Total ground state energy (Hartree): -1824.890611228553
```

6.1 VQE Simulation Results

We run the algorithm with 150 iterations. The algorithm sucessufully converges to the computed part energy in ~35 seconds with a relative error of 0.0000014 that is within 10^{-5} Hartree.

The relative error of VQE's ground state energy with the ground state energy of the NumPyMinimumEigensolver is 0.000000765 which is within 10^{-6} Hartree.

The relative error of VQE's ground state energy with the classical reference solution is 0.00140 which is within 10^{-2} Hartree.

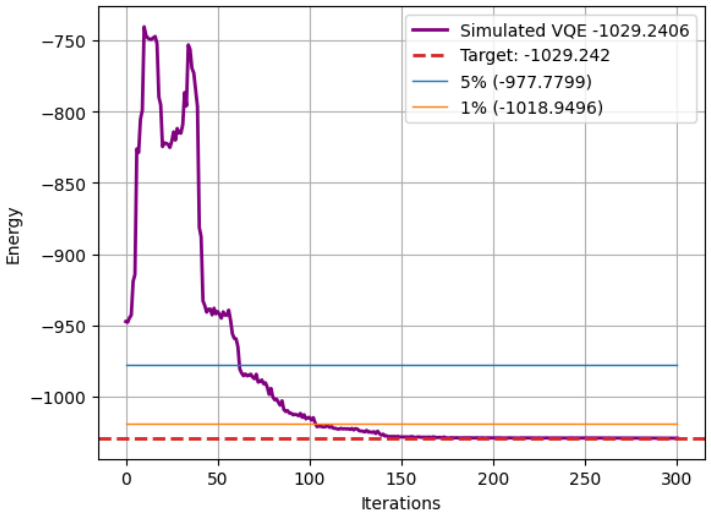

Figure 12: VQE Simulation for CO2 @ Cu (I)

6.2 Deparameterisation of ansatz

Again most the parameters were in the vicinity of $-\pi/2$. We freeze these parameters and now we are left with only 2 parameters to optimize for. The optimization needed 40 iterations (~9 seconds, a 74.2 percent decrease in the runtime) with a relative errror of 0.0000000405 (97 percent decrease).

The relative error of VQE's ground state energy with the classical reference solution is 0.00140 (a 0.053 percent decrease).

6.3 Results on Noisy Backend

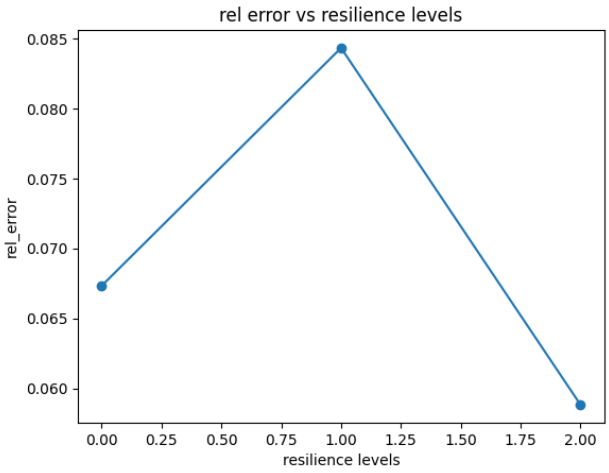

Figure 13: Results with deparameterised circuit on noisy simulator

The lowest relative error was achieved at resilience level = 3 with a value of 0.0588 which is within 6 percent the actual computed part energy. A similar trend is seen here as with $Mn(II)$ (rise in the relative error with level=1 which is more than level=0 (no

mitigation)).

7 Results for CO2 @ Mn (II) (Hardware)

We evaluated VQE on the real hardware for $CO_2@Mn(II)$ system. We use PennyLane [CT] for this purpose and it has pennylane-braket-plugin. Specifically, Rigetti — Aspen-M-3 [Tea] device which is based on superconducting qubits. The device contains 79 qubits but here we only use 4. We use pennyLane's grouping module to group hamiltonian terms and reduce circuit evaluations from 100 to 25. We use the deparameterised circuit and only run for 3 iterations with SPSA optimizer.

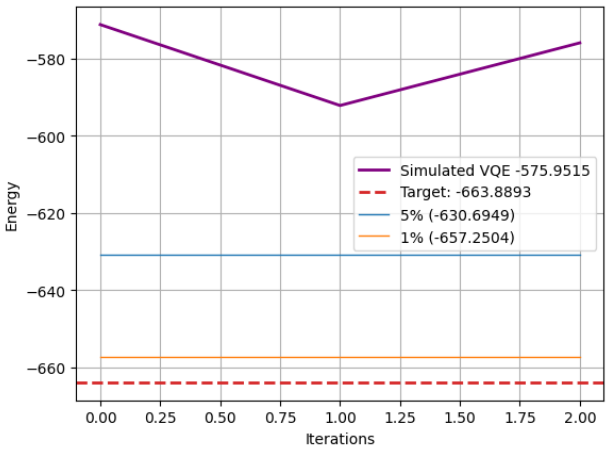

Figure 14: Results with Rigetti — Aspen-M-3

The algorithm halted with a relative error of 0.132. Unsuprisingly, the result has a very high relative error and needs more iterations to converge successfully to the ground state (which is costly in terms of money and time).

The relative error of VQE's ground state energy with the classical reference solution is 0.0732 which is within 101 (7.3 percent).

8 Conclusion

We investigated the minimum of the Potential Energy Surface (PES) based on the recent paper by Boy Choy and David J. Wales. We used a Hardware-efficient ansatz with varying depths for BeH_2 molecule and use the VQE algorithm. We used a deparameterisation approach to freeze R_y gates with standardized parameter values which helped in simplifying the energy landscape while maintaining the accuracy of the global minimum. For BeH_2, deparameterisation significantly reduced the number of trainable parameters while retaining the accuracy of ground state energy.

We extended the deparameterisation procedure to carbon capture on MOFs and explored the minimum of PES with CO_2 with 2 metal ions $Mn(II)$ and $Cu(I)$ which led to interesting results. For both the systems, we were able to reduce the parameters to 2 from 8 and 10 for the ansatz of $Mn(II)$ and $Cu(I)$ respectively. We simulated our ansatzes on noisy simulators as well as Braket's local and remote devices and obtained promising results. We employed error mitigation techniques in noisy simulators which converged the ground state energy to within 6 percent of the actual.

It is an exciting idea to employ quantum computing to profile molecular energy landscapes, and we intend to apply the techniques used here to investigate problem

inspired circuit ansatzes and compare them with hardware-efficient ansatzes in subsequent work.

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