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de Telecomunicació de Barcelona



Quantum Simulation

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by
Albert López Escudero

In partial fulfillment
of the requirements for the
DEGREE IN ELECTRONICS ENGINEERING

Advisor: Vincenzo de Maio & Ivona Bandric

Reviewer: Javier Rodriguez Fonollosa

Barcelona, December 2024

Resum

Cada exemplar del Treball de Fi de Grau (TFG) ha de contenir un Resum, que és un breu extracte del TFG. En termes d'estil, el Resum hauria de ser una versió reduïda del projecte: una introducció concisa, un compendi dels resultats i les principals conclusions o arguments presentats en el projecte. El Resum no ha de superar les 150 paraules i cal que estigui traduït al català, castellà i anglès.

Resumen

Cada ejemplar del Trabajo de Fin de Grado (TFG) debe incluir un Resumen que es un breve extracto del TFG. En cuanto al estilo, el Resumen debería ser una versión reducida del proyecto: una introducción breve, un resumen de los resultados principales y las conclusiones o argumentos principales presentados en el proyecto. El Resumen no debe exceder las 150 palabras y debe estar traducido al catalán, castellano e inglés.

Summary

Each copy of the Bachelor's Thesis (TFG) must include a Summary, which is a concise abstract of the TFG. In terms of style, the Summary should be a condensed version of the project: a brief introduction, a summary of the main results, and the conclusions or key arguments presented in the project. The Summary should not exceed 150 words and must be translated to catalan, spanish and english.

A Dedication page may be included in your thesis just before the Acknowledgments page, but it is not a requirement.

Acknowledgements

It is appropriate, but not mandatory, to declare the extent to which assistance has been given by members of the staff, fellow students, technicians or others in the collection of materials and data, the design and construction of apparatus, the performance of experiments, the analysis of data, and the preparation of the thesis (including editorial help). In addition, it is appropriate to recognize the supervision and advice given by your advisor.

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Abbreviations

ETSETB Escola Tècnica Superior d'Enginyeria de Telecomunicació de Barcelona

EU European Union

GEF Grau en Enginyeria Física

GREELEC Grau en Enginyeria Electrònica de Telecomunicació

GRETST Grau en Enginyeria de Tecnologies i Serveis de Telecomunicació

Introduction

In recent decades, computing has undergone a significant transformation, reaching physical limits in the improvement of classical hardware. These challenges have driven research in quantum computing, an emerging technology with the potential to revolutionize various fields due to its ability to perform calculations exponentially more efficiently in certain problems. Among these applications, quantum molecular simulation stands out as a promising area, enabling the study of complex chemical systems that are intractable for classical methods.

The main objective of this project is to develop a quantum simulator capable of efficiently modeling molecules using advanced quantum algorithms, with a specific focus on implementing the Variational Quantum Eigensolver (VQE) algorithm. This algorithm combines quantum circuits for state preparation and classical optimizers that adjust parameters to minimize the system's energy. Additionally, the project introduces innovations in the design of adaptive quantum circuits, the integration of simultaneous optimizations of nuclear and electronic coordinates, and visualization tools for analyzing the optimization process.

1.1 Work goals

The primary goal of this project is to contribute a novel methodology to the field of molecular simulations by:

- Developing a quantum simulation program capable of efficiently modeling molecules using quantum algorithms.
- Introducing innovative code that implements adaptive circuit construction and advanced optimization strategies.
- Demonstrating the effectiveness of this approach by simulating selected molecular systems and comparing the results with classical computational methods.

- Enhancing the integration between quantum and classical computations to optimize both electronic and nuclear degrees of freedom.

1.2 Requirements and specifications

To achieve these objectives, the following requirements and specifications have been established:

- **Quantum Computing Frameworks:** Utilize quantum computing libraries such as PennyLane and JAX for quantum circuit simulation and automatic differentiation.
- **Algorithm Implementation:** Implement the VQE algorithm with adaptive circuit construction, allowing the selection of the most significant excitations based on energy gradients.
- **Optimization Techniques:** Employ efficient optimizers, including gradient-based methods like gradient descent and advanced techniques like the Quantum Natural Gradient optimizer.
- **Hamiltonian Construction:** Accurately build molecular Hamiltonians for various molecular geometries and ensure compatibility with standard quantum chemistry basis sets.
- **Visualization Tools:** Develop modules for visualizing energy convergence, parameter evolution, and molecular geometries throughout the optimization process.
- **Computational Resources:** Ensure the code is optimized for performance, making effective use of computational resources and supporting parallel execution where possible.
- **Extensibility:** Design the codebase to be modular and extensible, allowing future enhancements and adaptation to other molecular systems or quantum algorithms.

1.3 Methods and procedures

This project employs innovative methods and procedures to enhance molecular simulations using quantum computing. The implementation reflects a cohesive integration of adaptive circuit construction, advanced optimization strategies, and a seamless blend of quantum and classical computation, as demonstrated by the project’s modular codebase.

Adaptive Circuit Construction

Traditional VQE implementations rely on fixed ansätze, which may fail to capture the complexities of molecular systems efficiently. In this project, adaptive circuit construction is implemented in the `ansatz_preparer.py` module. The quantum circuit is dynamically constructed by selecting excitations (operators) from a predefined pool, based on their

contribution to lowering the system's energy. This selection is guided by energy gradient computations provided by `optimizer.py` and `hamiltonian_builder.py`. This approach ensures computational efficiency by including only the most impactful excitations, significantly accelerating convergence to the ground state energy.

Advanced Optimization Techniques

Optimizing quantum circuit parameters is critical for the success of VQE. The `optimizer.py` and `opt_mol.py` modules incorporate both gradient-based and gradient-free optimization methods. Techniques such as the Gradient Descent Optimizer and Quantum Natural Gradient Optimizer are employed to address the geometric structure of the parameter space, ensuring faster and more stable convergence. Additionally, the optimization process extends to nuclear coordinates, implemented in `opt_mol.py`, allowing for simultaneous refinement of electronic structures and molecular geometries. This hybrid optimization loop is a key innovation, enabling the algorithm to explore the coupled energy landscape effectively.

Integration of Quantum and Classical Computation

The seamless integration of quantum and classical computations is achieved using frameworks like PennyLane. This integration, implemented across `hamiltonian_builder.py`, `ansatz_preparer.py`, and `optimizer.py`, allows for efficient computation of energy gradients with respect to quantum circuit parameters and nuclear coordinates. These automatic differentiation tools facilitate robust optimization and enable handling of complex molecular systems that are challenging for classical methods.

