



Analysis, Study and Improvement on Molecular Quantum Simulation Processes

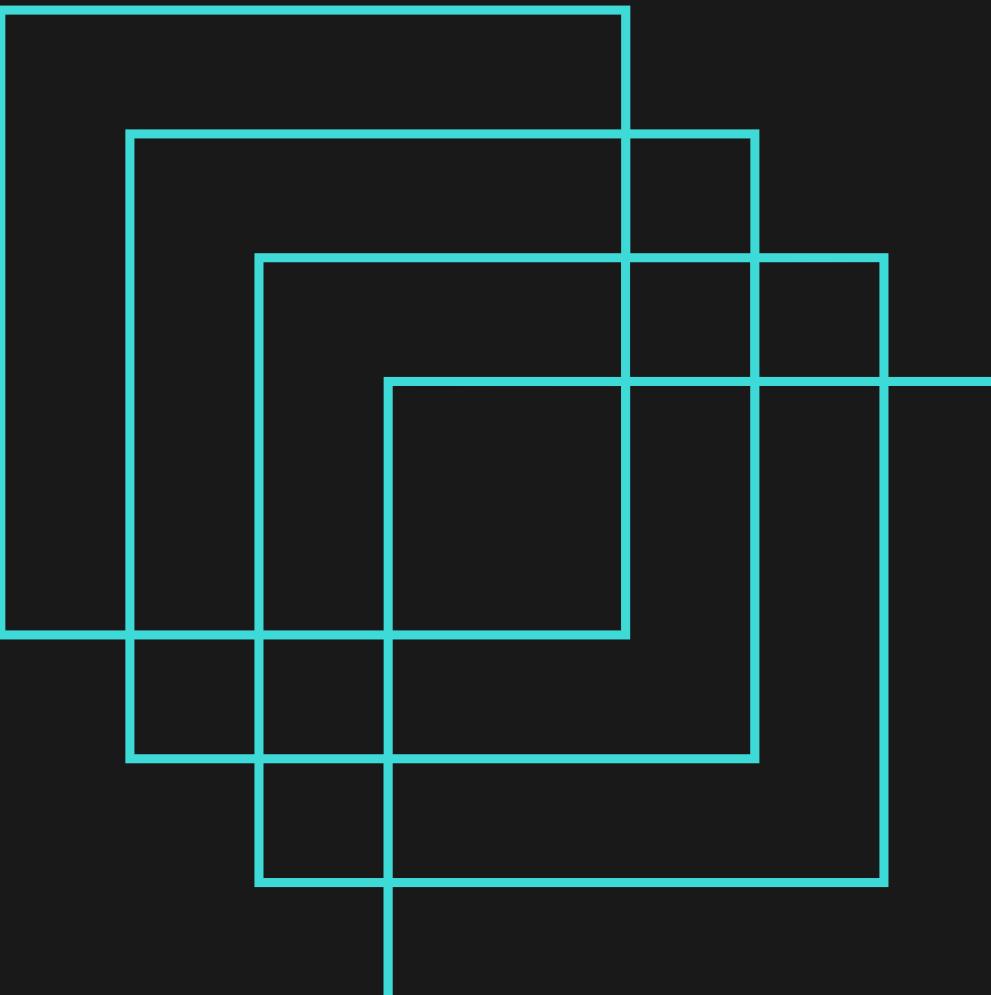
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Project Github Link:

<https://github.com/lmpawan10/Qiskit-Hackathon>

Group 11



Syllabus

- 1 Introduction
- 2 Objectives
- 3 Methodology
- 4 VQE - Optimization Subroutine
- 5 Further Developments

Introduction

Hamiltonian representation:

$$\mathbb{H} = - \underbrace{\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2}_{K_e} - \underbrace{\sum_I \frac{\hbar^2}{2m_I} \nabla_I^2}_{K_I} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V_{ee}} + \underbrace{\sum_{i,I} \frac{Z_I e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{R}_I|}}_{V_{eI}} + \underbrace{\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|}}_{V_{II}}$$

Hamiltonian of a molecule describes its total energy.

Replacing all the constants by 1,

$$\mathbb{H} = - \sum_i \frac{1}{2} \nabla_i^2 - \sum_I \frac{1}{2m_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Introduction

Born-Oppenheimer approximation:

Due to the significant difference in mass between nuclei and electrons, the electronic motion in a molecule can be treated independently of the nuclear motion

$$\hat{H} = - \sum_i \frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + E_{II}$$

Introduction

First Quantization:

We assume the two-electron wavefunction can be described as the Hartree product,

$$\psi_a(\mathbf{r}_1) \otimes \psi_b(\mathbf{r}_2)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = c_1 \psi_a(\mathbf{r}_1) \otimes \psi_b(\mathbf{r}_2) + c_2 \psi_c(\mathbf{r}_1) \otimes \psi_d(\mathbf{r}_2) + \dots$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i_1, i_2, \dots, i_N=1}^M c_{i_1, i_2, \dots, i_N} \psi_{i_1}(\mathbf{r}_1) \otimes \psi_{i_2}(\mathbf{r}_2) \otimes \dots \otimes \psi_{i_N}(\mathbf{r}_M)$$

Introduction

Second Quantization:

- Arrange the M orbitals into a binary string.
- Denote occupied and unoccupied orbitals as 1 and 0 respectively.

$$\mathbb{H} = \sum_{pq}^M h_{pq} c_p^\dagger c_q + \frac{1}{2} \sum_{pqrs}^M h_{pqrs} c_p^\dagger c_q^\dagger c_r c_s + E_{II}$$

$$h_{pq} = \int \psi_p^*(\mathbf{x}) \left[-\frac{1}{2} \nabla^2 + \sum_I \frac{Z_I}{|\mathbf{x} - \mathbf{R}_I|} \right] \psi_q(\mathbf{x}) d\mathbf{x} = \int \psi_p^*(\mathbf{x}) h_1(\mathbf{x}) \psi_q(\mathbf{x}) d\mathbf{x}$$

$$h_{pqrs} = \iint \frac{\psi_p^*(\mathbf{x}_1) \psi_q^*(\mathbf{x}_2) \psi_r(\mathbf{x}_2) \psi_s(\mathbf{x}_1)}{|\mathbf{x}_1 - \mathbf{x}_2|} d\mathbf{x}_1 d\mathbf{x}_2$$

Objectives

- To successfully calculate the energy of a molecule system.
- To optimize the Hamiltonian of a molecule with techniques like active space partitioning.
- To study the behaviour of a system under different orbital state conditions

