Peter Grünberg Institut (PGI)
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The Variational Quantum Eigensolver in Quantum Chemistry with PennyLane

Stefania-Rebekka Symeonidou

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Abstract

This thesis explores quantum chemistry using the Variational Quantum Eigensolver (VQE), developed with the help of PennyLane's quantum chemistry library. Our focus was on exploring molecular structures and energy landscapes.

With an adaptive VQE implementation, we generated approximate multi-electron wave functions by optimizing a quantum circuit on a simulator. We started from a Hartree-Fock state and applied the UCCSD (Unitary Coupled Cluster Singles and Doubles) Ansatz to entangle electrons and lower the Hamiltonian's expectation value.

The journey began with H_2, where the VQE accurately predicted its equilibrium distance and energy. We then extended our analysis to more complex molecules like LiH, BeH_2, and H_2O, successfully determining their equilibrium geometries and energies, which match existing literature.

However, we discovered anomalies in the energy surfaces of BeH_2 and H_2O at larger internuclear distances, leading us to question the choice of initial states for these scenarios.

In summary, this work demonstrated the VQE's potential for accurate molecular simulations. While it excels in capturing ground states for various molecules, challenges remain for large internuclear distances. This sheds light on the evolving landscape of quantum technologies applied to understanding molecular systems.

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Declaration

I declare that for my thesis I utilized ChatGPT to refine the English in my thesis. I have never copied entire paragraphs nor have I utilized ChatGPT for any other purpose.

Contents

1 Introduction

In the modern times, computers play an essential role in nearly every facet of our lives, from powering our smartphones to driving scientific discoveries. Despite the exponential growth in computational power, certain complex problems have remained intractable due to the limitations of classical computers. This stagnation in progress has motivated the quest for innovative computational methods capable of addressing these challenges. One promising approach is the development of quantum computers, which utilize the principles of quantum mechanics to perform computations that were previously deemed impossible.

Quantum computation is based on the idea of using quantum mechanics to perform computations, instead of classical physics. This means that instead of using bits encoded as 0 and 1, we can employ qubits, which can exist in a superposition of these two states. As a result, our algorithms become faster and more space-efficient. In fact, an ordinary computer can be used to simulate a quantum computer, but this simulation is impossible to be performed efficiently [1]. Thus, quantum computers can be expected to outperform classical computers on specific classes of problems. This kind of computer was first proposed by Richard Feynman in 1982 [2] and is one of the big challenges facing 21st century science and technology.

In the last decades major progress has been achieved in the area of experimental implementation of Quantum Computers. Various few qubit processors and classical simulators of quantum processors are now accessible through the cloud. Furthermore, quantum software platforms are evolving rapidly, with offerings such as IBM's Qiskit, Google's Cirq, and Xanadu's PennyLane now readily accessible.

A highly promising application of quantum computation is quantum chemistry. Quantum computers can simulate properties of molecules more efficiently and with fewer approximations than classical computers. This is of great interest for many industrial processes. Libraries like PennyLane provide useful functionalities for quantum differentiable programming, combining insights from quantum computing, computational chemistry, and machine learning [3].

This thesis will commence with the theoretical foundations of quantum chemistry, such as the Hartree-Fock method. Ground state calculations for small molecules will be performed, and the optimal geometries of these molecules will be evaluated to demonstrate how useful quantum computation can be for quantum chemistry. To achieve this, we will use PennyLanes library for quantum chemistry to construct the Variational Quantum Eigensolver (VQE), a quantum-classical algorithm which makes use of machine learning techniques to optimize given input parameters and thus enhances approximation precision compared to the Hartree-Fock method. Our primary emphasis will be on theory, and we will conduct the simulations employing PennyLanes's integrated simulator. Thus, we are able to simulate small molecules up to 12 qubits.

2 Theory

2.1 The Hartree-Fock Theory

Central to quantum chemistry is the Hartree-Fock (HF) theory. It is an approximation method used to derive a simplified version of the Schrödinger equation for molecules. This allows for the calculation of the wave functions, so called orbitals, for the electrons within the system. We will first present the theory in a general manner and then illustrate it using the example of H_2. The goal of this section is to introduce, how a first approximation of the molecular orbitals and the ground state energy of a molecule can be calculated. This first approximation can then be used to compute the qubit Hamiltonian and set initial values for the VQE algorithm that we intend to utilize.

When examining a quantum system, our focus lies in solving the time-dependent Schrödinger equation, which describes the underlying physics:

$$\hat{H}(\vec{r},t)\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) \tag{2.1}$$

It is applicable on isolated, non-relativistic systems, as the molecules in Chapter 4 are. When the Hamiltonian is time-independent equation 2.1 can be reduced to the time-independent Schrödinger equation by making the Ansatz $\psi(\vec{r},t) = \sum_k C_k\psi_k(\vec{r})e^{-iE_kt/\hbar}$, where ψ_k are the so called stationary states:

$$\hat{H}(\vec{r})\psi_k(\vec{r}) = E_k\psi_k(\vec{r}) \tag{2.2}$$

Equation 2.2 is an eigenvalue problem, which is much easier to solve, than the time-dependent Schrödinger equation (eq. 2.1). The Hamiltonian $\hat{H}$ varies based on the underlying system.

For an molecule equation 2.2 depends on the coordinates of all electrons and all nuclei. The Hamiltonian, consisting of kinetic and potential terms, would take the form:

$$\begin{aligned}
\hat{H} &= \hat{T}_{N_c} + \hat{T}_e + \hat{V}_{N_cN_c} + \hat{V}_{N_ce} + \hat{V}_{ee} \\
&= \underbrace{-\sum_A \frac{\hbar^2}{2m_A}\nabla_A^2}_{\hat{T}_{N_c}} \underbrace{-\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2}_{\hat{T}_e} \\
&\quad \underbrace{+\sum_{A<B} \frac{Z_AZ_Be^2}{4\pi\epsilon_0|\vec{R}_A-\vec{R}_B|}}_{\hat{V}_{N_cN_c}} \underbrace{-\sum_{iA} \frac{Z_Ae^2}{4\pi\epsilon_0|\vec{R}_A-\vec{r}_i|}}_{\hat{V}_{N_ce}} \underbrace{+\sum_{i<j} \frac{e^2}{4\pi\epsilon_0|\vec{r}_j-\vec{r}_i|}}_{\hat{V}_{ee}}
\end{aligned} \tag{2.3}$$

where i,j denote electrons and A,B nuclei (indexes: N_c=nuclei, e=electron). $\hbar$ denotes the reduced Planck constant, e the electronic charge, m the electron and nuclear mass, and ϵ_0 the vacuum permittivity. Furthermore $\vec{r_i}$ is the position of an electron and $\vec{R}_A$ is that of a nucleus, Z_A is the nuclear charge number [4]. The terms in the hamiltonian represent the kinetic energy of the nuclei ($\hat{T}_{N_c}$) and electrons ($\hat{T}_e$), followed by the potential energy associated with nuclear-nuclear ($\hat{V}_{N_cN_c}$), nuclear-electron ($\hat{V}_{N_ce}$), and electron-electron interactions ($\hat{V}_{ee}$).

Thus, to solve equation 2.2 for an arbitrary molecule (or multi-electron system), a large number of variables has to be taken into account. Solutions are known for single-electron systems like the hydrogen atom, but no analytic solutions are known for multi-electron systems [5]. To simplify and solve the problem, four major approximations need to be made:

1. Born-Oppenheimer approximation
2. Hartree-Fock/mean-field approximation
3. LCAO-MO (**L**inear **C**ombination of **A**tomic **O**rbitals-**M**olecular **O**rbital) Ansatz
4. approximation of **A**tomic **O**rbitals (AO's) by finite basis sets

In the subsequent sections, these approximations will be introduced step-by-step until a numerically solvable equation, known as the Roothaan-Hall equation, is reached.

Example 2.1.1 *H_2*
So let us write down the problem we want to solve for H_2 (eq. 2.2), and reduce it step-by step through the next sections. The H_2 molecule consist of two nuclei, each with one electron, and nuclear charge number $Z_H = 1$. Thus the time-independent Schrödinger equation depends on the positions of the two nuclei and the two electrons:

$$\hat{H}\psi_k(\vec{r}_1,\vec{r}_2,\vec{R}_1,\vec{R}_2) = E_k\psi_k(\vec{r}_1,\vec{r}_2,\vec{R}_1,\vec{R}_2) \tag{2.4}$$

with the Hamiltonian

$$\begin{aligned}\hat{H}(\vec{r}_1,\vec{r}_2,\vec{R}_1,\vec{R}_2) &= \hat{T}_{N_c} + \hat{T}_e + \hat{V}_{N_cN_c} + \hat{V}_{N_ce} + \hat{V}_{ee}\\ &= -\frac{\hbar^2}{2m_H}\nabla^2_{H^{(1)}} - \frac{\hbar^2}{2m_H}\nabla^2_{H^{(2)}} - \frac{\hbar^2}{2m_e}\nabla^2_1 - \frac{\hbar^2}{2m_e}\nabla^2_2\\ &+ \frac{Z_HZ_He^2}{4\pi\epsilon_0|\vec{R}_2-\vec{R}_1|}\\ &- \frac{Z_He^2}{4\pi\epsilon_0|\vec{R}_1-\vec{r}_1|} - \frac{Z_He^2}{4\pi\epsilon_0|\vec{R}_1-\vec{r}_2|} - \frac{Z_He^2}{4\pi\epsilon_0|\vec{R}_2-\vec{r}_1|} - \frac{Z_He^2}{4\pi\epsilon_0|\vec{R}_2-\vec{r}_2|}\\ &+ \frac{e^2}{4\pi\epsilon_0|\vec{r}_2-\vec{r}_1|}\end{aligned} \tag{2.5}$$

Taking a look at this problem, it is obvious why analytic solutions cannot be derived for molecules. Even the simplest molecule (H_2) requires 12 variables.

2.1.1 Born-Oppenheimer Approximation

The first approximation needed is the Born-Oppenheimer appoximation. Within the Born-Oppenheimer approximation, we treat the nuclear and electronic variables separately. This is done by making the Ansatz $\psi_k(\vec{r}, \vec{R}) = \phi_{e,k}(\vec{r}; \vec{R})\phi_{N,k}(\vec{R})$. Here $\vec{r}$ and $\vec{R}$ stand for all electronic and all nuclear positions, respectively. The molecular orbitals $\phi_{e,k}$ may depend on the nuclear positions, but only in a constant matter. This corresponds to fixing nuclear coordinates and neglecting the nuclear motion in comparison to the electronic motion. It is a legitimate assumtion, as the mass of electrons is way smaller than the mass of nuclei ($m_e << m_{N_c}$).

By freezing the nuclei, the kinetic nuclear term in the Hamiltonian vanishes and we obtain the **electronic structure problem** in first quantization:

$$\hat{H}_e \phi_{e,k}(\vec{r}; \vec{R}) = E_{e,k}(\vec{R})\phi_{e,k}(\vec{r}; \vec{R}) \tag{2.6}$$

with

$$\hat{H}_e(\vec{r}; \vec{R}) = \hat{T}_e + \hat{V}_{N_c N_c} + \hat{V}_{N_c e} + \hat{V}_{ee} \tag{2.7}$$

$\hat{H}_e$ is referred to as the electronic Hamiltonian, and depends on the kinetic energy of the electrons ($\hat{T}_e$), the Coulomb interaction between the nuclei and electrons ($\hat{V}_{N_c e}$), and electron-electron interactions ($\hat{V}_{ee}$). Here the term of nuclear coulomb interaction $\hat{V}_{N_c N_c}$ represents a constant, as it only depends on nuclear coordinates. The $\phi_{e,k}$ represent the molecular orbitals. $E_{e,k}(\vec{R})$ is the potential energy surface [6].

Once the electronic eigenstates are determined, it is possible to revisit and consider the nuclei in order to derive the vibrational and rotational states:

$$\hat{H}_{N_c} = \hat{T}_{N_c} + E_{e,k}(\vec{R}) \qquad \hat{H}_{N_c}\phi_{N_c}(\vec{R}) = E_{N_c}\phi_{N_c}(\vec{R}) \tag{2.8}$$

In this context, $\hat{H}_{N_c}$ represents the nuclear Hamiltonian, which includes both the nuclear kinetic energy and the electronic energy eigenstates.