Innovations in Code Implementation

Key innovations in our code include:

- **Dynamic Operator Selection:** A procedure to compute energy gradients for each operator in the pool and select the one with the highest impact, thus adaptively constructing the quantum circuit.
- **Hybrid Optimization Loop:** An iterative loop that updates both quantum circuit parameters and nuclear positions, enhancing the ability to find the global minimum energy configuration.
- **Efficient Gradient Computation:** Advanced numerical methods in `optimizer.py` compute gradients for nuclear coordinates, enabling efficient geometry optimization.
- **Visualization and Analysis Tools:** The *visualizer.py* module provides comprehensive visualization tools for analyzing energy evolution and 3D representations of molecular geometries.

- **Modularity and Extensibility:** The modular code structure, described in *main.py* and related modules, facilitates easy adaptation to different molecules, basis sets, and quantum devices, supporting future research.

Utilization of Existing Frameworks and Contribution to the Field

The project builds on established frameworks such as PennyLane and leverages existing algorithms like the VQE. The *hamiltonian_builder.py* module utilizes PennyLane’s tools for molecular Hamiltonian construction, while the adaptive circuit construction and hybrid optimization approaches extend these capabilities significantly. By introducing novel methodologies and improving computational efficiency, this project makes a meaningful contribution to the fields of quantum chemistry and quantum computing.

1.4 Work plan

Normally the figures and tables are put in `\figure` and `\table` environments, that can float freely in the document. You can identify each float with a `\label`

GANTT DIAGRAM

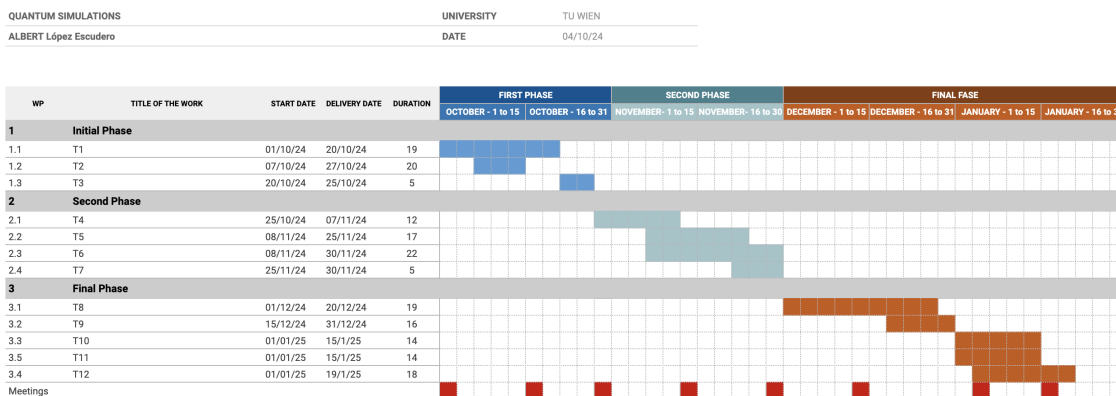


Figure 1.1: Project’s Gantt diagramGantt diagram of the project. For more information read the manual [skalagantt] of Skala..

State of the Art of the Technology Used or Applied in this Thesis

In recent years, computing has undergone significant evolution, reaching a point where improving the hardware of traditional devices presents considerable challenges. This has driven research in quantum computing, a technology that promises to revolutionize the field by enabling much more efficient calculations and superior processing capabilities. In applications such as molecular simulation, quantum computing has proven to be remarkably more efficient than classical computing, justifying investment in its development.

However, one of the main obstacles of quantum computing is the high cost associated with its devices. To run programs on a quantum computer, it must operate at extremely low temperatures, close to 0.1 Kelvin, which significantly increases the cost and technical complexity. Therefore, methods are being investigated to improve and optimize these devices, making them more accessible and viable for broader use.

Currently, one of the most practical ways to harness quantum computing's potential is through **quantum simulation**. Quantum simulation allows us to study complex quantum systems using either quantum simulators or classical computers. By emulating the behavior of quantum systems, we can explore quantum algorithms and applications effectively without necessarily requiring a fully functional quantum computer.

In this project, we focus on the operation of quantum simulators applied to molecular simulation, an area where quantum computing offers significant advantages. The main objective is to develop a program capable of simulating different molecules in a simple and efficient manner.

To this end, we will review the basic concepts of quantum mechanics that are essential to understand the fundamentals and potential of quantum computing, and explore the techniques of quantum simulation that allow us to harness quantum computing capabilities even with current technological limitations.

2.1 Quantum Simulation

Quantum simulation has emerged as an advanced and essential technique for studying complex quantum systems, especially those that are inaccessible or present great challenges for direct analysis using classical methods. Based on the proposal of Richard Feynman, who postulated that a computer built from quantum elements could overcome the limitations of classical computers in simulating quantum phenomena, quantum simulation has progressed significantly. It encompasses both digital and analog simulations and has expanded its applicability in various scientific areas.

There are mainly two approaches in quantum simulation: **Digital Quantum Simulation (DQS)** and **Analog Quantum Simulation (AQS)**. DQS employs the quantum circuit model, where systems are represented by qubits that evolve through quantum gates to reproduce the dynamics of the target system. This approach is universal, as it can, in principle, simulate any quantum system, although not always efficiently. On the other hand, AQS involves creating a quantum system that directly emulates the Hamiltonian of the system under study, allowing certain properties of the simulated system, such as time evolution, to be reproduced approximately. This method is particularly useful when a qualitative representation is required rather than high precision.

In addition to these approaches, there are algorithms inspired by quantum information theory that facilitate the classical simulation of quantum systems. Techniques such as **Matrix Product States (MPS)** and **Projected Entangled Pair States (PEPS)** allow representing particle systems on classical computers more efficiently than standard classical methods, optimizing the calculation of properties of complex quantum systems.