Methodology

Project Block-Flow Diagram



Methodology

Ground-State Energy Approximation:

- Hartree Fock Method
- **Density Functional Theory**

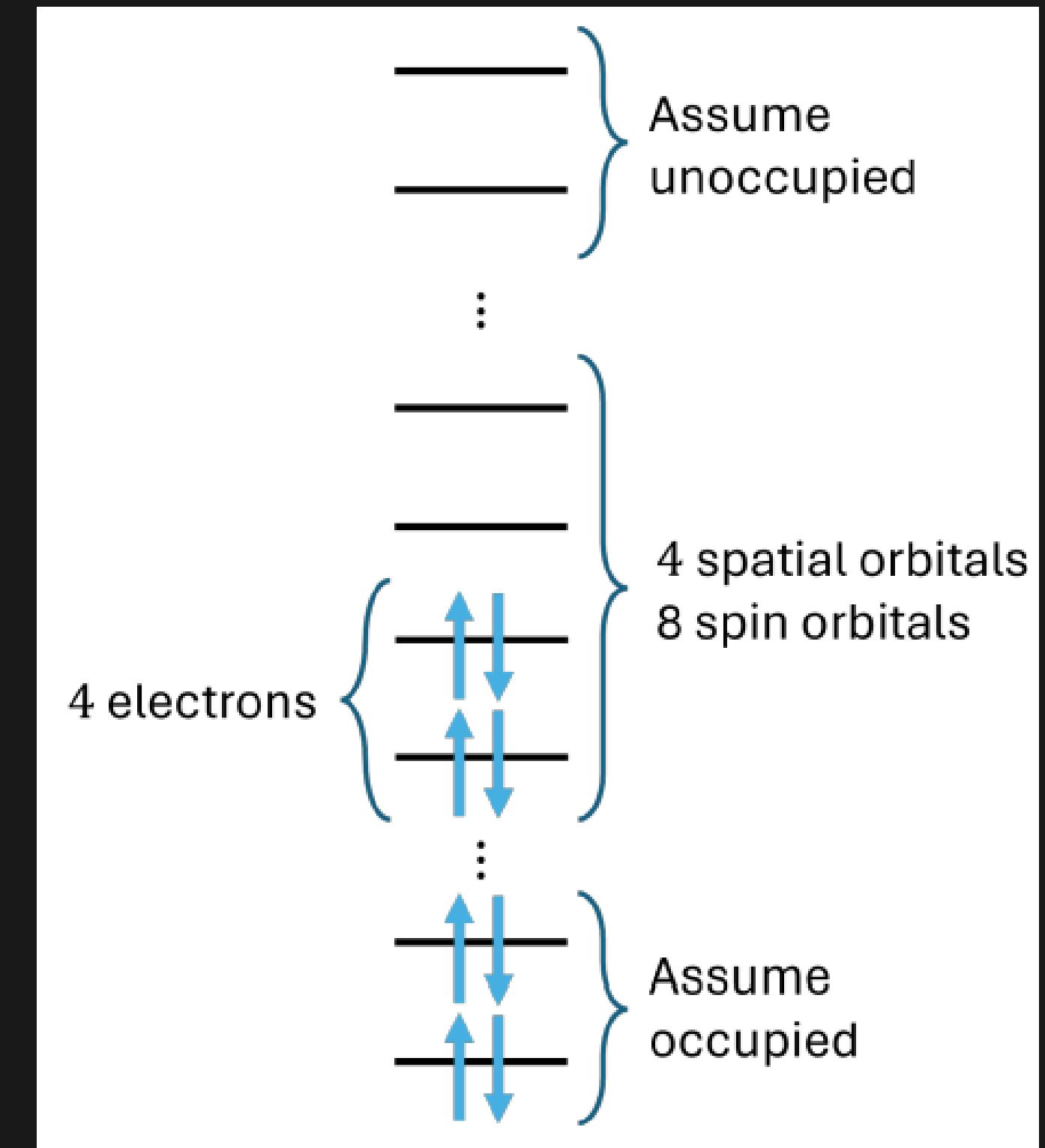
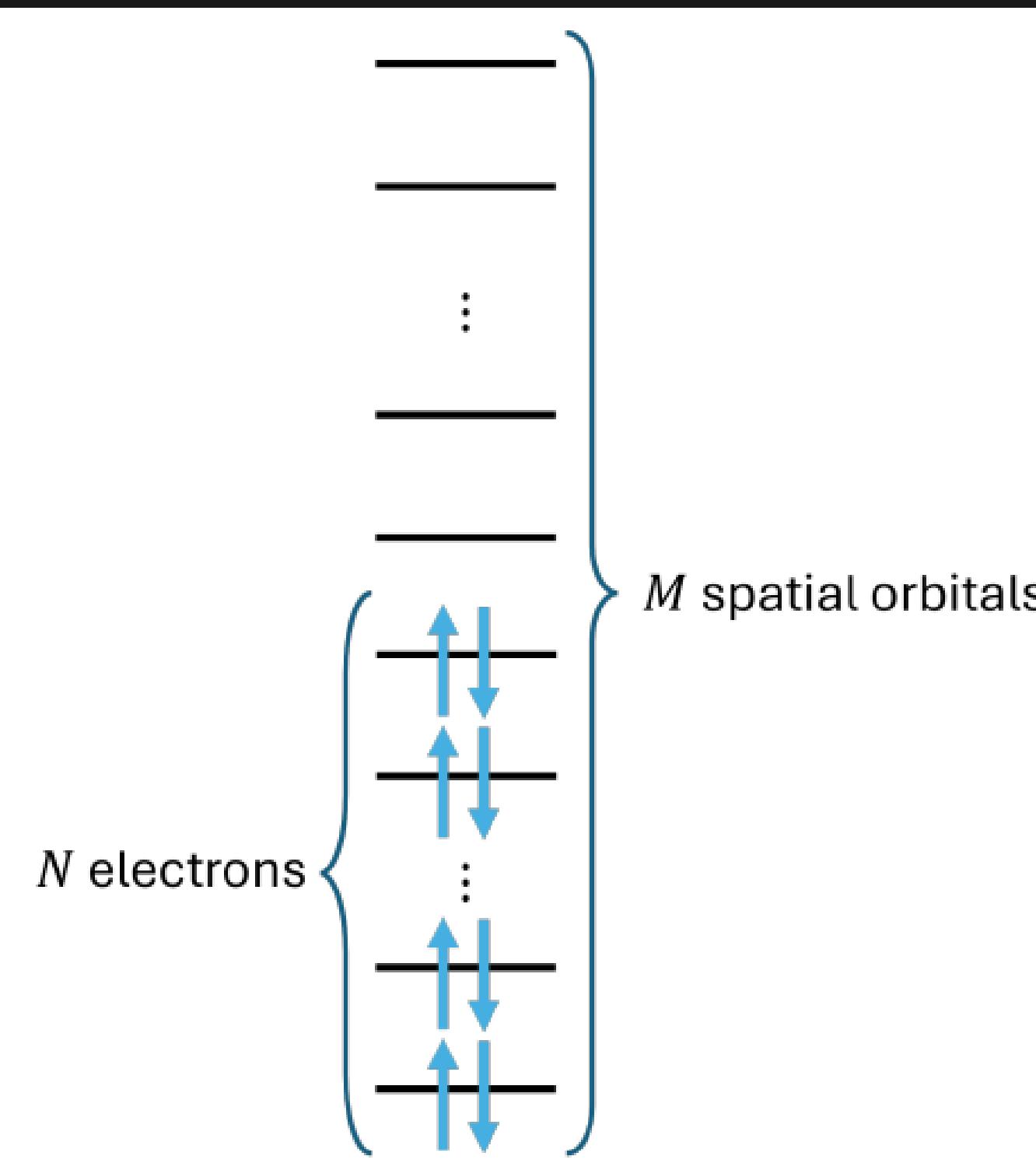
Methodology