Since we will solely focus on the electronic eigenstates, we won't delve further into the theory of vibrational and rotational states. Furthermore, for the sake of simplicity, we will omit the index "e" and "k" in the context of the electronic structure problem from this point onward.

Example 2.1.2 H_2
Equation 2.4 reduces to the electronic structure problem:

$$\hat{H}_e \phi_{e,k}(\vec{r}_1, \vec{r}_2; \vec{R}_1, \vec{R}_2) = E_{e,k}(\vec{R}_1, \vec{R}_2)\phi_{e,k}(\vec{r}_1, \vec{r}_2; \vec{R}_1, \vec{R}_2) \tag{2.9}$$

with the Hamiltonian

$$\begin{aligned}\hat{H}_e(\vec{r}_1,\vec{r}_2;\vec{R}_1,\vec{R}_2) &= \hat{T}_e + \hat{V}_{N_cN_c} + \hat{V}_{N_ce} + \hat{V}_{ee} \\ &= -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 \\ &+ \frac{Z_H Z_H e^2}{4\pi\epsilon_0|\vec{R}_2-\vec{R}_1|} \\ &- \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_1-\vec{r}_1|} - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_1-\vec{r}_2|} - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_2-\vec{r}_1|} - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_2-\vec{r}_2|} \\ &+ \frac{e^2}{4\pi\epsilon_0|\vec{r}_2-\vec{r}_1|}\end{aligned} \tag{2.10}$$

2.1.2 Hartree-Fock (mean-field) approximation

Considering the Born-Oppenheimer approximation, the electronic structure problem remains intractable. Our primary challenge arises from the electron-electron interaction term (V_{ee}).

To simplify the problem, we must also separate variables that describe individual electrons (one-electron picture). In doing so, we are still required to satisfy the antisymmetry condition for fermions as mandated by the Pauli exclusion principle. An approximate wavefunction ($\Phi \approx \phi_{e,k}$) for many-electron systems is formulated by taking the antisymmetrized product of functions that describe individual electrons

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix} \tag{2.11}$$

the so called Slater determinant [4]. $\frac{1}{\sqrt{N!}}$ is a normalization constant where N is the number of electrons in the system. In the Hartree–Fock theory only a single Slater determinant is used as approximation to the electronic multi-particle wave function $\phi_{e,k}$. In more accurate theories, so called Post-Hartree-Fock methods, a linear combination of Slater determinants is used. We will come back to that in section 2.4.

Approximating the electronic multi-electron wave function with a single Slater determinant means, that Coulomb correlations between electrons are neglected. Nevertheless Fermi correlations are considered, as described below [7]. This means, that within the Hartree-Fock (HF) approximation the single, independent electrons, in the Coulomb potential of the frozen nuclei, feel the other electrons only as a mean field.

The $\phi_j(\mathbf{x}_j)$ in equation 2.11 are the one-electron spin-orbitals. The electronic coordinates $\mathbf{x}_j$ denote the spatial coordinates ($\vec{r_j}$), as well as the spin variable of an electron (s_j). Those two variables can be separated too ($\phi_j(\mathbf{x}_j) = \phi_i(\vec{r_j})\sigma(s_j)$), where $\sigma(s_j)$ can denote a spin up or spin down state. As our focus is solely on the spatial orbitals $\phi_i(\vec{r_j})$ and spin orbitals are orthonormal, we will omit the spin variable from this point onward. This permits each spatial orbital to be occupied twice (by one spin up and one spin down electron), in accordance with the Pauli exclusion principle. It results in N/2 spatial orbitals that need to be determined (restricted HF theory).

Therefore, the problem once more simplifies to identifying the N/2 spatial orbitals, also referred to as molecular orbitals. The simplified equation is called the restricted Hartree-Fock equation

$$\hat{F}\phi_i(\vec{r}_1) = \epsilon_i \phi_i(\vec{r}_1) \tag{2.12}$$

where $\hat{F}$ is the Fock operator and $\vec{r}_1$ the coordinates of the first electron, but can be the spatial coordinates of any electron. In this thesis our focus lies in determining the molecular orbitals, rather than calculating the eigenvalues. This is because the overall ground state energy for a specific molecular state is established through the expectation value of the total Hamiltonian in Born-Oppenheimer approximation(eq. 2.7) in state Φ (eq. 2.11). The Fock operator is an approximation, only considering one electron in the field of the nuclei and all other electrons. It does also neglect the constant nuclear-nuclear coulomb interaction term

$$\begin{aligned}
\hat{F} &= \hat{h}_1 + \sum_{j=1}^{N/2} \left(2\hat{J}_j - \hat{K}_j\right) \\
\hat{h}_1 &= -\frac{\hbar^2}{2m_e}\nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0|\vec{R}_A - \vec{r}_1|} \\
\hat{J}_j &= \int d\vec{r}_2 \frac{\phi_j^*(\vec{r}_2)\phi_j(\vec{r}_2)e^2}{4\pi\epsilon_0|\vec{r}_2 - \vec{r}_1|} \\
\hat{K}_j\phi_i(\vec{r}) &= \left[\int d\vec{r}_2 \frac{\phi_j^*(\vec{r}_2)\phi_i(\vec{r}_2)e^2}{4\pi\epsilon_0|\vec{r}_2 - \vec{r}_1|}\right]\phi_j(\vec{r}_1)
\end{aligned} \tag{2.13}$$

The operator $\hat{h}_1$ is called the core Hamiltonian and serves as an one-electron operator. It incorporates both the kinetic energy and the Coulomb interaction of the electron with the nuclei. The Fock operator's second term, a two-electron operator, is a simplified version of the Vee term. It becomes solvable through the separation of variables describing individual electrons (HF approximation). This two-electron operator is composed of the Coulomb operator $\hat{J}_j$ and the exchange operator $\hat{K}_j$. It depends on all the occupied spatial orbitals. The electron exchange term describes the correlation between electrons with parallel spin, the Fermi correlation. Since we are exclusively addressing spatial orbitals and disregarding spin orbitals, the factor of two in the Coulomb operator accounts for both spin orientations [8].

Thus, once again, we have simplified the problem to equation 2.12, which now requires solving. Equation 2.12 is a Pseudo-eigenvalue problem, as the Fock operator $\hat{F}$ also depends on the orbitals of the other electrons within the system.

Example 2.1.3 *H_2*
In the case of H_2 the approximate ground state wavefunction/Slater determinant is:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}[\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) - \phi_2(\mathbf{x}_1)\phi_1(\mathbf{x}_2)] \tag{2.14}$$

where the ϕ_i are still the molecular spin orbitals. These are equivalent to one spin-down electron and one spin-up electron, both in the 1s (binding) spatial molecular orbital. The problem (eq. 2.9) in Hartree-Fock approximation reduces to the Hartree-Fock equation, as described above:

$$\hat{F}\phi_{1s}(\vec{r_1}) = \epsilon_i \phi_{1s}(\vec{r_1}) \tag{2.15}$$

with the Fock-Matrix-operator for H_2 being

$$\begin{aligned}\hat{F} &= \hat{h}_1 + 2\hat{J}_1 - \hat{K}_1 \\ &= -\frac{\hbar^2}{2m_e}\nabla_1^2 \\ &\quad - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_1 - \vec{r}_1|} - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_2 - \vec{r}_1|} \\ &\quad + \int d\vec{r}_2 \frac{\phi_{1s}^*(\vec{r}_2)\phi_{1s}(\vec{r}_2)e^2}{4\pi\epsilon_0|\vec{r}_2 - \vec{r}_1|}\end{aligned} \tag{2.16}$$

2.1.3 Roothaan-Hall self-consistent field equations

Because the Hartree-Fock equation (eq. 2.12) is non-linear, we must introduce two additional assumptions to facilitate its solution. The fundamental concept is based on approximating the molecular orbitals using a given basis set, which simplifies the integrals in 2.13 for solvability. Consequently, a self-consistent equation known as the Roothaan-Hall equation can be deduced and solved through iterative methods.

The first assumption we are going to make is referred to as the ”Linear Combination of Atomic Orbitals - Molecular Orbitals” (**LCAO-MO**). As the name suggests, the molecular orbitals will be expressed as a linear combination of the nuclei-centered atomic orbitals (χ_ν) from the constituent atoms of the molecule.

$$\phi_i(\vec{r}) = \sum_{\nu} c_{\nu i}\chi_\nu(\vec{r}) \tag{2.17}$$

The coefficients $c_{\nu i}$ in this expansion are real and are the variables that will need to be optimized later, as we will discover [3]. The LCAO for the molecules analyzed in this thesis, will be presented in Section 3.2.

The final required approximation is the representation of atomic orbitals within a finite basis set. The underlying concept is that any function can be presented in the context of a complete basis set. However, achieving an exact representation demands an infinitely large basis set, which is not feasible for computational purposes. Experts have progressively refined basis sets for chemical applications and optimized the coefficients and exponents in equation 2.18 for isolated atoms. These identical coefficients are also utilized for molecules, even though the atoms are part of the molecule. In our case, we will approximate the atomic orbitals (STO=Slater type orbitals) using a Gaussian basis, comprising 3 Gaussians (**STO-3G** basis)

$$\begin{gathered}\chi(\vec{r}) = \mathcal{N}\sum_{i=1}^{3} a_i\psi_i(\vec{r},\alpha_i) \\ \psi_i(\vec{r},\alpha_i) = x^k y^m z^n e^{-\alpha_i r^2}\end{gathered} \tag{2.18}$$

$\mathcal{N}$ is a normalization constant, and the coefficients a_i, and exponents α_i rely on the approximated atomic orbital, with α_i defining the radial size of the basis function. These values can be obtained from multiple available libraries [3]. PennyLane uses a build in library, which can be changed to the ”basissetexchange” library. The exponents k,m, and n are natural numbers which must fulfill $l = k + m + n$, where l is the angular momentum quantum number. They define the angular shape and direction of the orbital. You can find the Gaussians that can be used for s, p, and d orbitals in Table 2.1, as an example.

There exist various other basis sets available for approximating atomic orbitals, apart from the STO-3G basis that we won't be considering in this thesis [9][10]. We use the Gaussian basis, because Gaussian functions are simple to evaluate analytically and numerically. The STO-3G is the simplest, commonly used basis set [3].

orbital form		k l m	possible Gaussian basis functions
s orbitals (l=0)		0 0 0	$e^{-\alpha r^2}$
p orbitals (l=1)	p_x	1 0 0	$xe^{-\alpha r^2}$
	p_y	0 1 0	$ye^{-\alpha r^2}$
	p_z	0 0 1	$ze^{-\alpha r^2}$
d orbitals (l=2)	d_{xx}	2 0 0	$x^2e^{-\alpha r^2}$
	d_{yy}	0 2 0	$y^2e^{-\alpha r^2}$
	d_{zz}	0 0 2	$z^2e^{-\alpha r^2}$
	d_{xy}	1 1 0	$xye^{-\alpha r^2}$
	d_{xz}	1 0 1	$xze^{-\alpha r^2}$
	d_{yz}	0 1 1	$yze^{-\alpha r^2}$

Table 2.1: Example of Gaussian basis functions for different angular momentum.