The applications of quantum simulation are broad and encompass multiple scientific fields. In condensed matter physics, it allows the study of models such as the Hubbard model and quantum phase transitions, fundamental for understanding phenomena like superconductivity. In quantum chemistry, it facilitates the calculation of molecular energies and complex chemical reactions. In high-energy physics and cosmology, it emulates particles in high-energy fields and cosmological phenomena. Furthermore, quantum simulation is instrumental in the analysis of open quantum systems and in the investigation of quantum chaos, allowing exploration of interactions with the environment and chaotic dynamics in the quantum realm.

However, quantum simulation faces significant challenges related to the precise control of the quantum simulator systems and the management of decoherence and errors, which can affect the accuracy of the results. The amount of required resources, such as the number of qubits and quantum gates, also depends on the size and complexity of the system to be simulated. It is estimated that quantum simulators require between 40 and 100 qubits to surpass the computational power of classical computers in specific problems. Despite these challenges, technological advances continue to improve the viability and efficiency of quantum simulation, promising to transform research in natural sciences and expand our understanding of quantum phenomena.

2.2 Key Concepts in Quantum Mechanics

It is essential to understand the difference between bits in classical computing and qubits in quantum computing to delve into this new technological paradigm.

In classical computing, the basic unit of information is the **bit**, which can take the value of 0 or 1. These bits are the foundation upon which conventional computers operate, processing information through combinations of these binary states.

In contrast, quantum computing uses the **qubit** or quantum bit as its basic unit. Unlike the classical bit, a qubit can exist in a superposition of states, meaning it can simultaneously represent the values 0 and 1 thanks to the principle of superposition in quantum mechanics. This property, along with phenomena such as quantum entanglement and interference, allows quantum computers to process information exponentially more efficiently for certain problems.

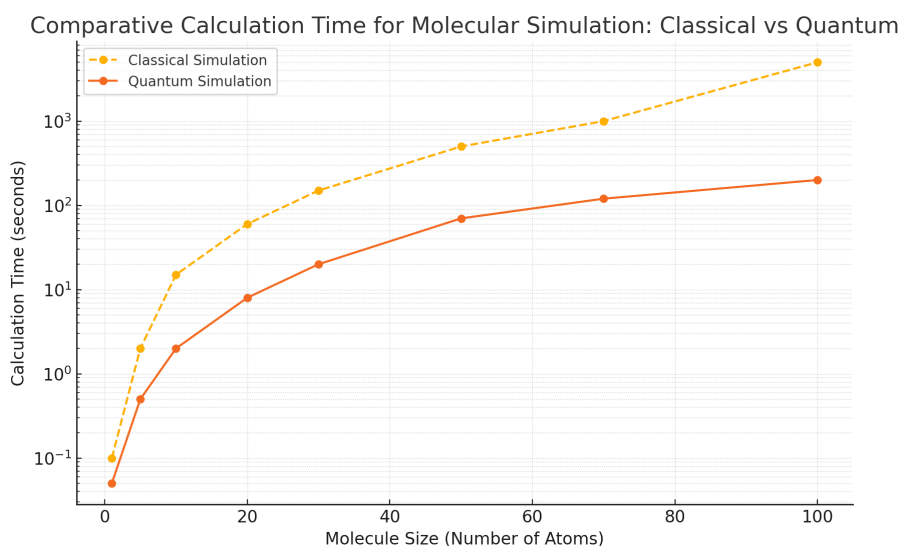


Figure 2.1: Comparison of computation time for molecular simulations: classical vs quantum.

Understanding how qubits operate and their differences from classical bits is essential to appreciate the revolutionary potential of quantum computing.

2.2.1 Qubit

The **qubit** is the basic unit of information in quantum computing. While the classical bit can only be in one of two states (0 or 1), a qubit can be in a superposition of both states simultaneously. This is due to the principle of quantum superposition, one of the fundamental characteristics of quantum mechanics.

Mathematically, a qubit is represented as a linear combination of the basis states $|0\rangle$ and $|1\rangle$:

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle$$

where α and β are complex numbers that satisfy the normalization condition $|\alpha|^2 + |\beta|^2 = 1$. These coefficients indicate the probability amplitudes of finding the qubit in the states $|0\rangle$ or $|1\rangle$ upon measurement.

In addition to superposition, qubits can exhibit **quantum entanglement**, a property that allows creating strong correlations between qubits that cannot be explained by classical physics. Entanglement is essential for the computational power of quantum computers, as it enables processing and storing an exponentially larger amount of information than classical systems.

For example, while a classical system of n bits can represent one of 2^n possible state combinations, a quantum system of n qubits can represent a superposition of all those combinations simultaneously. This capability is what allows quantum computers to tackle complex problems more efficiently.

However, manipulating and maintaining qubits is a significant technical challenge. Qubits are extremely sensitive and can be affected by interactions with the environment, leading to **quantum decoherence**. To minimize this effect and preserve quantum properties, it is necessary to keep systems in controlled conditions, such as very low temperatures, close to absolute zero.

2.2.2 Quantum Superposition

Quantum superposition allows a quantum system to exist in multiple states simultaneously until a measurement is performed. This characteristic is key to the functioning of quantum computers, as it enables processing a large amount of information in parallel.

In quantum systems, superposition is combined with **quantum interference**, where the probability amplitudes of states can reinforce or cancel each other out. This phenomenon is exploited in quantum algorithms to increase the probability of obtaining the correct result. For example, in Grover's algorithm, constructive interference amplifies the probability of the desired state, significantly improving the efficiency of searching for elements in an unsorted database.

Superposition is especially useful in simulating complex molecular systems. Quantum computers can naturally model the superpositions of electronic states in molecules, which is crucial for studying chemical reactions and molecular properties that are difficult to address with classical methods due to the exponential growth of computational resources required.

2.2.3 Quantum Decoherence

Quantum decoherence is one of the main challenges in quantum computing. It refers to the loss of a system's quantum properties, such as superposition and entanglement, due

to unwanted interactions with the environment. This loss causes the quantum system to transition toward classical behavior, affecting the accuracy and reliability of quantum calculations.

Qubits are extremely sensitive to external disturbances, such as electromagnetic fluctuations, vibrations, and temperature changes. These interactions can cause quantum states to mix with those of the environment, leading to a loss of coherence that is irreversible and degrades the stored quantum information.

To mitigate the effects of decoherence, various strategies are implemented:

- **System Isolation:** Designing physical systems that minimize unwanted interactions with the environment, using materials and techniques that protect qubits from external disturbances.
- **Quantum Error Correction:** Implementing error correction codes that allow detecting and correcting errors without directly measuring the qubit's state, thereby preserving quantum information.
- **Dynamic Control:** Applying techniques such as pulse refocusing and dynamic pulse sequences that actively compensate for disturbances and extend the coherence time of qubits.