Advantages of DFT:

- Inclusion of electron-correlation parameter
- Computationally efficient
- Large scale system implementation

Methodology

Active Space:



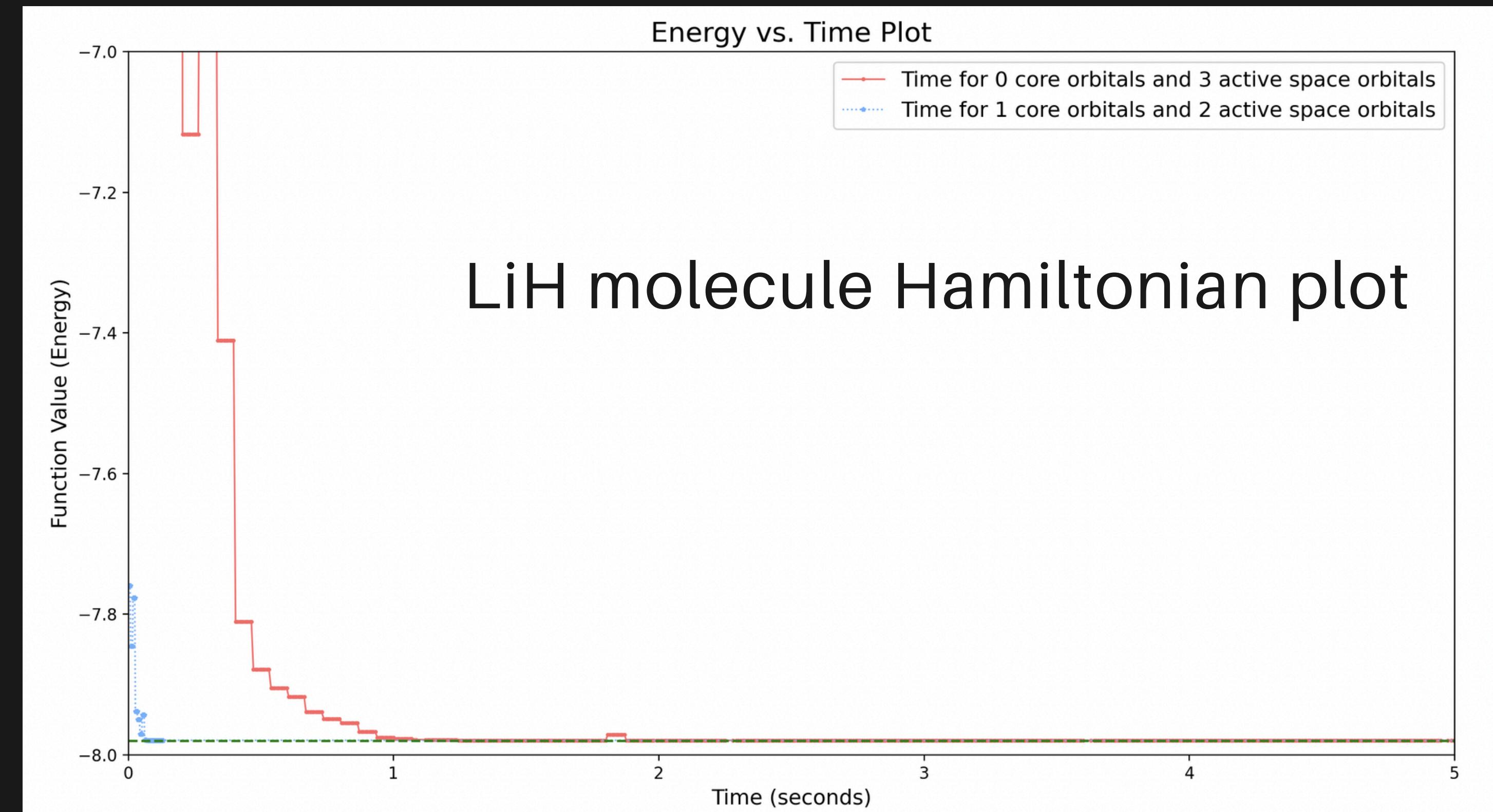
Methodology

Active Space:

Assumption:

The high orbitals are always empty, and the lowest orbital are always occupied.