Expressing the molecular orbitals within our LCAO approach and Gaussian basis set, we can now reduce equation 2.12 to an equation aimed at determining the coefficients $c_{\nu i}$ from equation 2.17. Inserting our LCAO Ansatz in the HF equation 2.12, multiplying the equation by an atomic orbital χ_μ^* and integrating over $\int d\vec{r}$ results in the **Roothaan-Hall equation**

$$\sum_\nu F_{\mu\nu}C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu}C_{\nu i} \Rightarrow \mathbf{FC} = \mathbf{SCE} \tag{2.19}$$

where **F** is the Fock-Matrix, **C** the coefficient matrix, **S** the overlap matrix of the atomic orbitals, and **E** the diagonal matrix of the energie eigenvalues with entries

$$\begin{aligned} F_{\mu\nu} &= \int \chi_\mu^*(\vec{r})\hat{F}\chi_\mu(\vec{r})d\vec{r} \\ S_{\mu\nu} &= \int \chi_\mu^*(\vec{r})\chi_\mu(\vec{r})d\vec{r} \end{aligned} \tag{2.20}$$

The entries $C_{\nu i}$ in the coefficient matrix are the variables for which we aim to solve in equation 2.19. By diagonalizing the overlap matrix (**D** is the diagonal overlap matrix), we can simplify the problem into an eigenvalue problem that can be solved using standard techniques in linear algebra

$$\tilde{\mathbf{F}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\mathbf{E} \tag{2.21}$$

where

$$\mathbf{S} = \mathbf{VDV^T} \qquad \mathbf{X} = \mathbf{VD^{-1/2}V^T} \qquad \mathbf{C} = \mathbf{X}\tilde{\mathbf{C}} \qquad \tilde{\mathbf{F}} = \mathbf{X^TFX} \tag{2.22}$$

The primary challenge stems from the fact that the Fock matrix still depends on the coefficient matrix. Hence, we computationally solve this equation 2.21 through iteration [3]. The procedure is as follows:

1. Set the initial value of the coefficient matrix as $\tilde{\mathbf{C}}_\mathbf{0} = 0 = \mathbf{C_0}$, meaning the only contribution to the energy arises from the core Hamiltonian ($\hat{F}(\mathbf{C_0}) = \hat{h}_1$). This means we start by neglecting any interaction between the electrons.

2. Compute the result for the initial Fock-Matrix $\tilde{\mathbf{F}}_\mathbf{0}$, and then solve 2.21 by diagonalizing $\tilde{\mathbf{F}}_\mathbf{0}$.

3. Check if the obtained coefficient matrix is consistent with the input coefficient matrix ($\tilde{\mathbf{C}}_\mathbf{1} \overset{?}{=} \tilde{\mathbf{C}}_\mathbf{0}$).

4. If this condition is met, our process is complete. Otherwise, update the initial guess with $\tilde{\mathbf{C}}_\mathbf{1}$ and iterate repeatedly until the two matrices match ($\tilde{\mathbf{C}}_\mathbf{k} = \tilde{\mathbf{C}}_\mathbf{k+1}$).

Therefore, solving the Roothaan-Hall equation is called a self-consistent method. What we essentially do is gradually adjust the interaction between the electrons, progressing step by step until the interaction is exactly right to result in the lowest energy state. This conclusion stems from the fact that solving this equation is equivalent to identifying the molecular orbitals (approximated by a single Slater determinant) that minimize the expectation value of the Hamiltonian, under the condition of independent electrons occupying the lowest-energy orbitals [3][11]. In the approximation of molecular orbitals using a single Slater determinant, the lowest energy state is referred to as the Hartree-Fock state, and the corresponding energy is called the Hartree-Fock energy.

Regarding the convergence of this method, the SCF procedure (Self-Consistent Field method) typically achieves convergence within 10 to 20 iterations when an appropriate initial guess is supplied. Nevertheless, in instances where the gap between the highest occupied and lowest unoccupied orbital is narrow (which does not apply to the molecules discussed in this thesis), the SCF procedure might encounter challenges in rapid convergence. It could oscillate between multiple solutions, converge to a higher-lying solution, or even reach a saddle-point solution [11].

Example 2.1.4 *H_2*
Now, let us come back to our example. For H_2 the LCAO-MO would consist of the occupied 1s orbitals of each constituent H atom of H_2:

$$\phi_i(\vec{r}) = c_{1i}\chi_1(\vec{r}) + c_{2i}\chi_2(\vec{r}) \tag{2.23}$$

where χ_1 is the 1s hydrogen orbital centered in atom $H^{(1)}$ and χ_2 is the 1s hydrogen orbital centered in atom $H^{(2)}$, respectively. What is required to define the Ansatz here is the geometry of the molecule, specifically the distances r_{H-H} between the nuclei. In this thesis, we establish the origin of the coordinate system at the midpoint between the two hydrogen atoms and position the molecule along the z-axis ($\vec{R}_1 = [0, 0, -r_{H-H}/2]$, $\vec{R}_2 = [0, 0, r_{H-H}/2]$).

The 1s orbitals of hydrogen are well-known solutions of the Schrödinger equation. As mentioned before, in order to make the integrals below computationally tractable, we need to approximate them using three Gaussians of the s-orbital form (table 2.1) (STO-3G basis). The coefficients and exponents for the STO-3G basis of hydrogen can be found in table 3.1.

The SCF procedure for determining c_{1i} and c_{2i} (eq. 2.23) unfolds as follows:

1. *Calculate the four overlap integrals $S_{\mu\nu}$ (eq. 2.20) for the overlap matrix* $\mathbf{S}$.

2. *Diagonalize* $\mathbf{S}$ *and obtain* $\mathbf{X}$.

3. *Calculate the initial Fock matrix (*$\mathbf{F}(\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0})$*, where* $\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0} = \mathbf{C}_\mathbf{0}$*), by solving the four integrals:*

$$\begin{aligned} F_{\mu\nu}(\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0}) &= \int \chi_\mu^*(\vec{r})\hat{F}(\tilde{\mathbf{C}}_\mathbf{0} = 0)\chi_\nu(\vec{r})d\vec{r} \\ &= \int \chi_\mu^*(\vec{r}) \left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_1 - \vec{r}_1|} - \frac{Z_H e^2}{4\pi\epsilon_0|\vec{R}_2 - \vec{r}_1|} \right] \chi_\nu(\vec{r})d\vec{r} \end{aligned} \tag{2.24}$$

   and then calculate $\tilde{\mathbf{F}}(\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0}) = \mathbf{X}^\mathbf{T}\mathbf{F}(\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0})\mathbf{X}$.

4. *Solve the eigenvalue problem* $\tilde{\mathbf{F}}(\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0})\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\mathbf{E}$*(eq. 2.21) by diagonalizing* $\tilde{\mathbf{F}}(\tilde{\mathbf{C}}_\mathbf{0} = \mathbf{0})$*, and obtain* $\tilde{\mathbf{C}}_1$ *and* $\mathbf{E}_1$.

5. *If the obtained coefficient matrix* $\tilde{\mathbf{C}}_1$ *is consistent with the input coefficient matrix* $\tilde{\mathbf{C}}_\mathbf{0}$*, our process is complete. Otherwise, update the initial guess with* $\tilde{\mathbf{C}}_\mathbf{1}$ *and repeat step 3 to 6 until the two matrices match (*$\tilde{\mathbf{C}}_\mathbf{k} = \tilde{\mathbf{C}}_\mathbf{k+1}$*).*

What we ***expect*** *for* H_2 *is to find a bonding (*$\phi_+ = A\left[\chi_1 + \chi_2\right]$*) and an antibonding (*$\phi_- = B\left[\chi_1 - \chi_2\right]$*, where A and B are constants) molecular 1s-orbital [12]. For these molecular orbitals, the coefficients of the LCAO must be identical due to the symmetry of* H_2*. Both hydrogen atoms need to contribute in an equivalent manner. The orbitals we find will be presented in section 3.2.*

2.2 Hamiltonian in second quantization

In quantum computation, for the purpose of representing a fermionic system using qubits, we must employ the second-quantization approach, also referred to as occupation number representation, and subsequently translate the resultant fermionic problem to qubits. In this section, our attention will be directed towards the former aspect. The discussion of the latter will be covered in section 2.3. Additionally, starting from this point, natural units will be utilized ($\hbar = m_e = e = 1$).

The second-quantization approach is conducted within the framework of the Born-Oppenheimer approximation. The antisymmetry inherent to fermionic systems is captured through operator properties, and states are expressed in terms of occupation numbers. Consequently, there's no requirement for the states themselves to be antisymmetrized. Specifically, an electronic state is represented as $|n_1, n_2, \cdots, n_M\rangle$, where M denotes the number of spin-orbitals (N occupied orbitals + virtual orbitals). For fermionic systems, the values of n_p can be one if the spin-orbital ϕ_p is occupied, and zero otherwise, in accordance with the Pauli exclusion principle. To perceive the analogy, one can contrast this electronic state with the Slater determinant in equation 2.11. Each Slater determinant corresponds to a distinct electronic state. Any potential electronic state can be formulated as a superposition of states of this kind.

Every operator in second quantization can be depicted using fermionic ladder operators a_p,$a_p^\dagger$

$$\begin{aligned} a_p^\dagger |n_1, \dots, n_p, \dots, n_M\rangle &= \delta_{n_p,0}(-1)^{\sum_{q<p} n_q} |n_1, \dots, (n_p+1), \dots, n_M\rangle \\ a_p |n_1, \dots, n_p, \dots, n_M\rangle &= \delta_{n_p,1}(-1)^{\sum_{q<p} n_q} |n_1, \dots, (n_p-1), \dots, n_M\rangle \end{aligned} \tag{2.25}$$

They are called the creation and annihilation operator, respectively, and fulfill the anticommutation relations

$$[a_p, a_q] = \left[a_p^\dagger, a_q^\dagger\right] = 0 \qquad \left[a_p, a_q^\dagger\right] = \delta_{pq} \tag{2.26}$$

In equation 2.25, the factor $(-1)^{\sum_{q<p} n_q}$ accounts for the antisymmetry (exchange symmetry). The Kronecker delta handles the Pauli exclusion principle.

Utilizing this understanding, the Hamiltonian in second-quantized form can be represented using these operators as follows:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \tag{2.27}$$

The electronic Hamiltonian in second quantized form also includes the constant nuclear repulsion term: $\hat{H}_e = \hat{H} + V_{N_c N_c}$. We will neglect this term for now, but it will be included in the Hamiltonian and energy calculations in Chapters 3 and 4. Here, h_{pq} and h_{pqrs} represent the one- and two-electron integrals, respectively, that are essential for constructing the molecular Hamiltonian. These integrals can be computed by performing integrations over molecular spin orbitals ϕ as follows:

$$\begin{aligned} h_{pq} &= \int \phi_p(\mathbf{x})^* \left(-\frac{\nabla^2}{2} - \sum_{i=1}^{N} \frac{Z_i}{|\vec{r} - \vec{R}_i|} \right) \phi_q(\mathbf{x}) d\mathbf{x} \\ h_{pqrs} &= \int \frac{\phi_p(\mathbf{x}_1)^* \phi_q(\mathbf{x}_2)^* \phi_r(\mathbf{x}_2) \phi_s(\mathbf{x}_1)}{|\vec{r}_1 - \vec{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \tag{2.28}$$

Here, $\mathbf{x}$ encompasses both spatial and spin degrees of freedom, in analogy to section 2.1.2. Once more, we will disregard spin dependence and center our attention on spatial orbitals. We can achieve this by modifying our summations in equation 2.27, as spin integration primarily results in certain integrals being set to zero due to orthonormality. The one-electron integral incorporates contributions from electronic kinetic energy and the electron-nuclear Coulomb interaction of one electron with all nuclei. The two-electron integral accounts for the electron-electron Coulomb interaction [3] [13].

Using the LCAO approach (eq. 2.17), the integrals in equation 2.28 can be computed upon determining the coefficient matrix $\mathbf{C}$ (eq. 2.19). Subsequently, after establishing the coefficient matrix, we can formulate the optimized molecular orbitals (eq. 2.17), construct the molecular Hamiltonian in second-quantized form (eq. 2.27), and calculate the Hartree-Fock energy.

Example 2.2.1 *H_2*
For H_2, as elucidated in the preceding section, we expounded that the electrons can inhabit bonding and antibonding orbitals. Taking spin orientation into account, we discern four molecular spin orbitals. Consequently, a feasible two-electron state assumes the form $|n_1, n_2, n_3, n_4\rangle$, where the first two wavefunctions correspond to the bonding orbital with up-spin, bonding orbital with down-spin, and antibonding orbital with up and down spins, respectively. The lowest energy determinant (HF state) is simply $|1, 1, 0, 0\rangle$, as the bonding orbital boasts a lower energy.