Controlling and mitigating decoherence are essential for the advancement of quantum computing and its application in areas like molecular simulation, where the precision of calculations is fundamental.

2.3 The Hamiltonian in Quantum Mechanics

The Hamiltonian is a fundamental concept originating from classical mechanics, introduced by William Rowan Hamilton in 1833. Hamiltonian mechanics is a reformulation of classical mechanics that provides powerful tools for studying the dynamics of systems. The Hamiltonian function represents the total energy of the system, expressed in terms of generalized coordinates and momenta, and is given by the sum of the kinetic and potential energies.

In quantum mechanics, the **Hamiltonian operator** plays a central role in describing the energy and time evolution of quantum systems. It represents the total energy of the system, including both kinetic and potential energies, and is essential for formulating the Schrödinger equation.

2.3.1 Mathematical Definition

The Hamiltonian operator, commonly denoted as \hat{H} , is a self-adjoint operator acting on the Hilbert space associated with the quantum system. For a single particle in one dimension, the Hamiltonian is expressed as:

$$\hat{H} = \hat{T} + \hat{V}$$

where:

- \hat{T} is the kinetic energy operator.
- \hat{V} is the potential energy operator.

In terms of the position \hat{x} and momentum \hat{p} operators, these are defined as:

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\hat{V} = V(\hat{x})$$

Here, m is the mass of the particle, \hbar is the reduced Planck constant, and $V(\hat{x})$ is the potential energy function depending on position.

2.3.2 Role in the Schrödinger Equation

The Hamiltonian is central to the Schrödinger equation, which describes how the quantum state of a system evolves over time. The time-dependent Schrödinger equation is expressed as:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

where $|\psi(t)\rangle$ is the state vector of the system at time t . For time-independent systems, the Schrödinger equation reduces to the eigenvalue equation:

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

Here, E represents the eigenvalues of the Hamiltonian, corresponding to the allowed energy levels of the system, and $|\psi\rangle$ are the associated eigenstates.

2.3.3 Hamiltonian in Multi-Particle Systems

For systems with multiple particles, the Hamiltonian includes additional terms representing interactions between particles. For example, for a system of two particles, the Hamiltonian is expressed as:

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{V}_1 + \hat{V}_2 + \hat{V}_{12}$$

where:

- \hat{T}_1 and \hat{T}_2 are the kinetic energy operators of particles 1 and 2, respectively.
- \hat{V}_1 and \hat{V}_2 are the individual potential energy operators.
- \hat{V}_{12} represents the potential interaction between the two particles.

2.3.4 Importance in Quantum Simulations

In quantum simulations, especially in algorithms like the Variational Quantum Eigensolver (VQE), the Hamiltonian is decomposed into a sum of simpler terms, often expressed in terms of Pauli operators. This decomposition facilitates implementation on quantum circuits and allows estimating the system's energy through measurements on qubits.

Understanding the structure and properties of the Hamiltonian is essential for modeling and simulating quantum systems, as it determines the possible energies and dynamics of the system under study.

2.4 Algorithms

Once we have understood the basic concepts, we focus on the quantum algorithms used in particle simulation. These algorithms make use of quantum logic gates, which are detailed in Appendix A.

2.4.1 VQE: Variational Quantum Eigensolver

The VQE is a hybrid quantum-classical algorithm designed to find the minimum energy of a quantum system, such as a molecule. This algorithm combines quantum state preparation with classical optimization. It leverages the quantum properties of qubits to find the ground state of the molecule more rapidly, followed by classical optimization to refine the solution.

Stages of the Algorithm

The VQE is based on the variational principle, which states that the expected energy of any approximate state $|\psi(\theta)\rangle$ is always greater than or equal to the energy of the true ground state E_0 :

$$E(\theta) = \langle \psi(\theta) | H | \psi(\theta) \rangle \geq E_0$$

1. Quantum State Preparation A parameterized quantum circuit known as an *ansatz* is used, defined by a set of adjustable parameters $\vec{\theta}$. This circuit applies a sequence of quantum gates, such as rotations and entangling gates, to generate a quantum state:

$$|\psi(\vec{\theta})\rangle$$

2. Measurement of the Expected Energy For a given quantum state $|\psi(\vec{\theta})\rangle$, the expected energy of the system under a Hamiltonian H is measured:

$$E(\vec{\theta}) = \langle \psi(\vec{\theta}) | H | \psi(\vec{\theta}) \rangle$$

The Hamiltonian H is decomposed into terms of Pauli operators representing the electronic and nuclear interactions in the system.

3. Classical Optimization The parameters $\vec{\theta}$ are iteratively adjusted using a classical optimizer to minimize $E(\vec{\theta})$.

4. Iteration of the Process The steps of state preparation, measurement, and optimization are repeated until $E(\vec{\theta})$ converges to a minimum value. This value corresponds to the ground state energy of the system.

2.4.2 Adaptive Circuits

Adaptive circuits dynamically optimize quantum circuits by iteratively selecting components that most effectively reduce the system’s energy. In this project, we implemented an adaptive strategy where the ansatz is constructed step-by-step by incorporating excitations (operators) from a predefined pool. Operators are chosen based on their gradient contributions to lowering the system’s energy, ensuring that computational resources are focused on the most impactful degrees of freedom. This approach accelerates convergence, reduces circuit complexity, and maximizes efficiency.

The variational principle underpins this method, guaranteeing that any trial state $|\psi(\theta)\rangle$ yields an energy $E(\theta)$ that serves as an upper bound to the true ground state energy E_0 , i.e., $E(\theta) \geq E_0$. By iteratively refining the ansatz with the most relevant operators, the adaptive approach reduces the dimensionality of the problem at each step, avoiding wasted computational and optimization efforts on irrelevant regions of the parameter space.

In quantum chemical problems, the excitation space grows combinatorially with the number of molecular orbitals, making it increasingly challenging to navigate and optimize as system size increases. Including all possible single and double excitations would create an unmanageable parameter landscape. The adaptive ansatz mitigates this challenge by strategically traversing the solution space, selecting only the operators that contribute meaningfully to capturing electronic correlations. This targeted methodology not only improves scalability but also ensures that each optimization step contributes directly to achieving a more accurate representation of the system’s ground state.