Methodology



Methodology

Advantages of active space partitioning :

- Improves convergence
- Focuses more on a particular degree of freedom
- Computational cost reduction

Methodology

Simulation results for LiH molecule:

Table: Runtime and Energy comparison table for LiH molecule with 6-31G* basic

Number of Core Orbitals	Number of Active space orbitals	Energy (Hartee; 1 Hartree ≈ 27.2114 eV)	Total runtime (secs)
0	3	-7.979959198213003	3.1057791709899902
0	4	-7.980096	300+
1	2	-7.979549500610695	0.552283763885498
1	3	-7.978685811586303	2.7422380447387695
1	4	-7.980064348409336	20.006736755371094
1	5	-7.982995054328841	98.23914504051208

Methodology

Simulation results for LiH molecule:

Table: Runtime and Energy comparison table for LiH molecule with sto-3g basic

Number of Core Orbitals	Number of Active space orbitals	Energy (Hartee; 1 Hartree \approx 27.2114 eV)	Total runtime (secs)
0	3	-7.861989407601333	1.8872809410095215
0	4	-7.8621820765	300+
1	2	-7.860763646360443	0.24502110481262207
1	3	-7.861471364945881	1.876662015914917
1	4	-7.86229668686881	42.69442391395569
1	5	-7.88062969740972	196.66403698921204

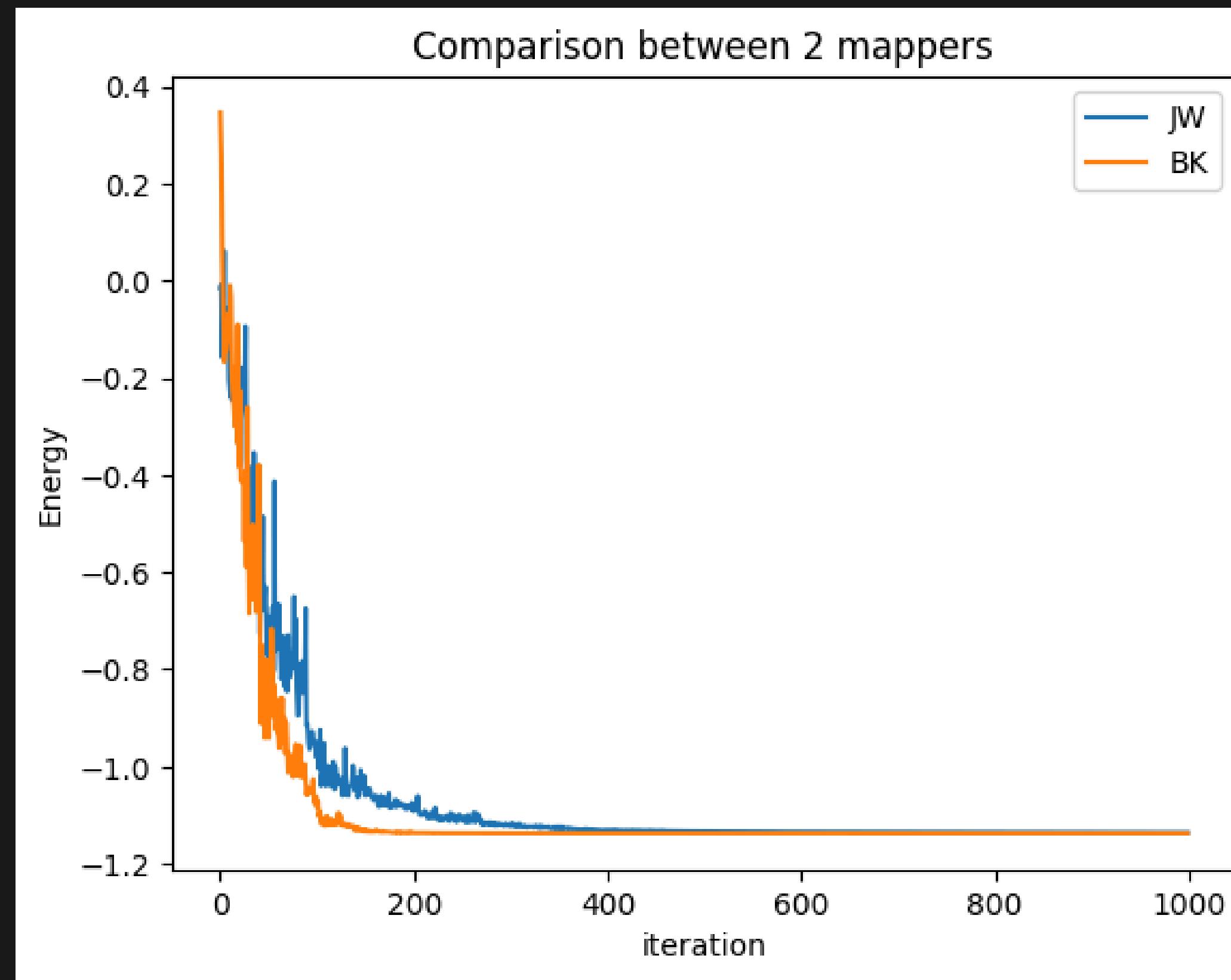
Methodology

Conversion to Polynomial Hamiltonian:

- JW (Jordan Wigner encoding)
- BK (Bravyi-Kitaev encoding)