The complete Hamiltonian in second-quantization is then as follows:

$$\begin{aligned} \hat{\mathrm{H}} =& h_{11} a_1^\dagger a_1 + h_{22} a_2^\dagger a_2 + h_{33} a_3^\dagger a_3 + h_{44} a_4^\dagger a_4 \\ &+ h_{1221} a_1^\dagger a_2^\dagger a_2 a_1 + h_{3443} a_3^\dagger a_4^\dagger a_4 a_3 + h_{1441} a_1^\dagger a_4^\dagger a_4 a_1 + h_{2332} a_2^\dagger a_3^\dagger a_3 a_2 \\ &+ \left(h_{1331} - h_{1313}\right) a_1^\dagger a_3^\dagger a_3 a_1 + \left(h_{2442} - h_{2424}\right) a_2^\dagger a_4^\dagger a_4 a_2 \\ &+ \Re\left(h_{1423}\right) \left(a_1^\dagger a_4^\dagger a_2 a_3 + a_3^\dagger a_2^\dagger a_4 a_1\right) + \Re\left(h_{1243}\right) \left(a_1^\dagger a_2^\dagger a_4 a_3 + a_3^\dagger a_4^\dagger a_2 a_1\right) \\ &+ \Im\left(h_{1423}\right) \left(a_1^\dagger a_4^\dagger a_2 a_3 - a_3^\dagger a_2^\dagger a_4 a_1\right) + \Im\left(h_{1243}\right) \left(a_1^\dagger a_2^\dagger a_4 a_3 - a_3^\dagger a_4^\dagger a_2 a_1\right) \end{aligned} \tag{2.29}$$

It's evident that certain one- and two-electron integrals vanish as a consequence of spin integration, while others vanish due to spatial symmetry [4]. For example, only one-electron integrals of same spin orbitals, do not vanish. Moreover, they are contingent upon the distance between the nuclei.

The first row of operators in the Hamiltonian 2.30 contains the one-electron operators, responsible for the energy contribution of each molecular orbital to the overall *energy of the system. The second and third rows encompass the coulomb and exchange operators, respectively, while the final two rows involve the double excitation operators [14]. The third row's coefficients are antisymmetrized, which reflects the exchange antisymmetry of fermions.*

Using the indistinguishability of electrons, we obtain $h_{pqrs} = h_{qpsr}$ *and* $a_p^\dagger a_q^\dagger a_r a_s = a_q^\dagger a_p^\dagger a_s a_r$. *Additionaly we observe, that* $h_{pqrs} = \overline{h_{srqp}}$. *These two equations were fundamental in deriving the real and imaginary double excitation terms in the final two rows [15].*

Using the normalization of spin integration, and the fact that orbitals 1 and 2, as well as 3 and 4, share the same spatial orbitals, leading to some integrals being identical [4], we can derive a simplified version of equation 2.29. It's worth noting that for the stable molecule H_2, *the molecular orbitals and, consequently, the coefficients are real, making the imaginary components of equation 2.29 disappear:*

$$\begin{aligned}\hat{\mathrm{H}} =& h_{11}(a_1^\dagger a_1 + a_2^\dagger a_2) + h_{33}(a_3^\dagger a_3 + a_4^\dagger a_4) \\ &+ h_{1221} a_1^\dagger a_2^\dagger a_2 a_1 + h_{3443} a_3^\dagger a_4^\dagger a_4 a_3 + h_{1441}(a_1^\dagger a_4^\dagger a_4 a_1 + a_2^\dagger a_3^\dagger a_3 a_2) \\ &+ (h_{1331} - h_{1313})(a_1^\dagger a_3^\dagger a_3 a_1 + a_2^\dagger a_4^\dagger a_4 a_2) \\ &+ h_{1423}\left(a_1^\dagger a_4^\dagger a_2 a_3 + a_3^\dagger a_2^\dagger a_4 a_1 + a_1^\dagger a_2^\dagger a_4 a_3 + a_3^\dagger a_4^\dagger a_2 a_1\right)\end{aligned} \tag{2.30}$$

2.3 Fermion-qubit mappings

As previously mentioned, once the Hamiltonian is obtained in second quantization, it becomes essential to transform the problem into qubits to enable its representation on a quantum computer. One common mapping method is the Jordan-Wigner transformation. Converting a state in this convention is straightforward. An occupied orbital corresponds to an up-spin qubit, and an unoccupied one to a down-spin qubit (e.g., $|1,1,0,0\rangle \Rightarrow |\uparrow,\uparrow,\downarrow,\downarrow\rangle$). Consequently, we can represent any element of the occupation number basis.

However, the challenge lies in mapping the operators. We need to map fermionic operators to operators that act on qubits. Qubit operators are bosonic operators like the Pauli operators $\{\mathbb{1}, \sigma^x, \sigma^y, \sigma^z\} = \{\mathbb{1}, X, Y, Z\}$:

$$\mathbb{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.31}$$

The mapping process needs to preserve the required fermionic exchange symmetries. Appropriate qubit operators are the $\sigma_j^{\pm} = \sigma_j^x \pm i\sigma_j^y$ rotations, which convert an up-spin to a down-spin ($\hat{a}_j \to \sigma_j^-$) and a down-spin to an up-spin ($\hat{a}_j^\dagger \to \sigma_j^+$), respectively. Moreover, we include Pauli-Z operators to uphold the exchange symmetry (the fermionic anti-commutation relations), resulting in the following transformation:

$$\begin{aligned} a_p &= \frac{1}{2} Z_1 \otimes \cdots Z_{p-1} \otimes (X_p - iY_p) \\ a_p^\dagger &= \frac{1}{2} Z_1 \otimes \cdots Z_{p-1} \otimes (X_p + iY_p) \end{aligned} \tag{2.32}$$

The challenge with the Jordan-Wigner mapping is the requirement for a large number of single-qubit gates (Pauli-Z operators). Bravyi and Kitaev introduced an alternative mapping that encodes this anti-symmetrization more efficiently. Additionally, various alternative approaches have been proposed to enhance the Jordan-Wigner mapping in terms of qubit needed. However, for our objectives, we won't delve further into these mappings, as the Jordan-Wigner mapping is sufficient [4].

Example 2.3.1 H_2
While the qubit Hamiltonian can become quite complex in the general case, it is relatively simple in the H_2 case:

$$\begin{aligned} \hat{H} =& b_1\mathbb{1} + b_2 Z_1 + b_3 Z_2 + b_4 Z_3 + b_5 Z_4 \\ &+ b_6 Z_1 Z_2 + b_7 Z_1 Z_3 + b_8 Z_1 Z_4 \\ &+ b_9 Z_2 Z_3 + b_{10} Z_2 Z_4 + b_{11} Z_3 Z_4 \\ &+ b_{12} \left(X_1 Y_2 Y_3 X_4 + Y_1 X_2 X_3 Y_4 - X_1 X_2 Y_3 Y_4 - Y_1 Y_2 X_3 X_4 \right). \end{aligned} \tag{2.33}$$

The constants b_i are parameters that we won't detail here. However, it's important to note that they are expressed in units of Hartree, and dependent on the internuclear distance. Furthermore, when the complete electronic Hamiltonian is considered, including the nuclear repulsion term, the only thing that changes is the constant b_1. This is obvious since the nuclear repulsion term is only a constant, not an operator.

The determined values for the complete electronic Hamiltonian will be provided in section 3.2. It is apparent that the qubit Hamiltonian encompasses operators involving one, two, and four qubits. These correspond to the operators in the first, second/third, and fourth lines of equation 2.33, respectively. This alignment mirrors the structure found in the second-quantized Hamiltonian (eq. 2.30).

To elucidate how these terms are derived from the second-quantized Hamiltonian, let's provide an example for the one-, two-, and four-qubit operators:

$$\begin{aligned}
a_1^\dagger a_1 &= \frac{1}{4}\left[X_1 + iY_1\right]\left[X_1 - iY_1\right] \\
&= \frac{1}{4}\left[X_1X_1 - iX_1Y_1 + iY_1X_1 + Y_1Y_1\right] \\
&= \frac{1}{2}\mathbb{1} + \frac{1}{2}Z_1 \\
\\
a_1^\dagger a_2^\dagger a_2 a_1 &\overset{[a_1,a_2]=0=[a_2^\dagger,a_1]=0}{=} a_1^\dagger a_1 a_2^\dagger a_2 \\
&= a_1^\dagger a_1\left[\frac{1}{4}Z_1Z_1\left[X_2 + iY_2\right]\left[X_2 - iY_2\right]\right] \\
&= a_1^\dagger a_1\left[\frac{1}{2}\mathbb{1} + \frac{1}{2}Z_2\right] \\
&= \frac{1}{4}\left[\mathbb{1} + Z_1 + Z_2 + Z_1Z_2\right] \\
\\
a_1^\dagger a_4^\dagger a_2 a_3 &= a_1^\dagger a_4^\dagger\left[\frac{1}{4}Z_1\left[X_2 - iY_2\right]Z_1Z_2\left[X_3 - iY_3\right]\right] \\
&= a_1^\dagger a_4^\dagger\left[\frac{1}{4}\left[X_2 - iY_2\right]\left[X_3 - iY_3\right]\right] \\
&= -\frac{1}{16}[X_1X_2X_3X_4 \\
&\quad + iX_1X_2X_3Y_4 - iX_1X_2Y_3X_4 - iX_1Y_2X_3X_4 + iY_1X_2X_3X_4 \\
&\quad + X_1X_2Y_3Y_4 + X_1Y_2X_3Y_4 - X_1Y_2Y_3X_4 - Y_1X_2X_3Y_4 + Y_1X_2Y_3X_4 + Y_1Y_2X_3X_4 \\
&\quad - iX_1Y_2Y_3Y_4 + iY_1X_2Y_3Y_4 + iY_1Y_2X_3Y_4 - iY_1Y_2Y_3X_4 \\
&\quad + Y_1Y_2Y_3Y_4]
\end{aligned} \tag{2.34}$$

We utilized the anticommutation relations and multiplied operators that act on the same qubits. It's noticeable that the one-electron operator results in a diagonal qubit operator, implying a system of non-interacting fermions. This also holds true for the two-qubit operator, which is a product of two one-qubit operators following the same pattern. Yet, when examining the four-qubit operators, a non-diagonal outcome emerges. This signifies that the four-qubit operators describe interactions between the electrons [16].

Hence, it becomes evident what each term of the Hamiltonian in equation 2.33 signifies. These terms can be understood in analogy with the second-quantized Hamiltonian.

2.4 The Variational Quantum Eigensolver

After exploring the process of constructing the qubit Hamiltonian within the Hartree-Fock approximation, which is essential for representing our system on a quantum computer, we can now proceed to outline the actual approach we employed to compute the ground states of certain small molecules.

As previously mentioned, exact solutions are generally not feasible for most electronic structure problems (eq. 2.6). The Hartree-Fock method provides an initial approximation for the molecular orbitals and ground state energies, facilitating the creation of the qubit Hamiltonian. However, this approximation of the molecular orbitals (HF-state; eq. 2.11) and thus the ground state energies (HF-energy) is rather crude, as it neglects the Coulomb correlation among the electrons. This leads to a total electronic energy different from the exact solution of the non-relativistic Schrödinger equation within the Born–Oppenheimer approximation. In quantum chemistry, the goal is to obtain solutions that closely resemble the exact values. To achieve this, quantum computing techniques can be leveraged to attain improved approximations for molecular orbitals and ground states by entangling qubits in a quantum circuit.

One of these techniques, known as Post-Hartree-Fock methods, is the Variational Quantum Eigensolver (VQE). In this approach, the circuit is initialized in the HF-state, and gates are applied to entangle the qubits. This concept aligns with the idea of considering more than one Slater determinant for the wavefunction in equation 2.11. The entanglement leads to more accurate molecular orbitals, minimizing the expectation value of the Hamiltonian created with the molecular orbitals within the Hartree-Fock approximation. Consequently, a better approximation of the ground state is obtained. The entangling gates are parameterized by a variable θ, resulting in a parameter-dependent wave function. The observation that the ground state energy (energy in the true ground state) is lower than the energy in the initial state (HF-state) is encapsulated by the Variational Theorem:

$$E(\theta) = \langle \Phi(\theta) | \hat{H} | \Phi(\theta) \rangle \geq E_0 \tag{2.35}$$

where Φ is normalized [3][17]. By optimizing the parameter θ, we determine the smallest eigenstate of the utilized Hamiltonian. This approach yields an approximate ground state energy that is closer to the true ground state energy compared to the HF-energy. Figure 2.1 provides a visual representation of the different approximative energy levels.