2.5 Optimizers

In the realm of quantum simulation algorithms like the **Variational Quantum Eigensolver** (VQE), optimizers are essential components that facilitate the minimization of the expected energy of a quantum system. Following the preparation of quantum states and the measurement processes described earlier, optimizers are employed in the classical computation stage to adjust the parameters of the quantum circuit, known as the *ansatz*.

The theoretical purpose of optimizers in this project is to solve a continuous optimization problem. They aim to find the optimal set of parameters $\vec{\theta}$ that minimize the cost function $E(\vec{\theta})$, which represents the expectation value of the Hamiltonian H with respect to the quantum state $|\psi(\vec{\theta})\rangle$:

$$E(\vec{\theta}) = \langle \psi(\vec{\theta}) | H | \psi(\vec{\theta}) \rangle$$

Optimizers utilize mathematical techniques to navigate the high-dimensional parameter space effectively. Depending on the specific characteristics of the problem, different optimization methods can be employed:

- **Gradient-based methods:** These methods compute the gradient of the cost function with respect to the parameters and use this information to guide the search towards the minimum energy. Examples include gradient descent and its variants.
- **Gradient-free methods:** In cases where calculating the gradient is impractical or the cost function is noisy, gradient-free methods like Nelder-Mead or COBYLA can be used.
- **Second-order methods:** These methods, such as the BFGS algorithm, approximate the second derivatives (Hessian) of the cost function to achieve faster convergence.

Within the iterative loop of the VQE algorithm, the optimizer updates the parameters $\vec{\theta}$ after each quantum measurement based on the chosen optimization strategy. This process continues until convergence is achieved, meaning the expected energy $E(\vec{\theta})$ reaches a minimum value that approximates the ground state energy of the system.

Integrating optimizers into the quantum-classical workflow is crucial because they connect quantum computations with classical numerical methods. They enable effective exploration of the parameter space, addressing challenges such as multiple local minima and flat regions in the energy landscape that are inherent in quantum systems.

By employing appropriate optimization techniques, this project aims to enhance the efficiency and accuracy of molecular simulations. Optimizers play a pivotal role in leveraging the capabilities of quantum computing to achieve results that are difficult to obtain with classical computational methods alone, thus contributing to the advancement of quantum simulation despite current technological limitations.

Methodology / project development

In this chapter, the methodology used in the completion of the work will be detailed. Its aim is to offer a thorough account of the approaches and techniques used, ensuring replicability and academic rigor. It will not only cover the research methods and measurement techniques employed but will also delve into the specifics of software and hardware development. Whether the project involves qualitative analysis, quantitative measurements, computational modeling, or physical prototyping, this chapter should elucidate how each component contributes to the overall objectives.

In addition to describing the methods themselves, the chapter will also provide justifications for why specific methods were chosen over others. For example, it may explain the choice of a particular programming language, statistical test, or experimental setup. The chapter will also address the limitations of the methodology and how these have been mitigated or accounted for. Readers should come away with a clear understanding of how the project's development has been carried out, why certain choices were made, and how these methods serve to fulfill the initially established objectives.

3.1 Tools and Frameworks Selection

3.1.1 Framework Selection

To make the decision on which framework to use, we compared the documentation of the two quantum simulation frameworks available in the market: PennyLane and Qiskit. These are the most comprehensive frameworks with similar features available at the time of creating this project. After reviewing the documentation, we ultimately chose to use PennyLane for two reasons.

The first reason was the amount of documentation related to quantum simulation. Once we started looking into how others were using these resources, we realized that in the field of molecular simulation, the existing documentation—both theoretical and especially practical—was substantially greater. This provided us with more examples to begin developing our project.

The second reason for our choice was the frequent major changes implemented by Qiskit. We realized that while Qiskit is a tool that promises to be very good, it has historically undergone significant structural changes.

For these reasons, this project has been developed using the PennyLane framework. Below, we will observe how the project has been developed and explain the reasons behind the decisions made.

3.2 Project Structuring

After deciding on the interface to use and implementing the first version of the code, we decided to reorganize the project to make it more precise and modular. This structure offers the possibility to easily add more lines of code and functionalities.

3.2.1 Code Organization

```
quantum_simulation_project/  
config/  
    config_functions.py: Configuration functions for the project.  
    molecules.json: Molecule data.  
    __pycache__: Python cache files.  
main.py: Main program file.  
modules/  
    ansatz_preparer.py: Quantum ansatz preparation.  
    hamiltonian_builder.py: Molecular Hamiltonian construction.  
    molecule_manager.py: Molecular data management.  
    opt_mol.py: Molecular optimization.  
    optimizer.py: Optimization algorithms.  
    visualizer.py: Visualization tools.  
    __pycache__: Python cache files.  
temp_results_autograd/  
    energy_evolution.png: Energy evolution graph.  
    filtered_report_autograd.txt: Filtered results report.  
    final_geometries_3D.png: Image of the final 3D geometries.  
    nuclear_coordinates.png: Nuclear coordinates.  
    output.txt: Program data output.  
    profile_output_autograd.txt: Autograd profile output.  
test/: Directory for tests.
```

This file serves as the entry point of the program. It initializes the initial conditions, sets up the molecule's configuration, defines optimization options, and orchestrates the execution of the quantum simulation and geometry optimization process. It is the first file to execute when running the application.

Auxiliary Modules (`modules/`): This directory contains various modules that encapsulate the core logic and operations of the project:

- `ansatz_preparer.py`: Includes functions for constructing the quantum circuit from the variational ansatz, preparing states, and applying excitations.
- `hamiltonian_builder.py`: Responsible for generating the molecular Hamiltonian based on nuclear coordinates and the selected electronic basis.
- `molecule_manager.py`: Manages information related to the molecule, such as its charge, multiplicity, number of electrons, and required orbitals.
- `opt_mol.py`: Functions that orchestrate the molecular optimization process, invoking the optimizer and recording the simulation's progress.
- `optimizer.py`: Implements the optimization logic, combining routines for evaluating the cost (energy) with the selected optimization algorithms, updating parameters, and geometries.
- `visualizer.py`: Generates graphical outputs and reports that display the evolution of energy, nuclear coordinates, and other relevant data during optimization.