Methodology

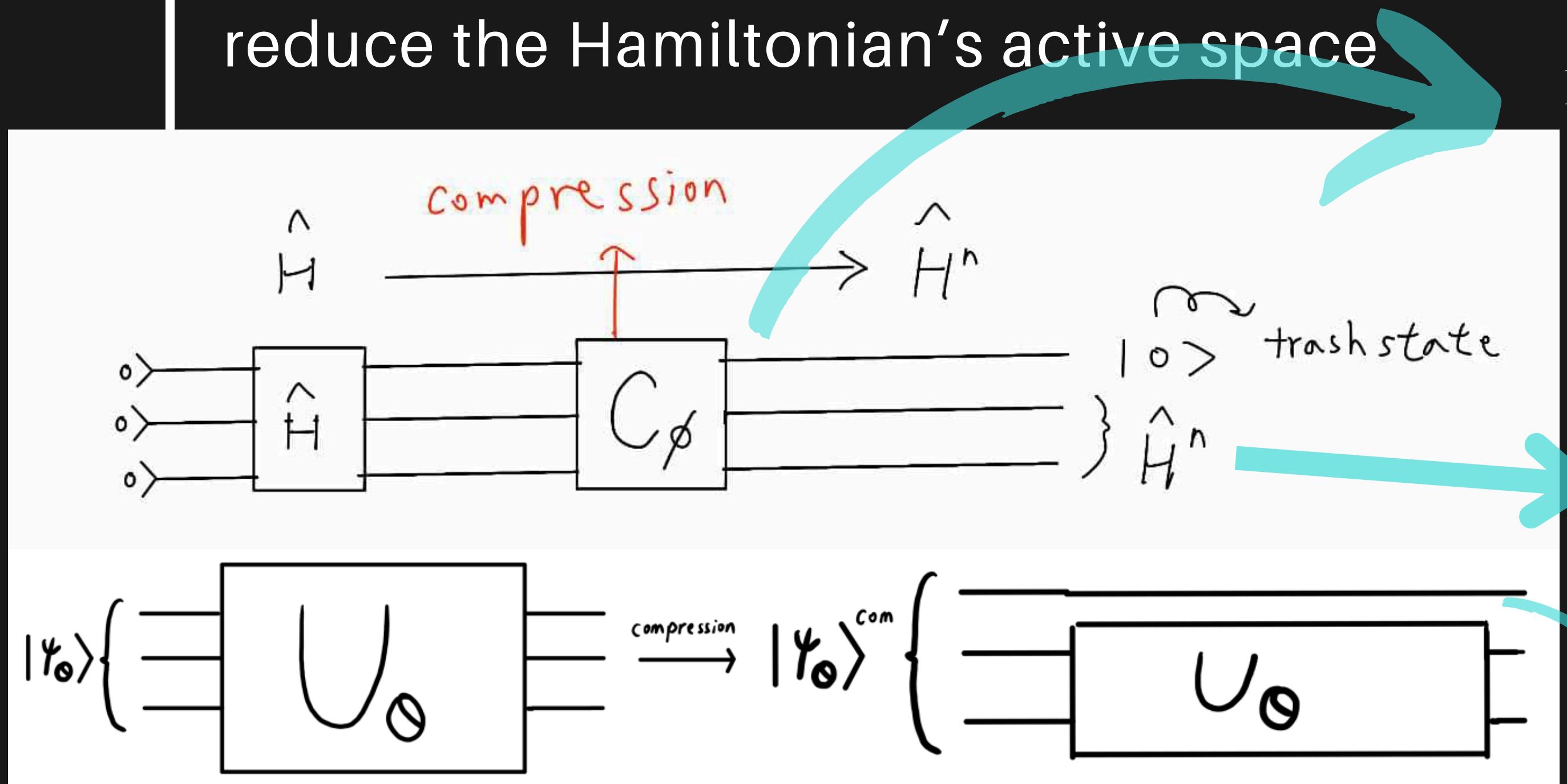
Jordan Wigner and Bravyi-Kitaev encoding(Energy vs. Iteration plot)



3

Hamiltonian Compression

Using The Quantum Autoencoder to
reduce the Hamiltonian's active space



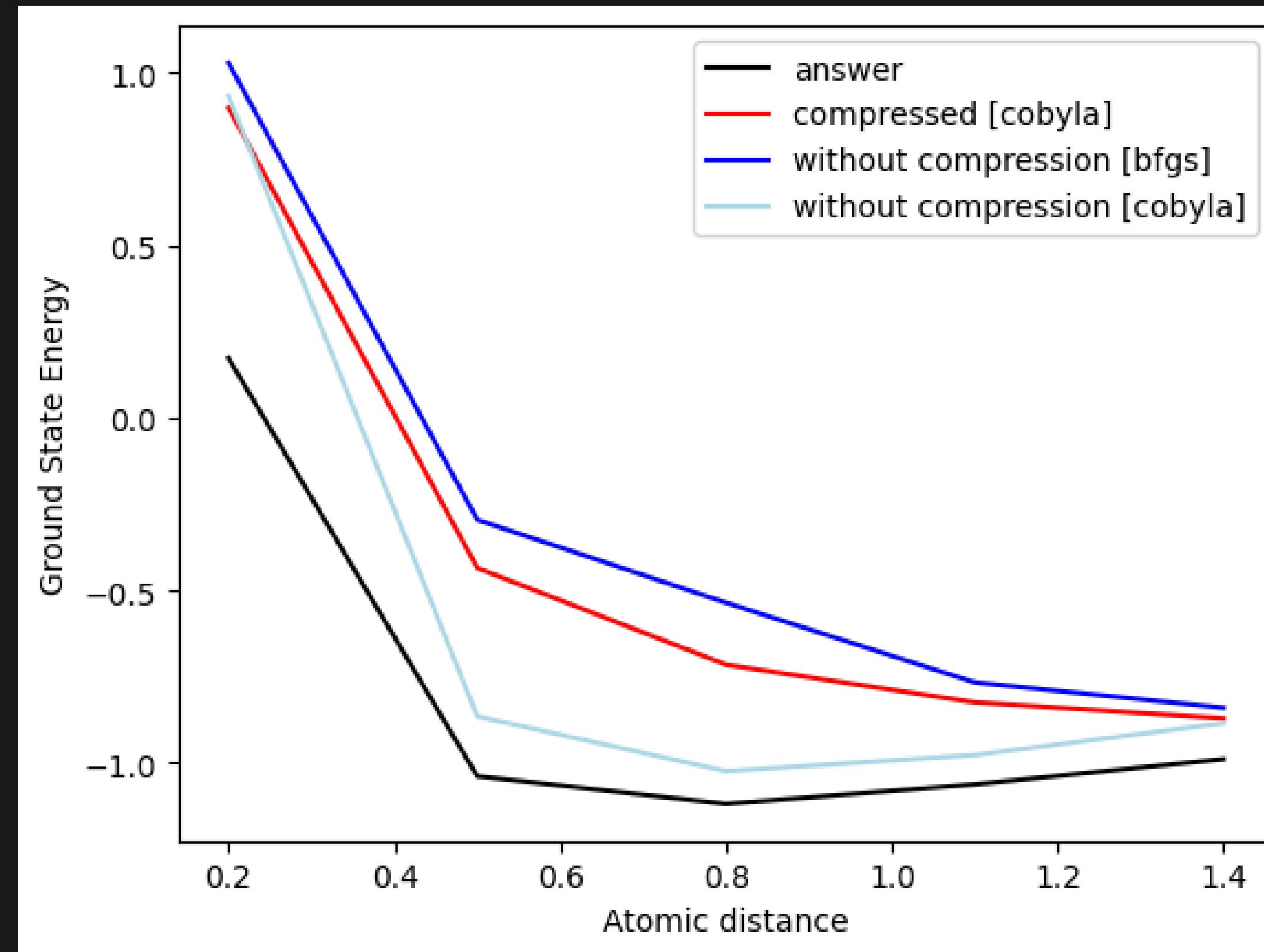
More variational sub-
steps, more
computational costs