The Hartree-Fock energy represents the most crude approximation and serves as an upper bound for the energy. Achieving the Hartree-Fock limit, which represents the best approximation attainable within the HF-approximation, requires expanding the atomic basis set to full completeness. The difference between the HF limit and the exact energy, which considers complete correlation effects (full CI method= eq. 2.36) and employs a full basis set, is referred to as the correlation energy. This term encompasses the contribution to the energy arising from Coulomb correlation [7]. The energies obtained through the VQE methodology presented in this thesis

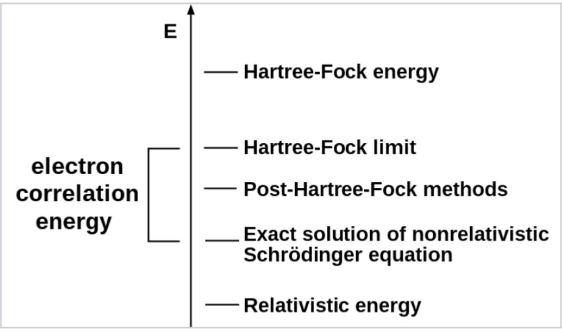


Figure 2.1: Electron correlation energy and illustration of approximate energie obtained by solving the the Schrödinger equation for various approximation levels (source: [7]).

will lie between these two limits.

2.4.1 The VQE algorithm

Now, let's investigate how the VQE actually operates. As mentioned earlier, VQE is a quantum-classical algorithm designed to minimize the so-called cost function, which, in our case, represents the system's energy. The minimization process is divided into two parts: the first part is executed on a quantum computer, while the second part runs on a classical computer.

1. **Quantum Part:**
   The quantum computer sets up a small quantum circuit, initialized in the Hartree-Fock state. This circuit applies entangling gates/rotations to the qubits, based on an Ansatz, to modify this initial state. Then the resulting expectation value of the Hamiltonian in this state is measured and passed to the classical computer.
   One standard approximation used for an accurate corrected wavefunction, compared to the Hartree-Fock state, is the Unitary Coupled Cluster (UCC) method. It approximates the many-electron wavefunction Φ, not by a single Slater determinant (as in the HF-approximation; eq. 2.11), but by a linear combination of all possible Slater determinants of a complete set of spin orbitals, including excited state Slater determinants:

   $$\Phi = c_0|\Phi_{HF}> + \sum_{a,r} c_a^r|\Phi_a^r> + \sum_{a<b,r<s} c_{ab}^{rs}|\Phi_{ab}^{rs}> + \cdots \tag{2.36}$$

   Here, the first term on the right side is the HF-state, the second term describes all determinants with a single-particle excitation from state a to r, the third term describes all double excitations from the states a and b to states r and s, and so on. In this thesis, we use the UCCSD (**U**nitary-**C**upled-**C**luster-**S**ingles and **D**oubles) approximation, which includes only the Hartree-Fock, single-excitation, and double-excitation Slater determinants. It is the most common approximation of Φ (eq. 2.36) [6].
   The gate Ansatz for our circuit in UCCSD corresponds to applying all possible single- and double-excitation rotations to the qubits, changing the initial state.

These rotations depend on the angle θ. Single excitations are represented by two-qubit gates, while double excitations are represented by four-qubit gates:

$$\begin{aligned}
\textbf{single exitation}\quad & G(\theta) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(\theta/2) & -\sin(\theta/2) & 0 \\ 0 & \sin(\theta/2) & \cos(\theta/2) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \\
& \text{with ordering} \quad |00\rangle, |01\rangle, |10\rangle\, |11\rangle \\
& \Rightarrow G(\theta)|01\rangle = \cos(\theta/2)|01\rangle + \sin(\theta/2)|10\rangle \\
& \Rightarrow G(\theta)|10\rangle = \cos(\theta/2)|10\rangle - \sin(\theta/2)|01\rangle
\end{aligned} \tag{2.37}$$

$$\begin{aligned}
\textbf{double exitation}\quad & G^{(2)}(\theta)|0011\rangle = \cos(\theta/2)|0011\rangle + \sin(\theta/2)|1100\rangle \\
& G^{(2)}(\theta)|1100\rangle = \cos(\theta/2)|1100\rangle - \sin(\theta/2)|0011\rangle
\end{aligned} \tag{2.38}$$

A single excitation corresponds to entangling the states $|01\rangle$ and $|10\rangle$, which differ by the excitation of a single particle. On the other hand, a double excitation corresponds to entangling states $|1100\rangle$ and $|0011\rangle$, where the transformation from $|1100\rangle$ to $|0011\rangle$ is interpreted as the "excitation" of two particles from the first pair of qubits to the second pair of qubits [3].

2. **Classical Part:**
   Receiving the resulting expectation value of the Hamiltonian, the classical computer employs optimization techniques to determine optimized parameters (θ) that minimize the energy cost function.
   One common optimization method used here is a gradient-based method, which works well with automatic differentiation in Pennylane. This method, known as the gradient descent optimizer (machine learning technique), finds the minimum energy by adjusting the input parameter θ along the steepest slope of the energy landscape:

$$\theta \to \theta - \eta \frac{\partial E(\theta)}{\partial \theta} \tag{2.39}$$

   where η represents the step size. The choice of η is crucial, it should be large enough for fast convergence but small enough to avoid overshooting the minimum [18].
   The optimized parameter is then fed back into the quantum part, and a new expectation value for the energy is calculated. This process is repeated iteratively until the energy converges to its minimum.

2.4.2 The challenges of VQE

The Variational Quantum Eigensolver (VQE) algorithm efficiently combines quantum and classical computations to approximate the ground state energy and molecular orbitals. However, there are three primary challenges that we want to highlight, associated with the VQE approach [3]:

1. **Choice of Ansätze**: There are multiple possible choices for the initial state and the unitary transformation of the state (gates). It's crucial to make wise selections here. In this work, we use the Hartree-Fock state as the initial state, which is a good approximation near equilibrium. This choice helps the VQE algorithm converge faster than starting with a random state. Additionally, we use the UCCSD Ansatz, as described above, because it is the most simple approximation of the wavefunction. These are the commonly used Ansätze.

2. **Computing the Expectation Value of the Hamiltonian**: Another significant challenge lies in calculating the expectation value of the Hamiltonian. When running the circuit with a simulator, PennyLane transforms the Hamiltonian H into a matrix, and the quantum state (Φ) into a vector. Subsequently, it performs matrix-vector multiplication to determine the expectation value. On the other hand, when utilizing a Quantum Device for execution, the Hamiltonian can be expressed as a sum of individual terms ($\hat{H} = \sum_i \hat{H}_i$). Each of these terms is measured independently. To optimize resource usage, the same set of qubits can be repurposed for each term by repeatedly preparing the quantum state. This allows for the computation of the expectation value as the sum of individual measurements ($< \hat{H} >= \sum_i < \hat{H}_i >$).

In the Chapter 4, we will provide an example of the VQE implementation in this thesis, once again focusing on H2.

2.5 ADAPT-VQE

Moreover, while the fixed Ansatz described above may perform well in many scenarios, it lacks efficiency for specific molecules, especially larger ones. In such cases, reducing the circuit depth becomes crucial to enhance efficiency. An effective strategy, which we will employ in this thesis, is the ADAPT-VQE algorithm. This algorithm dynamically adjusts the Ansatz based on the specific molecule under investigation.

The approach involves defining a pool of gates (in our case, all possible single and double gates), applying each gate to the initial state, and then selecting the gate that yields the largest gradient, that means the one contributing the most to the change in energy. This selected gate is then optimized using the traditional VQE method, and the resulting gate parameters are fixed, defining a new initial state. This process iterates until a convergence criterion is met [3]. In our case, the convergence criterion is approximately zero gradient, indicating that the energy change becomes negligible with the addition of more gates. This criterion signifies that the optimization process has effectively minimized the energy.

3 Construction of the molecular Hamiltonian

After having discussed the theoretical foundations, we want to explain how the VQE was implemented in this thesis. The first thing we need for the implementation is the molecular Hamiltonian. In this chapter, we will examine the Hamiltonians and molecular orbitals we constructed for a fixed molecular geometry. The implementation and the results of the VQE will be presented in Chapter 4.

Our implementation utilizes PennyLane, particularly making use of the relatively recent quantum chemistry module "qchem" within PennyLane. This setup allows us to employ the VQE method and compute ground states for four small molecules: two diatomic molecules (H_2 and LiH) and two triatomic molecules (BeH_2 and H_2O). Notably, one of these molecules possesses a 3-dimensional geometry, showcasing the versatility of our approach across various system configurations.

3.1 PennyLane for quantum chemistry

PennyLane is incredibly helpful for implementing a VQE for ground state calculations, particularly in constructing the molecular Hamiltonian. It provides built-in methods for constructing atomic and molecular orbitals, building Fock matrices, and solving the SCF equations for the optimized orbitals. This means we can simply construct the molecular Hamiltonians with PennyLane and use them in the VQE afterwards.

Furthermore, PennyLane allows us to compute derivatives of these objects through automatic differentiation, which is essential for the optimization method of our VQE. This method differentiates functions, requiring resources comparable to those needed for function evaluation, making the implementation efficient. Consequently, it has gained significant attention in machine learning [3].

3.2 Qubit Hamiltonian with Pennylane

As the qubit Hamiltonian describes our system, it is the most crucial component of the ground state calculation. Therefore, it is essential to examine closely the Hamiltonians we constructed using PennyLane.

The construction follows the methods described in the previous sections. For a given molecule and geometry, first, the optimized molecular orbitals are calculated (section 2.1.3). Then, the Hamiltonian in second quantization is derived (section 2.2), and, finally, the Jordan-Wigner transformation is applied (section 2.3). We will present the constructed Hamiltonians and all the further necessary data for the construction, starting with the hydrogen molecule.

In Chapter 4.2, we will calculate the ground state energy of all the molecules presented in this chapter, for multiple geometries. Since the Hamiltonians and molecular orbitals have the same form but different coefficients for different geometries, we will not present all of them here.

3.2.1 Hydrogen molecule - H_2

For the hydrogen molecule (H_2), we previously presented the Linear Combination of Atomic Orbitals (LCAO) in the example in section 2.1.3. For simplicity and consistency, we will write it down here using bra-ket notation:

$$|\phi_i >= c_{1i}|1s >_{H^{(1)}} + c_{2i}|1s >_{H^{(2)}} \tag{3.1}$$

The coefficients and exponents of the STO-3G basis set for a hydrogen 1s-orbital are sourced from the build in library of PennyLane, and you can find them in table 3.1.

atomic orbital	i	a_i	α_i
	1	0.1543289673	3.425250914
1s	2	0.5353281423	0.6239137298
	3	0.4446345422	0.1688554040

Table 3.1: Coefficients a_i and exponents α_i for the STO-3G approximation of a 1s hydrogen orbital. Index i is the Gaussians index (always 1 to 3).