Temporary Results Directories (`temp_results_autograd`): Several directories with names starting with `temp_results_autograd` store output data, time logs, and visualizations generated for different simulations and configurations. For documentation purposes, these directories are treated as a single repository for temporary results.

Dependencies (`requirements.txt`): This file lists the required libraries and their versions to reproduce the project's execution environment. Keeping it updated ensures reproducibility of the simulation across different systems, facilitating the installation of necessary dependencies.

3.2.2 Version Control

Version control was managed using Git, allowing detailed tracking of changes and facilitating continuous collaboration with the supervisors on the project. Primarily, at the start of the project, a single branch was used to develop the project and explore the framework's possibilities. Once a stable version was achieved, branches were created to conduct tests and develop new functionalities. The first branches created were for the different interface versions. In each branch, the code was refined so that the same code would run across the various interfaces. Finally, only the interface changes that proved most suitable for the project were merged back into the main branch.

3.3 Development and Implementation

The *Variational Quantum Eigensolver* (VQE) was chosen as the primary method to estimate the ground state energy of the studied quantum system. VQE combines limited quantum

processing (measurements and applicability in moderately deep circuits) with classical optimization techniques. Its selection is justified by:

- **Suitability for NISQ devices:** VQE is particularly well-suited for noisy intermediate-scale quantum (NISQ) devices, as it requires circuits of relatively low depth.
- **Flexible Ansatz:** It allows the use of various adaptive variational ansätze that capture essential electronic correlations.
- **Direct coupling to classical optimizers:** The VQE cost function (the expected energy) can be minimized with a wide range of classical methods, making it easy to experiment with different optimizers.

The core principle of VQE is the variational theorem, which guarantees that the expected energy of the ansatz is always an upper bound to the true ground state energy. By optimizing the ansatz parameters, the algorithm progressively approaches the actual energy minimum. We have already explained the concept of VQE in the state of the art chapter; now we will explain how we have implemented it in our project and how we have integrated it.

Principle of VQE: The VQE is based on the variational principle, which states that the expected energy of any approximate state $|\psi(\theta)\rangle$ is always greater than or equal to the real ground state energy E_0 :

$$E(\theta) = \langle \psi(\theta) | H | \psi(\theta) \rangle \geq E_0$$

We have already discussed this concept, but it is necessary to emphasize it as it is the foundation of the entire algorithm. The idea is to find the parameters θ that minimize the expected energy, thereby approaching the real value of the ground state energy.

Next, we will detail how the VQE is implemented in our project, explaining how each component has been developed for trying to achieve the best performance and results.

3.3.1 Hamiltonian Construction Process

1. Definition of Molecular Geometry:

The geometry is specified by the atomic symbols and the Cartesian coordinates of each atom in the molecule:

Geometry Definition

```
1 symbols = ['H', 'H']
2 x_init = np.array([0.0, 0.0, 0.0, 0.0, 0.0, 0.74])
```

2. Hamiltonian Construction:

The `build_hamiltonian` function generates the molecular Hamiltonian using PennyLane's functions:

Hamiltonian Build

```

1 def build_hamiltonian(x, symbols, charge=0, mult=1, basis_name='sto-3g'):
2     x = np.array(x)
3     coordinates = x.reshape(-1, 3)
4     hamiltonian, qubits = qml.qchem.molecular_hamiltonian(
5         symbols, coordinates, charge=charge, mult=mult, basis=basis_name
6     )
7     h_coeffs, h_ops = hamiltonian.terms()
8     h_coeffs = np.array(h_coeffs)
9     hamiltonian = qml.Hamiltonian(h_coeffs, h_ops)
10    return hamiltonian

```

Note: A basis set, such as 'sto-3g', is selected, which is a predefined set of basis functions to represent atomic orbitals in a simplified manner. This makes the simulation more efficient.

Function Description:

This function generates the qubit Hamiltonian of a molecule by transforming the electronic Hamiltonian in second quantization into the Pauli matrix framework. Additionally, it allows for the incorporation of net charge effects, spin multiplicity, and an active space defined by a specific number of electrons and orbitals, optimizing the quantum simulation of molecular systems.

3.3.2 Adaptive Ansatz Construction and Operator Selection

As we said before, the adaptive ansatz construction builds upon the conventional variational approach by strategically selecting only those excitations that offer the most significant energy reductions. Instead of starting from a large, fixed set of parameters, the algorithm begins with the Hartree-Fock state and incrementally introduces new excitations based on their calculated impact on lowering the system's energy. This methodology provides both theoretical and practical advantages in handling the complexity of the solution space.

The selection process begins with a predefined *operator pool*, typically composed of single and double excitation operators relevant to the molecular system. At the start of the procedure, no variational parameters are assigned, and the system is initialized in the reference Hartree-Fock state. At each iteration, the algorithm evaluates the energy gradients associated with adding each operator from the pool:

1. **Gradient Calculation:** For every candidate operator \hat{O}_i in the pool, the partial

derivative of the energy with respect to the parameter controlling \hat{O}_i is computed. This step identifies how sensitive the energy is to introducing that particular excitation.

2. **Operator Ranking and Filtering:** All candidate excitations are ranked according to the absolute value of their gradients. Operators that produce negligible energy changes are discarded, while those offering substantial decreases are selected for inclusion.
3. **Incremental Ansatz Growth:** The selected operator(s) is then added to the ansatz. A new parameter is introduced and optimized, increasing the dimensionality of the parameter space *only where it matters*. This targeted expansion ensures that each additional parameter contributes meaningfully to lowering the energy.
4. **Pool Update and Iteration:** After adding the chosen operators, the process repeats. The operator pool is re-examined at subsequent steps, but it now excludes previously chosen operators unless they are included as parameterized parts of the ansatz. Over multiple iterations, the ansatz evolves adaptively, honing in on the most relevant subset of excitations.

A simplified code snippet, consistent with the project's structure, may appear as follows:

Adaptive Operator Selection

```
1 gradients = compute_operator_gradients(operator_pool, selected_excitations, params, hamiltonian)
2 selected_gate, max_grad_value = select_operator(gradients, operator_pool, convergence_threshold)
3 if selected_gate:
4     selected_excitations.append(selected_gate)
5     params = np.append(params, 0.0) # Add new parameter for the chosen operator
6     print(f"Added operator {selected_gate} with gradient {max_grad_value:.5e}")
7 else:
8     print("No significant operators found. Convergence or local minimum reached.")
```

In this code, the `compute_operator_gradients` function evaluates each operator's gradient, while the `select_operator` function applies a filtering criterion based on a defined `convergence_threshold`. Only the most promising excitation is incorporated into the ansatz at each step, ensuring a controlled and meaningful expansion of the parameter space.