More information
about active/inactive
space of the
Hamiltonian

Reducing the anstaz parameter space,

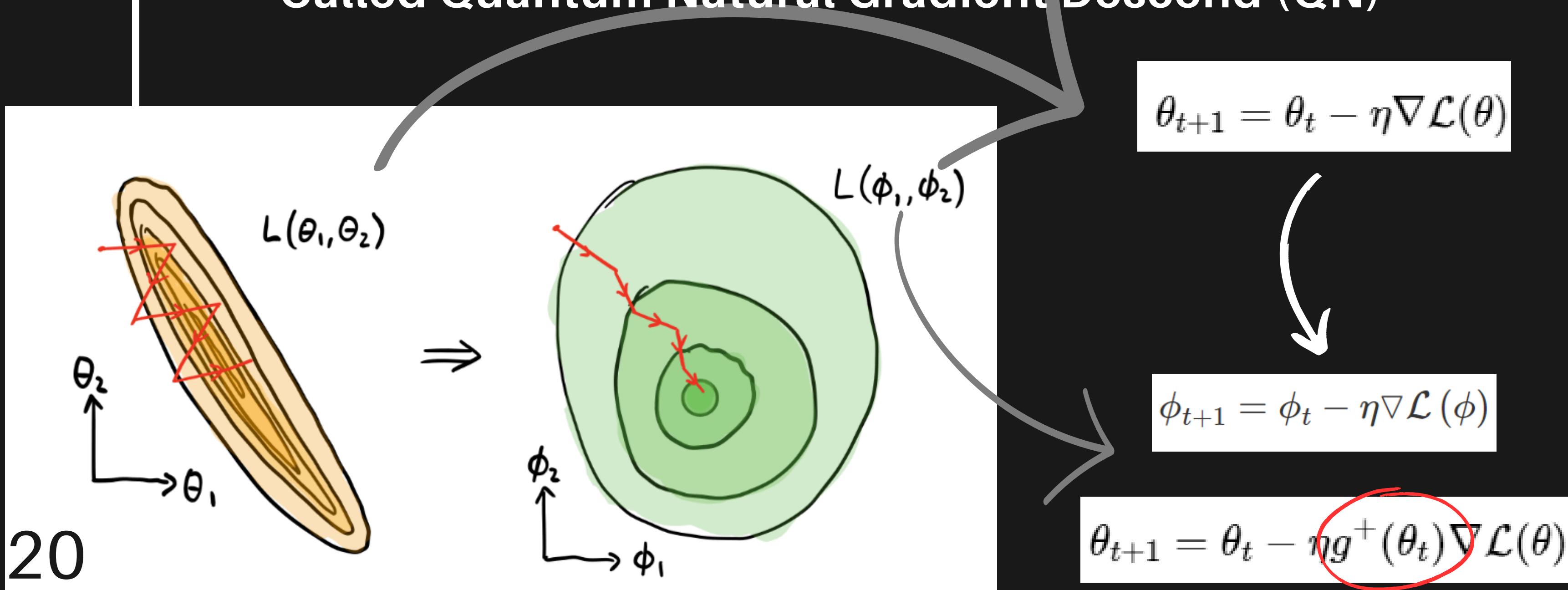
Hamiltonian Compression

Numerical result LiH molecule:

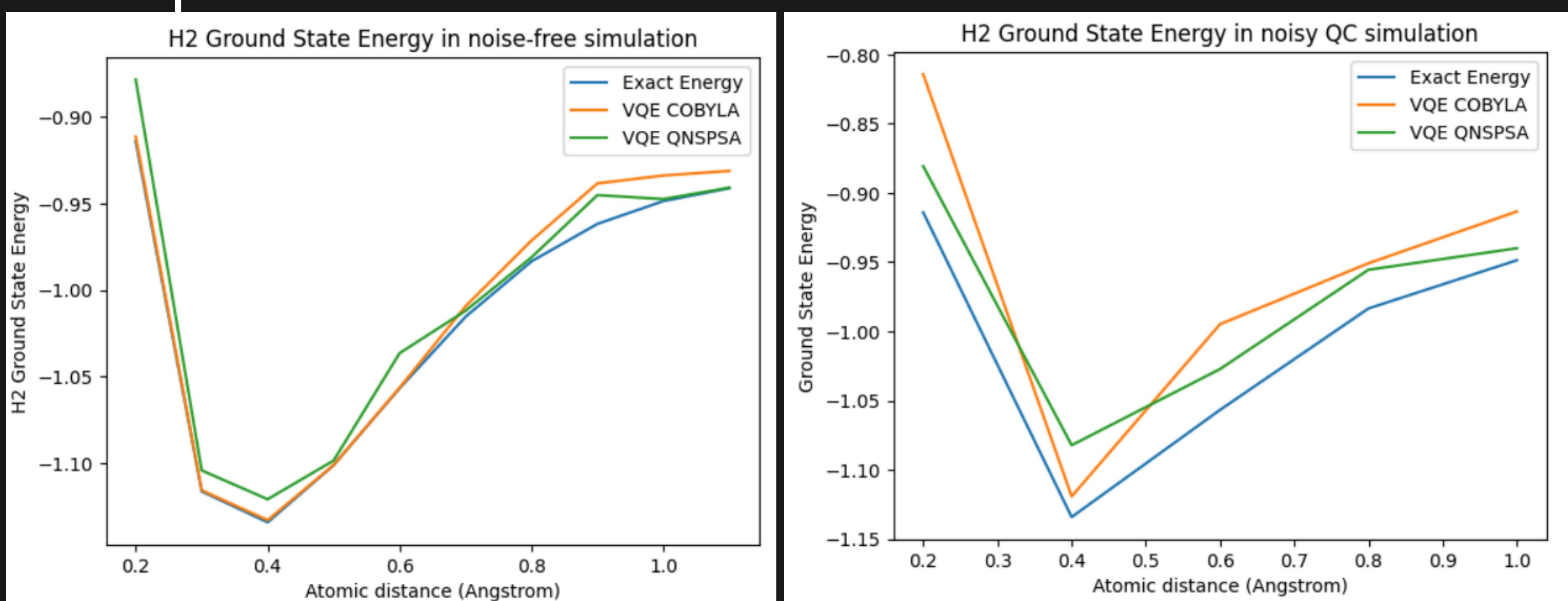


VQE - Optimization Subroutine

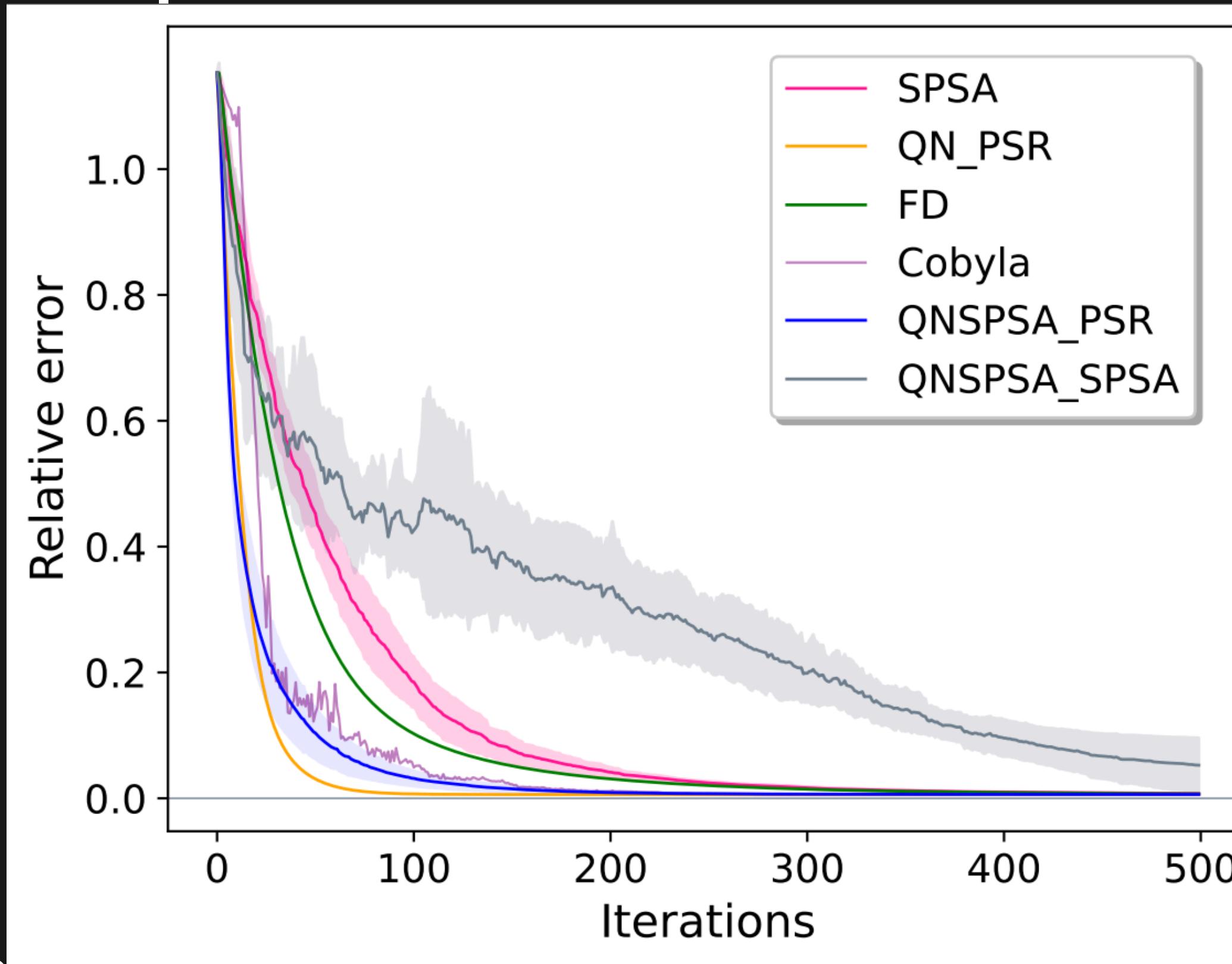
Study a new optimization algorithm taking into account the quantum geometry information of wave function
Called Quantum Natural Gradient Descend (QN)