The two optimized molecular orbitals in the LCAO approach (eq. 2.23), and consequently the qubit Hamiltonian, depend on the internuclear distance between the hydrogen atoms. We will now present these orbitals for an internuclear distance of 0.742 $\mathring{A}$. They are acquired using the Self-Consistent Field (SCF) method, which yields the following coefficients: It's evident that we obtain exactly what we expected: a bonding orbital (ϕ_+) and an antibonding orbital (ϕ_-), as explained in the example in section 2.1.3.

i	c_{1i}	c_{2i}
+	-0.54905874	-0.54905874
-	-1.21012637	1.21012637

Table 3.2: Optimized coefficients $c_{\nu i}$ for H_2 at $r_{H-H} = 0.742\mathring{A}$ (eq. 2.23). We do find two molecular orbitals ϕ_+ and ϕ_-

The resulting qubit Hamiltonian is

$$\begin{aligned}\hat{H}\left(r_{H-H}=0.742\mathring{A}\right) = & -0.0996\mathbb{1}+0.1711Z_1+0.1711Z_2-0.2225Z_3-0.2225Z_4\\ & +0.1686Z_1Z_2+0.1205Z_1Z_3+0.1658Z_1Z_4\\ & +0.1658Z_2Z_3+0.1205Z_2Z_4+0.1743Z_3Z_4\\ & +0.0453\left(X_1Y_2Y_3X_4+Y_1X_2X_3Y_4-X_1X_2Y_3Y_4-Y_1Y_2X_3X_4\right).\end{aligned} \tag{3.2}$$

where the coefficients are expressed in units of Hartree. These terms match those in equation 2.33, confirming our expectations. Moreover, the equality of the spatial orbitals for spin orbitals 1 and 2, as well as 3 and 4, which we utilized in Equation 2.30, is also evident in the coefficients derived here. This demonstrates the successful construction of the Hamiltonian with PennyLane. It is obvious that to represent this Hamiltonian in a quantum circuit, we need 4 qubits, as there are up to four Pauli operators.

The construction of the Hamiltonian for other molecules follows a similar procedure. The primary distinction lies in the Linear Combination of Atomic Orbitals (LCAO). In the case of larger atoms with more electrons and consequently more orbitals, we must consider higher-order orbitals. In our study, which includes molecules such as H_2, LiH, BeH_2, and H_2O, all of the atoms have atomic numbers lower than 10. Therefore, we need to consider orbitals up to the 2p-orbital. As a result, the Hamiltonians for these molecules contain a larger number of terms compared to H_2 in order to faithfully represent the entire system. In the case of heteronuclear molecules, it's important to note that different atoms contribute differently to the Hamiltonian. The molecular orbitals in the heteronuclear case will be concentrated more around one nucleus than the other. Additionally, the coefficients and exponents of the STO-3G approximation for atomic orbitals, which are sourced from the build in library of PennyLane, naturally differ for various atoms.

3.2.2 Lithium hydride - *LiH*

As we explained, the Linear Combination of Atomic Orbitals (LCAO) involves a linear combination of all atomic orbitals present in the molecule. For Lithium hydride (LiH), this means we have to consider the orbitals of both hydrogen and lithium. This results in the following LCAO:

$$\begin{aligned}|\phi_i> = & c_{1i}|1s>_H\\ & +c_{2i}|1s>_{Li}+c_{3i}|2s>_{Li}+c_{4i}|2p_x>_{Li}+c_{5i}|2p_y>_{Li}+c_{6i}|2p_z>_{Li}\end{aligned} \tag{3.3}$$

Since each of these atomic orbitals needs to be approximated using the STO-3G basis, the coefficients and exponents table becomes significantly larger, now involving six different orbitals. You can find the coefficients and exponents for the STO-3G basis of the lithium orbitals in Table 3.3. The coefficients and exponents for the hydrogen orbital can still be found in Table 3.1.
The geometry used for lithium hydride here is analogous to that of H_2. We place the origin in the middle between the two atoms and align the molecule with the z-axis. The optimized molecular orbitals and the qubit Hamiltonian are presented

atomic orbital	i	a_i	α_i
1s	1	0.1543289673	16.11957475
	2	0.5353281423	2.936200663
	3	0.4446345422	0.794650487
2s	1	-0.09996722919	0.6362897469
	2	0.3995128261	0.1478600533
	3	0.7001154689	0.0480886784
$2p_x$	1	0.155916275	0.6362897469
	2	0.6076837186	0.1478600533
	3	0.3919573931	0.0480886784
$2p_y$	1	0.155916275	0.6362897469
	2	0.6076837186	0.1478600533
	3	0.3919573931	0.0480886784
$2p_z$	1	0.155916275	0.6362897469
	2	0.6076837186	0.1478600533
	3	0.3919573931	0.0480886784

Table 3.3: Coefficients a_i and exponents α_i for the STO-3G approximation of the Li orbitals. Index i is the Gaussians index (always 1 to 3).

here for an internuclear distance of $1.57\mathring{A}$.
Since we have six different atomic orbitals, we expect to find six different molecular orbitals. This is exactly what we find with the SCF method. The results are presented in Table 3.4.

i	c_{1i}	c_{2i}	c_{3i}	c_{4i}	c_{5i}	c_{6i}
1	-0.0050695	-0.9912179	-0.0325277	0.0000000	0.0000000	0.0065452
2	0.5473847	-0.1691179	0.4525666	0.0000000	0.0000000	0.3470727
3	-0.1380414	-0.2096517	0.8000105	0.0000000	0.0000000	-0.6124250
4	0.0000000	0.0000000	0.0000000	0.9999995	0.0010043	0.0000000
5	0.0000000	0.0000000	0.0000000	0.0010043	-0.9999995	0.0000000
6	1.200391	0.0896222	-0.7147686	0.0000000	0.0000000	-0.9886064

Table 3.4: Optimized coefficients $c_{\nu i}$ for LiH at $r_{Li-H} = 1.57\mathring{A}$ (eq. 3.3).

We want to verify our resulting molecular orbitals for the simplest example.
As explained in [19], for the orbitals of LiH, we expect to find, within our optimized orbitals, a 1s orbital that is mostly affected by the 1s lithium orbital. This expectation arises from the fact that the Li 1s orbital energy lies below the H 1s orbital energy, and the 1s orbitals are tightly bound to their respective nuclei, resulting in only small interactions. Taking a look at Table 3.4, one can see that orbital one has the most substantial contribution from the Li 1s orbital, making it a suitable candidate for the 1s molecular orbital. This observation confirms that our algorithm is functioning correctly once again.

The calculated qubit Hamiltonian for LiH is as follows:

$$\begin{aligned}
\hat{H}\left(r_{Li-H} = 1.57\mathring{A}\right) = & -5.7271\mathbb{1} - 0.2993Z_1 - 0.2993Z_2 - 0.3904Z_3 \\
& - 0.3904Z_4 - 0.4257Z_5 - 0.4257Z_6 - 0.4257Z_7 \\
& - 0.4257Z_8 - 0.5680Z_9 - 0.5680Z_{10} \\
& + 0.1223Z_1Z_2 + 0.0529Z_1Z_3 + 0.0561Z_1Z_4 \\
& + 0.0620Z_1Z_5 + 0.0679Z_1Z_6 + 0.0620Z_1Z_7 \\
& + 0.0679Z_1Z_8 + 0.0828Z_1Z_9 + 0.1137Z_1Z_{10} \\
& + \mathcal{O}(Z_iZ_j) \\
& + 0.0120X_1X_3 - 0.0018X_2X_4 \qquad (3.4) \\
& - 0.0018Y_2Y_4 + 0.0120Y_1Y_3 \\
& - 0.0040(Y_2Z_3Y_4 + X_2Z_3X_4 + Y_1Z_2Y_3 + X_1Z_2X_3) \\
& - 0.0309Y_1Y_2X_9X_{10} \\
& + \mathcal{O}(X_i/Y_i/Z_i \quad X_j/Y_j/Z_j \quad X_k/Y_k/Z_k \quad X_l/Y_l/Z_l) \\
& - 0.0090Y_3Z_5Z_6Z_7Z_8Y_9 \\
& + \cdots \\
& + 0.0086X_1X_2Y_3Z_4Z_5Z_6Z_7Z_8Z_9Y_{10}
\end{aligned}$$

We have only provided a subset of terms here to illustrate that the Hamiltonian for LiH contains significantly more terms than that of the hydrogen molecule. The terms represented by $\mathcal{O}(Z_iZ_j)$ include interactions between different pairs of atomic orbitals (orbital i and j), where i and j range from 2 to 9 and 2 to 10, respectively. The remaining terms, represented by $\mathcal{O}(X_i/Y_i/Z_i \quad X_j/Y_j/Z_j \quad X_k/Y_k/Z_k \quad X_l/Y_l/Z_l)$ and the ellipsis $(\cdots)$, involve various combinations of 4, 6, 7, 8, 9, and 10 Pauli X, Y, and Z operators acting on different qubits. The coefficients are expressed in units of Hartree. You can find the full qubit Hamiltonian in the Appendix.

We can see that this is analogous to the H_2 Hamiltonian, but it considers more relevant molecular orbitals in the system. One question that may arise here is why the index runs only up to 10, implying that 10 qubits are involved, even though 12 would be needed to represent all six molecular orbitals, considering both up and down spins. The reason for this is that lithium has 3 electrons, resulting in a closed first shell. For simulations, we can neglect this closed shell and only consider the active electrons responsible for bonding, which amounts to 5 orbitals or 10 qubits.

This example illustrates that complexity increases rapidly when adding more electrons to a system. For instance, H_2 with 2 electrons only requires 4 qubits, while LiH with 4 electrons needs 10 qubits to represent its electronic structure accurately.

3.2.3 Beryllium hydride - BeH_2

Now let us consider beryllium hydride. BeH_2, composed of two hydrogen atoms and one beryllium atom, exhibits symmetry around the beryllium atom. The LCAO for beryllium hydride is similar to that of lithium hydride, but it includes an additional

H 1s orbital due to the presence of an extra hydrogen atom:

$$\begin{aligned} |\phi_i> = c_{1i}|1s>_{H^{(1)}} + c_{2i}|1s>_{H^{(2)}} \\ + c_{3i}|1s>_{Be} + c_{4i}|2s>_{Be} + c_{5i}|2p_x>_{Be} + c_{6i}|2p_y>_{Be} + c_{7i}|2p_z>_{Be} \end{aligned} \tag{3.5}$$

The STO-3G coefficients and exponents for the beryllium orbitals can be found in Table 3.5.

atomic orbital	i	a_i	α_i
1s	1	0.1543289673	30.16787069
	2	0.5353281423	5.495115306
	3	0.4446345422	1.487192653
2s	1	-0.09996722919	1.31483311
	2	0.3995128261	0.3055389383
	3	0.7001154689	0.0993707456
$2p_x$	1	0.155916275	1.31483311
	2	0.6076837186	0.3055389383
	3	0.3919573931	0.0993707456
$2p_y$	1	0.155916275	1.31483311
	2	0.6076837186	0.3055389383
	3	0.3919573931	0.0993707456
$2p_z$	1	0.155916275	1.31483311
	2	0.6076837186	0.3055389383
	3	0.3919573931	0.0993707456

Table 3.5: Coefficients a_i and exponents α_i for the STO-3G approximation of the Be orbitals. Index i is the Gaussians index (always 1 to 3).

BeH_2 is the first triatomic molecule we examine. It is known to arrange in an angle of 180° [20], making it one-dimensional and describable solely by the distance between the nuclei (r_{Be-H}), similar to the diatomic molecules we've previously examined. We establish the origin at the position of the beryllium atom and, once again, align the molecule with the z-axis. Here, we will present our results for a nuclear distance of $1.33\AA$.

Since we have 7 orbitals in the LCAO, we expect to find 7 molecular orbitals with the SCF method. These are shown in Table 3.6.
Since the molecule is symmetric around the origin, we expect to observe symmetry in the molecular orbitals as well, similar to the hydrogen molecule. In this case, the symmetry arises from the atomic H orbitals. The H atoms are symmetrically placed around the origin, specifically along the z-axis. Therefore, the contribution of both the 1s H orbitals should be the same for all the optimized molecular orbitals. As seen in Table 3.6, this is indeed the case, with c_{1i} and c_{2i} having the same values, except for the sign.