In numerical experiments, this targeted approach has demonstrated:

- **Faster Convergence:** Fewer parameters are introduced at each stage, allowing the optimizer to quickly reduce the energy without wading through irrelevant configurations.
- **Lower Resource Consumption:** By refining the search space, the quantum circuits remain relatively shallow, and classical optimization routines require fewer evaluations.

- **Scalability:** As molecular systems grow in complexity, the adaptive approach helps mitigate the exponential growth in parameter number, making it more feasible to handle larger systems within similar computational budgets.

3.3.3 Cost Function Definition

With the ansatz defined, the next step is to establish a cost function that evaluates the expected energy of the system given a set of parameters θ . In our implementation, this cost function is defined within `update_parameters_and_coordinates` and calculates the expected value of the molecular Hamiltonian:

Definition of the Cost Function

```
1 @qml.qnode(dev, interface=interface)
2 def cost_fn(params):
3     prepare_ansatz(params, hf_state, selected_excitations, spin_orbitals)
4     return qml.expval(hamiltonian)
```

This function is essential for evaluating $E(\theta)$. By calculating the expected value of the Hamiltonian, we can quantify how close our approximate state is to the true ground state.

3.3.4 Mixed Electronic and Geometric Optimization Strategy

In our project, we made a deliberate decision to integrate the refinement of both variational parameters θ and nuclear coordinates \mathbf{X} into a single iterative loop. Rather than treating these aspects separately, as is common in sequential optimization approaches, we chose to couple the electronic and geometric optimizations from the start. By doing so, we ensured that each electronic update immediately reflects the current molecular geometry, and each geometric adjustment leverages the most recent and accurate electronic wavefunction. This approach was guided by our goal of finding the global minimum of the molecular system's total energy more efficiently, ultimately steering the molecule towards its equilibrium geometry and ground state energy in a more coherent and resource-effective manner.

Rationale for Our Mixed Approach In many standard methodologies, the electronic structure is optimized at a fixed geometry before the geometry itself is optimized under that electronic configuration. We felt this separation was inefficient for our objectives, as it often leads to unnecessary iterations and suboptimal intermediate solutions. Recognizing that the electronic configuration and nuclear arrangement are intrinsically linked, we decided to continually update both in tandem. This choice was grounded in our understanding that capturing the interplay between the electronic distribution and molecular geometry as it unfolds would reduce computational overhead and converge more rapidly to a stable, physically meaningful equilibrium.

Our Iterative Optimization Steps

1. **Initialization:** We begin by defining the initial molecular geometry, nuclear coordinates \mathbf{X}_0 , and variational parameters θ_0 . For instance:

Initialization Example

```
1 symbols = ['H', 'H']
2 x_init = np.array([0.0, 0.0, 0.0, 0.0, 0.0, 0.74])
3 params = np.array([], requires_grad=True)
```

We selected these initial values based on known molecular structures and our desire to start from a configuration that is simple yet representative.

2. **Molecular Hamiltonian Update:** At each iteration, we recalculate the molecular Hamiltonian $\hat{H}(\mathbf{X})$ using the updated nuclear coordinates. This ensures that our cost function (the expected energy) accurately reflects the current geometry at every step, allowing us to maintain a closer link between the electronic solution and the evolving molecular shape.
3. **Operator Gradient Calculation and Selection:** For the electronic part, we compute energy gradients with respect to a pool of candidate excitation operators. We then select and add only the operator with the highest gradient contribution to the ansatz. This choice was made to keep the parameter space as manageable as possible, focusing our resources on the excitations that yield the greatest energy reductions. By gradually expanding the ansatz in this manner, we prevent an explosion in complexity and retain a more controlled optimization path.
4. **Nuclear Gradient Computation and Coordinate Updates:** To update the nuclear coordinates \mathbf{X} , we decided to compute the nuclear gradients numerically using finite differences. Concretely, for each coordinate direction, we slightly perturb \mathbf{X} and measure the resulting change in energy:

$$\nabla_{\mathbf{X}} E(\theta, \mathbf{X}) \approx \frac{E(\theta, \mathbf{X} + \delta \mathbf{u}) - E(\theta, \mathbf{X} - \delta \mathbf{u})}{2\delta}. \quad (3.1)$$

We adopted this finite-difference method to maintain flexibility and simplicity, and because it integrates seamlessly with our adaptive approach. After obtaining the gradients, we update the coordinates as:

$$\mathbf{X}_{\text{new}} = \mathbf{X}_{\text{old}} - \alpha \nabla_{\mathbf{X}} E(\theta, \mathbf{X}), \quad (3.2)$$

where α is a learning rate we chose based on preliminary tests to balance stability and speed of convergence. This direct control allowed us to refine the geometry efficiently without overshooting or requiring overly complex gradient estimations.

5. **Geometric Convergence Validation:** We established convergence criteria tailored to our desired precision and computational budget. For energy convergence,

we require that differences between subsequent iterations fall below a small threshold (e.g., 10^{-8} Ha). For geometric convergence, we set clear tolerances on changes in atomic positions and interatomic distances. Meeting both criteria ensures the geometry is near equilibrium and that no further improvements are necessary. This choice reflects our priority for a stable and physically meaningful final configuration rather than just a numerically optimized one.

6. **Visualization and Termination:** Throughout the process, we record the evolving energy, coordinates, and other metrics. We decided to include immediate visual feedback (such as energy vs. iteration plots and 3D molecular views) to quickly assess the effectiveness of our approach. This real-time monitoring helps us recognize potential issues early, adjust our strategies, and confirm when we have reached the desired convergence criteria. Once these conditions are met, we terminate the process, confident that the final geometry and electronic state are both well-optimized.

Why Our Iterative Coupling Is More Efficient By integrating electronic and geometric optimizations, we reduce the redundant recalculations and needless complexity that can arise in standard sequential methods. In our approach, each update to the electronic parameters leverages a geometry that is already moving towards equilibrium, and each geometric refinement uses an increasingly accurate electronic state. This synergy not only shortens the pathway to convergence but also helps us avoid getting stuck in suboptimal configurations. In our experience, this mixed strategy has proven more efficient and more closely aligned with the underlying physics of the system, delivering faster, more stable, and more accurate results than what we would expect from a traditional, decoupled optimization approach.