VQE - Optimization Subroutine



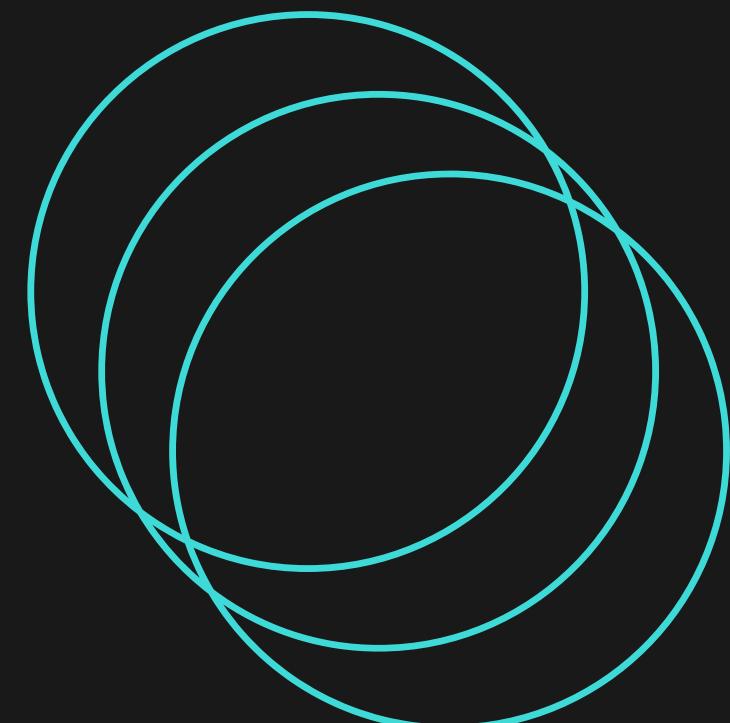
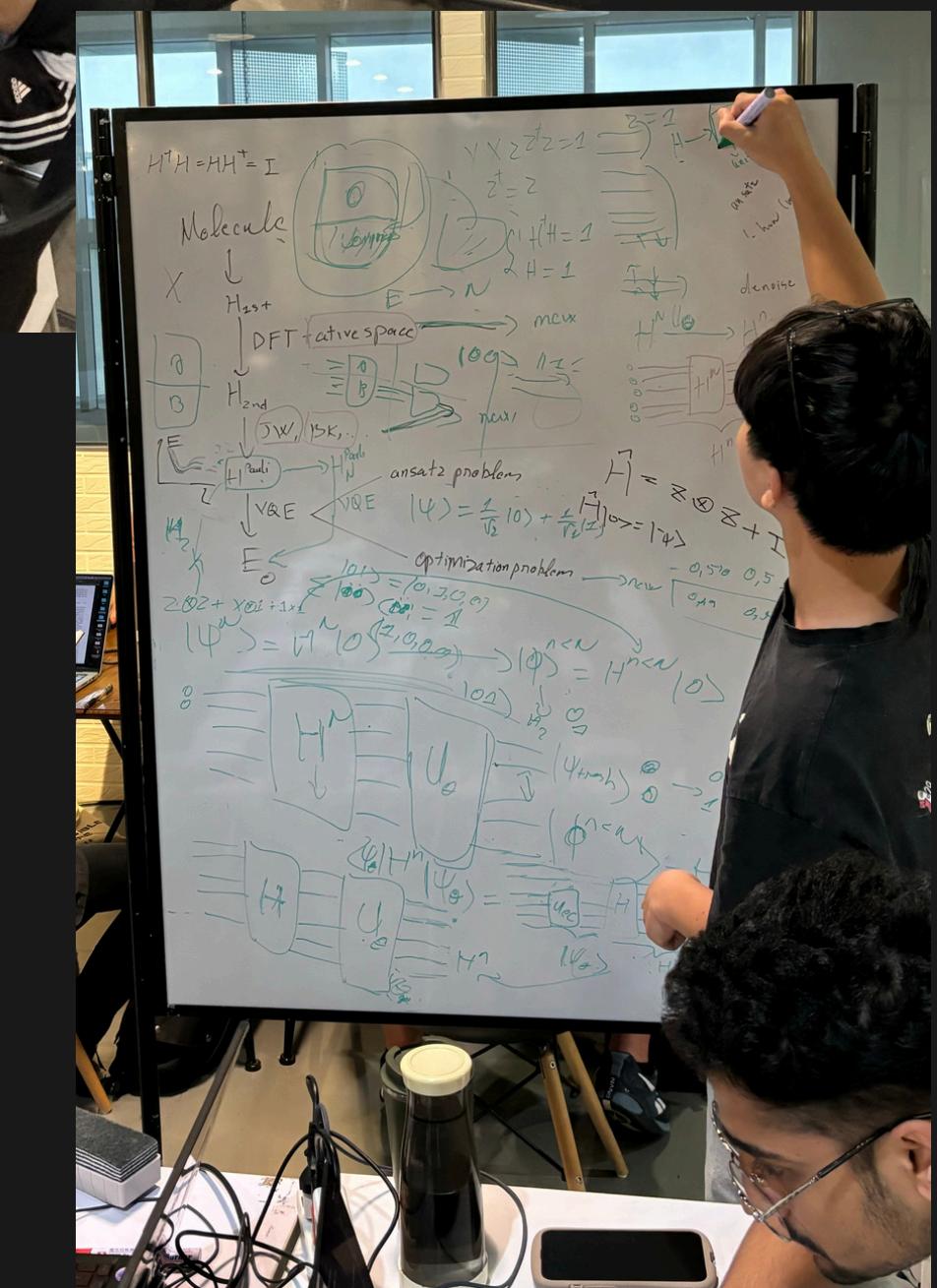
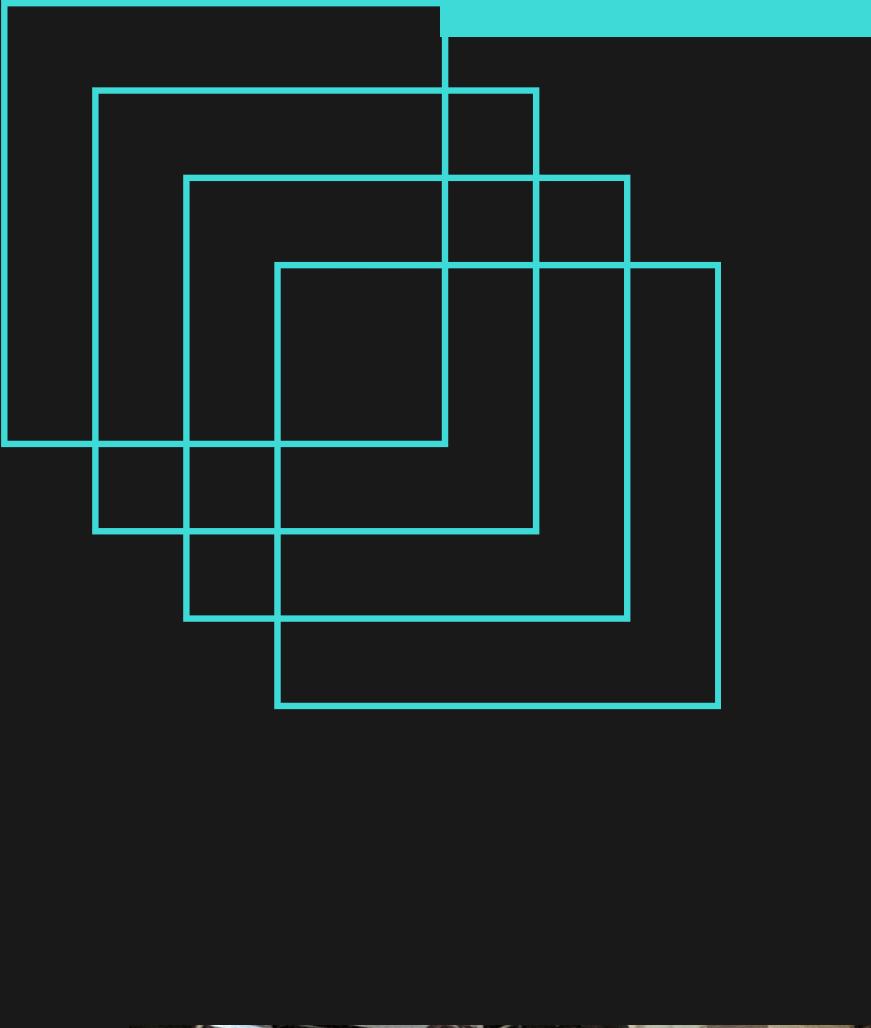
VQE - Optimization Subroutine



- **Current NISQ running time:** QNSPSA takes more time than classical method, SPSA, Cobyla
- **Faster convergence:** Nevertheless, in parallel quantum computing strategy, it is a different story
- **More Accurate:** Taking into account the quantum information able to make an improvement on accuracy

Further Advancements

- Using Randomize Measurement method instead of Swaptest in quantum compression
- Applying Quantum Autoencoder to deduce ansatz complexity
- Studying the effect of new optimization and quantum compression in different Hamiltonian



Thanks for Listening!