In the case of beryllium hydride, we have 7 orbitals, which would require 14 qubits for Hamiltonian representation. However, by neglecting the inner shell once again (2 1s orbitals for 1 spin up and 1 spin down), we can reduce the number

i	c_{1i}	c_{2i}	c_{3i}	c_{4i}	c_{5i}	c_{6i}	c_{7i}
1	0.0027788	0.0027788	-0.9917529	-0.0317595	0.0000000	0.0000000	0.0000000
2	0.3944653	0.3944653	-0.2244827	0.5564571	0.0000000	0.0000000	0.0000000
3	-0.4046822	0.4046822	0.0000000	0.0000000	0.0000000	0.0000000	0.5034959
4	0.0000000	0.0000000	0.0000000	0.0000000	1.0000000	0.0000725	0.0000000
5	0.0000000	0.0000000	0.0000000	0.0000000	-0.0000725	1.0000000	0.0000000
6	-0.8227281	-0.8227281	-0.2181327	1.2335410	0.0000000	0.0000000	0.0000000
7	1.0355076	-1.0355076	0.0000000	0.0000000	0.0000000	0.0000000	1.4589256

Table 3.6: Optimized coefficients $c_{\nu i}$ for BeH_2 at $r_{Be-H} = 1.33\mathring{A}$ (eq. 3.5).

of qubits to 12. Consequently, the Hamiltonian should have indices up to 12 and include terms with up to 12 Pauli operators. As expected, the Hamiltonian does indeed have this structure. However, due to its length and complexity, we won't present the Hamiltonian here as it wouldn't provide any significant advantage in understanding. You can find the full qubit Hamiltonian in the Appendix.

3.2.4 Water molecule - H_2O

The last and most complex molecule we want to examine is the water molecule. Similar to BeH_2, this molecule is symmetric around the oxygen atom. The LCAO approach for water is similar to that of beryllium hydride:

$$\begin{aligned} |\phi_i> = {} & c_{1i}|1s>_{H^{(1)}} + c_{2i}|1s>_{H^{(2)}} \\ & + c_{3i}|1s>_O + c_{4i}|2s>_O + c_{5i}|2p_x>_O + c_{6i}|2p_y>_O + c_{7i}|2p_z>_O \end{aligned} \tag{3.6}$$

The coefficients and exponents for the STO-3G approximation of the oxygen orbitals are presented in Table 3.7.

atomic orbital	i	a_i	α_i
1s	1	0.1543289673	130.7093214
	2	0.5353281423	23.80886605
	3	0.4446345422	6.443608313
2s	1	-0.09996722919	5.033151319
	2	0.3995128261	1.169596125
	3	0.7001154689	0.38038896
$2p_x$	1	0.155916275	5.033151319
	2	0.6076837186	1.169596125
	3	0.3919573931	0.38038896
$2p_y$	1	0.155916275	5.033151319
	2	0.6076837186	1.169596125
	3	0.3919573931	0.38038896
$2p_z$	1	0.155916275	5.033151319
	2	0.6076837186	1.169596125
	3	0.3919573931	0.38038896

Table 3.7: Coefficients a_i and exponents α_i for the STO-3G approximation of the O orbitals. Index i is the Gaussians index (always 1 to 3).

The difference between beryllium hydride and the water molecule lies in the geometry. The typical structure of H_2O is not linear but rather bent [20]. This increases complexity and introduces a second parameter that has to be considered when defining the geometry: the angle. We used the geometry shown in Figure 3.1. We will present our results for an internuclear distance of H and O of $0.958\mathring{A}$ and an angle of 104.5°.

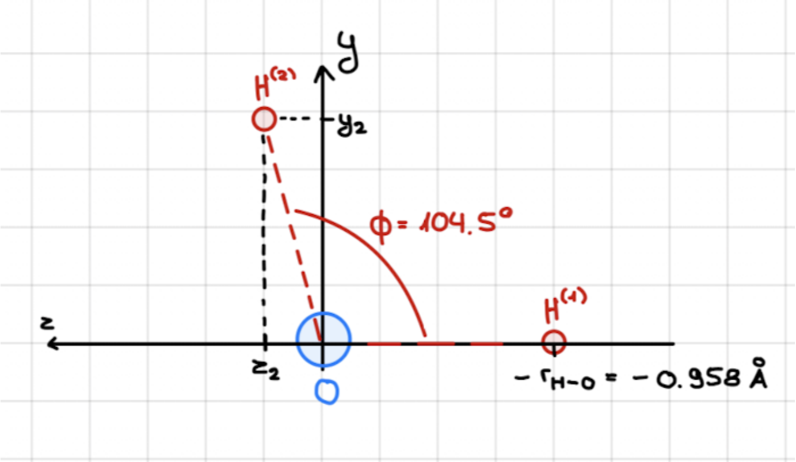


Figure 3.1: The geometry of H_2O used in this thesis.

Similarly to BeH_2, we expect to find 7 molecular orbitals with the SCF method. In Table 3.8, you can find our results.

i	c_{1i}	c_{2i}	c_{3i}	c_{4i}	c_{5i}	c_{6i}	c_{7i}
1	-0.0059629	-0.0059629	0.9941314	0.0265451	0.0000000	0.0034309	-0.0026565
2	0.1586638	0.1586638	-0.2328152	0.8337809	0.0000000	0.1022689	-0.0791851
3	-0.4450662	0.4450662	0.0000000	0.0000000	0.0000000	0.3712735	0.4795063
4	0.2781705	0.2781705	0.1031473	-0.5366643	0.0000000	0.6139744	-0.4753897
5	0.0000000	0.0000000	0.0000000	0.0000000	-1.0000000	0.0000000	0.0000000
6	-0.7965560	-0.7965560	-0.1322692	0.8833139	0.0000000	0.5869881	-0.4544947
7	0.8379779	- 0.8379779	0.0000000	0.0000000	0.0000000	0.6061462	0.7828486

Table 3.8: Optimized coefficients $c_{\nu i}$ for H_2O at $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$(eq. 3.6).

Once again, we see the symmetry of the molecule (2 H atoms) reflected in the atomic orbital contributions to the molecular orbitals. The coefficients c_{1i} and c_{2i} have the same values, except for the sign. One more interesting observation is that the only atomic orbital contributing to the 5th molecular orbital is the p_x orbital of the oxygen atom. The p_x orbital does not contribute to any other molecular orbital. Looking at Table 3.6 of the optimized BeH_2 orbitals, we see a similar phenomenon. The p_x and p_y orbitals of Be behave the same way. They contribute to two molecular orbitals but not to any others. This may be reflecting the fact that BeH_2 bonds along the z-axis, while H_2O bonds in the y-z plane. However, why is H_2O bent while BeH_2 is not? This is due to the fact that molecules adopt the configuration corresponding to the lowest energy state. We will demonstrate that the bonding angle of H_2O is indeed the angle of lowest energy in Chapter 4.2.

As the number of orbitals didn't change between BeH_2 and H_2O, the number of qubits required for the Hamiltonian representation remains the same. We need 14 qubits, which can be reduced to 12 by neglecting the full 1s shell of oxygen. Similar to the Hamiltonian of BeH_2, the Hamiltonian for H_2O also has terms with up to 12 Pauli operators. However, due to its length and complexity, we won't present the Hamiltonian here, as it wouldn't significantly enhance understanding. You can find it in the Appendix.

4 VQE in quantum chemistry

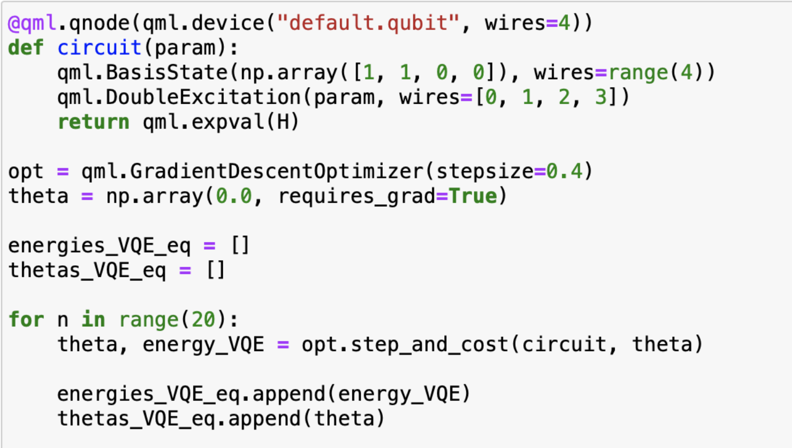
After constructing the qubit Hamiltonians and molecular orbitals, and verifying their correctness, we can now present our implementation of the VQE.

4.1 VQE implementation

In Section 2.4, we discussed the theoretical background of the VQE and its general operation. Now, we will explain how we implemented the VQE using PennyLane to approximate the ground state energies of H_2. We will provide our code and utilize graphics to demonstrate its proper functionality for a fixed internuclear distance. After presenting the VQE for H_2, we will illustrate its equivalent results to the ADAPT-VQE, which we employed for the other molecules due to its efficiency. Furthermore, we will present the resulting optimized quantum circuits for a fixed distance of all our molecules. In Section 4.2, we will showcase the energy surfaces of H_2, LiH, BeH_2, and H_2O, which we computed by determining the ground state energies for various internuclear distances, and angles for H_2O, using the VQE for H_2 and ADAPT-VQE for every other molecule. With the aid of these energy surfaces, we will define the equilibrium geometries of these molecules.

Let's begin with the VQE for the hydrogen molecule. The VQE implementation was inspired by Xanadu's PennyLane documentation paper [3]. For illustrative purposes, we employed the Hamiltonian presented in Equation 3.2. The corresponding code can be found in Figure 4.1. It's important to note that in all the figures from this point onwards, the qubits are numbered with indices starting from 0, whereas we previously used notation starting from 1.
Here, the qnode decorator specifies the device on which the quantum circuit runs. We utilized PennyLane's built-in "default.qubit" simulator. For more detailed functionalities of PennyLane, I refer you to the PennyLane documentation([21]). As we mentioned earlier, 4 qubits are required for Hamiltonian representation as hydrogen has 4 spin-orbitals, so we use 4 wires in the circuit. It is possible to reduce the number of qubits by utilizing symmetries (known as Qubit tapering), but we won't delve deeper into this theory, as the original number of qubits suffices for our purposes.

We initialize the circuit in the Hartree-Fock state of H_2 using PennyLane's 'BasisState' function. Then, we apply a double excitation gate (also via a PennyLane function), which represents the UCCSD Ansatz for H_2. While single excitations are also present in the Ansatz, the ADAPT-VQE will demonstrate that they are not essential for energy reduction in the case of H_2, thus are neglected here. The double excitation gate depends on a parameter θ, as shown in Equation 2.38. Subsequently,



```python
@qml.qnode(qml.device("default.qubit", wires=4))
def circuit(param):
    qml.BasisState(np.array([1, 1, 0, 0]), wires=range(4))
    qml.DoubleExcitation(param, wires=[0, 1, 2, 3])
    return qml.expval(H)

opt = qml.GradientDescentOptimizer(stepsize=0.4)
theta = np.array(0.0, requires_grad=True)

energies_VQE_eq = []
thetas_VQE_eq = []

for n in range(20):
    theta, energy_VQE = opt.step_and_cost(circuit, theta)

    energies_VQE_eq.append(energy_VQE)
    thetas_VQE_eq.append(theta)
```

Figure 4.1: VQE for computing the ground state energy of the hydrogen molecule for a given internuclear distance.

we measure the expectation value of the Hamiltonian in the prepared state using the method described in Section 2.4.

PennyLane allows computation of gradients with respect to all parameterized gates in a quantum circuit. Thus, we can compute the gradients of the expectation value of the Hamiltonian (cost function) with respect to the parameters θ (more than one for other molecules), allowing the implementation of the Gradient Descent Optimizer [3].

With the circuit prepared, we optimize the parameter θ using the Gradient Descent Optimizer with a step size η of 0.4 (eq. 2.39), starting from the Hartree-Fock state (initial guess $\theta = 0$). The choice of step size is based on the paper by Xanadu [3], and a comparison with Pia Döring's analysis on the step size for a VQE on H_2 [18]. This step size offers a good trade-off between accuracy and the number of required iterations. We used 20 iterations to determine the optimal parameter. Figure 4.2 makes clear that the VQE indeed converges within 20 iteartions.