3.4 Limitations and Mitigation Measures

Among the limitations of this approach are:

- **Scalability:** As the system grows in the number of electrons and orbitals, the complexity of Hamiltonian construction and the excitation space increases exponentially.
- **Quantum Noise and Errors:** On real devices, noise affects measurement fidelity. Our work, primarily simulation-oriented, plans to integrate mitigation techniques in future studies.
- **Ansatz Choice:** Although the adaptive ansatz helps, there is no guarantee that the excitation selection is optimal. Future work might explore more complex heuristics.

To mitigate these issues, we opted for reduced basis sets, strategies such as re-initializing the optimizer when increasing the parameter space, and verifying convergence through multiple criteria (energetic and geometric).

Results

This chapter should encompass your data analysis and findings. Additionally, include relevant tables, figures, and citations to support your results and interpretations. Here is a suggested list of topics to discuss:

4.1 Experiments and Tests

Describe the experiments conducted to assess the performance of your project. Explain how you collected and processed the data.

4.2 Data Visualization

Create visual representations of the results (e.g., scatter plots, bar charts). Interpret the visualizations and relate them to the research questions.

4.3 Limitations

Acknowledge any limitations in the data or analysis. Explain how these limitations may have influenced the results.

Sustainability Analysis and Ethical Implications

Starting from the academic year 2023-24, the TFG regulations of ETSETB require the inclusion of a sustainability report in the project's documentation. This analysis involves an assessment of environmental, social, and economic impacts, as well as potential ethical implications resulting from the completion of the TFG. In the case where the TFG involves a product/service/system/building, etc., that could be implemented, the analysis should also address the impacts that the proposal would have during the various stages of its lifecycle.

Detailed instructions on what the sustainability report should contain and how to prepare it can be found on the ATENEA platform.

IMPORTANT: Please note that the previous chapter on "Project Budget" is now integrated into the sustainability analysis, specifically in the cells "Economic Cell/Development of BT" and "Economic Cell/Project Execution".

Conclusions and Future Work

6.1 Conclusions

- Summarize the main results of your work.
- Discuss the degree of achievement in relation to the objectives set at the beginning of the work.
- Highlight the contributions of your work to the field of study.

6.2 Future Directions

- Identify areas for future research or development based on your work.
- Discuss possible ways to expand or improve the project.
- Consider questions that remained unanswered and opportunities for future exploration.

Logic Gates

A.1 Simple Logic Gates

Below are detailed the simple logic gates essential for constructing more complex quantum algorithms:

X Gate (Pauli-X) The **Pauli-X** gate is the quantum analog of the classical NOT gate. It performs a bit flip on the qubit, transforming the state $|x\rangle$ into $|\neg x\rangle$.

Representative Matrix

$$X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Effect on Basis States

- $X|0\rangle = |1\rangle$
- $X|1\rangle = |0\rangle$

Y Gate (Pauli-Y) The **Pauli-Y** gate performs a rotation of π around the y -axis. It transforms the state $|x\rangle$ into $i(-1)^x |\neg x\rangle$.

Representative Matrix

$$Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Effect on Basis States

- $Y|0\rangle = i|1\rangle$
- $Y|1\rangle = -i|0\rangle$

Z Gate (Pauli-Z) The **Pauli-Z** gate is known as the phase inversion gate. It transforms the state $|x\rangle$ into $(-1)^x |x\rangle$.

Representative Matrix

$$Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Effect on Basis States

- $Z|0\rangle = |0\rangle$
- $Z|1\rangle = -|1\rangle$

Hadamard Gate (H) The **Hadamard** gate creates an equal superposition of the computational basis states. It transforms the state $|x\rangle$ into $\frac{1}{\sqrt{2}}(|0\rangle + (-1)^x |1\rangle)$.

Representative Matrix

$$H = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

Effect on Basis States

- $H|0\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) = |+\rangle$
- $H|1\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) = |-\rangle$

A.2 Multi-Qubit Logic Gates

Controlled-NOT Gate (CNOT) The **CNOT** or **Controlled-X** gate is a two-qubit gate that flips the second qubit (target) if and only if the first qubit (control) is in the state $|1\rangle$. It transforms the state $|x, y\rangle$ into $|x, x \oplus y\rangle$, where \oplus denotes the XOR operation.

Representative Matrix

$$\text{CNOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Effect on Basis States

- $\text{CNOT}|00\rangle = |00\rangle$
- $\text{CNOT}|01\rangle = |01\rangle$
- $\text{CNOT}|10\rangle = |11\rangle$
- $\text{CNOT}|11\rangle = |10\rangle$

Single Excitation Gate (*SingleExcitation*) This gate performs a rotation in the two-dimensional subspace $\{|01\rangle, |10\rangle\}$. It transforms the state $|10\rangle$ into $\cos\left(\frac{\phi}{2}\right)|10\rangle - \sin\left(\frac{\phi}{2}\right)|01\rangle$.

Representative Matrix

$$U(\phi) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\left(\frac{\phi}{2}\right) & -\sin\left(\frac{\phi}{2}\right) & 0 \\ 0 & \sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Effect on Basis States

It affects the subspace $\{|01\rangle, |10\rangle\}$, performing a rotation parameterized by ϕ .

Double Excitation Gate (*DoubleExcitation*) This gate performs a rotation in the subspace of states $\{|0011\rangle, |1100\rangle\}$. It specifically affects these states, leaving the others unchanged.

Representative Matrix

$$U(\phi) = \begin{pmatrix} I_{12} & 0 & 0 \\ 0 & \begin{pmatrix} \cos\left(\frac{\phi}{2}\right) & -\sin\left(\frac{\phi}{2}\right) \\ \sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right) \end{pmatrix} & 0 \\ 0 & 0 & I_2 \end{pmatrix}$$

Effect on Basis States

It performs a rotation parameterized by ϕ in the subspace $\{|0011\rangle, |1100\rangle\}$.

These gates are implemented in PennyLane as `qml.SingleExcitation` and `qml.DoubleExcitation`, and are essential in quantum chemistry algorithms such as the *Unitary Coupled-Cluster Singles and Doubles* (UCCSD).