In Figure 4.2, we plotted the expectation value of the Hamiltonian in the prepared state (the VQE energy in purple), which depends on the parameter θ. Additionally, we plotted the parameter itself (black curve) to demonstrate that it converges as well. The convergence values are the minimal energy within the Hartree-Fock approximated Hamiltonian and the optimal VQE parameter that prepares the doubly excited state, minimizing the energy. We find an optimal parameter value of $\theta \approx 0.2263$. This indicates that the ground state of H_2 in the minimal basis set approximation (LCAO + STO-3G) is given by:

$$\begin{aligned} G^{(2)}(0.2263)|1100\rangle &= \cos(0.2263/2) \quad |1100\rangle - \sin(0.2263/2) \quad |0011\rangle \\ &= 0.994 \quad |1100\rangle - 0.113 \quad |0011\rangle \end{aligned} \tag{4.1}$$

The energy convergence clearly indicates that this is, indeed, the ground state: The initial state is the Hartree-Fock state $|1100\rangle$ with a Hartree-Fock energy of $E_{HF} = -1.11665 Ha$ for an internuclear distance of $r_{H-H} = 0.742 \mathring{A}$ (marked in orange in Figure 4.2). The minimum VQE energy is $E_{min,VQE} = -1.13726 Ha$, cor-

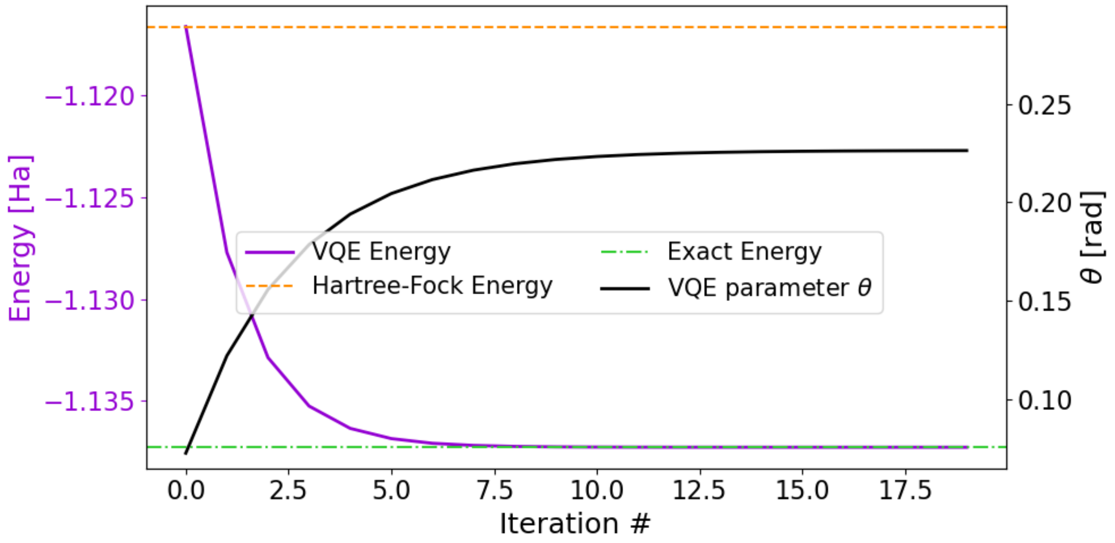


Figure 4.2: Convergence of the energy and parameter of the VQE for H_2 at $r_{H-H} = 0.742 \mathring{A}$.

responding to the state described in Equation 4.1. Remarkably, this value aligns perfectly with the exact energy $E_{exact} = -1.13726 Ha$ (marked in green), which represents the smallest eigenvalue of the Hamiltonian. We computed this exact energy through diagonalization via Givens-Rotations. Additionally, Figure 4.3 visually underscores this point by depicting the parameter's influence on the energy. It demonstrates that the Hartree-Fock state serves as an excellent approximation to the ground state, and the optimal parameter yields the lowest energy, surpassing the Hartree-Fock energy. This underscores the VQE's consistent and reliable performance.

By replicating this process for Hamiltonians at different internuclear distances,

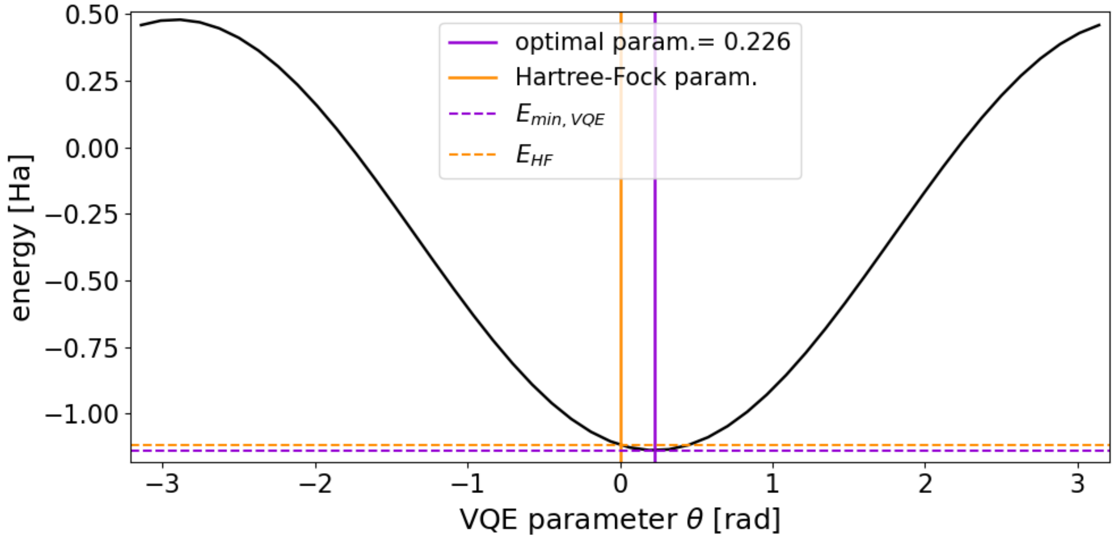


Figure 4.3: Parameter dependency of the VQE, found minimal parameter/energy and HF parameter/energy for $r_{H-H} = 0.742 \mathring{A}$.

we constructed the energy surface of H_2 as depicted in Figure 4.4. The discovered minimal VQE energies are highlighted in purple. The lowest point on this curve represents the equilibrium distance between the nuclei (r_{H-H}). We determined an equilibrium distance of $0.7356\mathring{A}$ corresponding to an energy of $-1.13731Ha$. Also visible in this figure are the VQE parameters associated with each energy point. It's noteworthy that as the distance increases, the parameter also increases, with no unusual behavior in between.

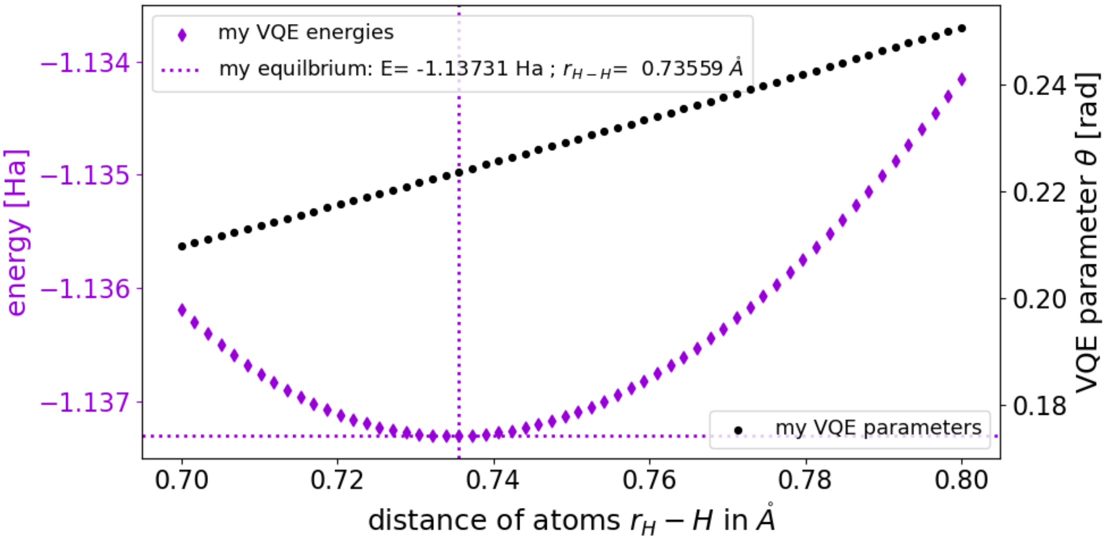
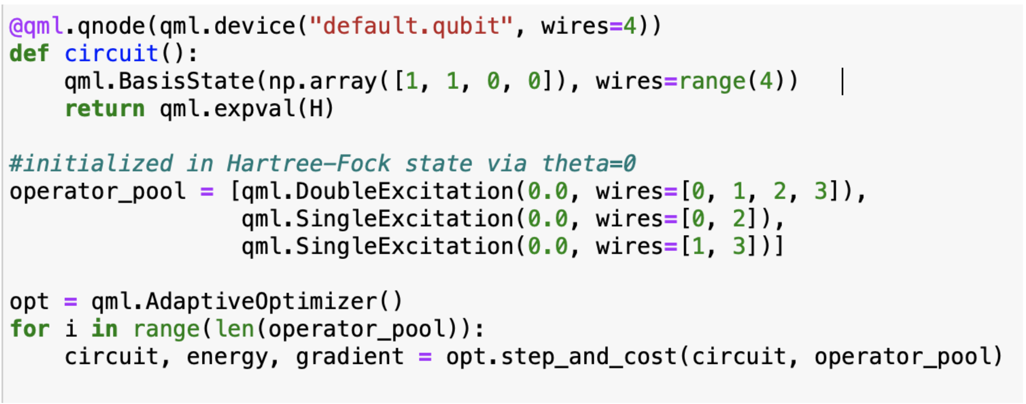


Figure 4.4: VQE Ground State Energy and Corresponding VQE Parameters vs. Internuclear Distance. The Equilibrium distance corresponds to the minimal energy.

Figure 4.11 portrays the same dependency over a broader range of distances, although with fewer data points. The equilibrium distance presented in this figure corresponds to the one calculated using the more precise representation (Figure 4.4). We will elaborate on Figure 4.11 later.

Now, let's compare this to the ADAPT-VQE. The ADAPT-VQE implementation was also inspired by Xanadu's PennyLane documentation paper [3] and can be found in Figure 4.5.

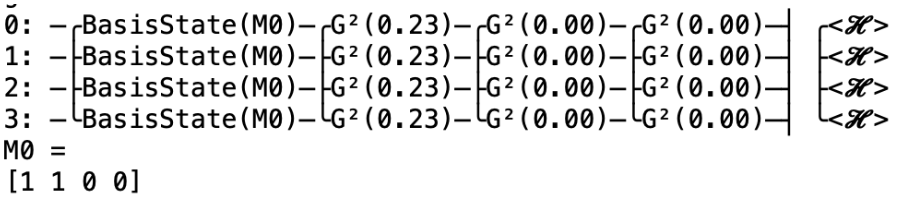


```
@qml.qnode(qml.device("default.qubit", wires=4))
def circuit():
    qml.BasisState(np.array([1, 1, 0, 0]), wires=range(4))
    return qml.expval(H)

#initialized in Hartree-Fock state via theta=0
operator_pool = [qml.DoubleExcitation(0.0, wires=[0, 1, 2, 3]),
                 qml.SingleExcitation(0.0, wires=[0, 2]),
                 qml.SingleExcitation(0.0, wires=[1, 3])]

opt = qml.AdaptiveOptimizer()
for i in range(len(operator_pool)):
    circuit, energy, gradient = opt.step_and_cost(circuit, operator_pool)
```

Figure 4.5: ADAPT-VQE for computing the ground state energy of the hydrogen molecule for a given internuclear distance.

The circuit initialization and creation are identical, except for the missing excitation gate. Instead, a gate pool is defined, encompassing all the single and double excitations possible for 4 qubits/spin-orbitals. Since the single excitation gates are two-qubit gates, we need to specify on which qubits they act. They all depend on a parameter and are initialized in the Hartree-Fock state (parameters=0). The most significant difference lies in the optimization process. Here, the "AdaptiveOptimizer" is employed, which performs the same steps we described in Section 2.4. It applies each of the gates in the gate pool to our initial state (HF-state) and then selects the gate with the largest gradient for optimization. The fixed parameter then defines a new initial state. This procedure is repeated until the energy gradient is sufficiently small (here: $< 6 \cdot 10^{-6}$).

The optimized state-preparing circuit for $r_{H-H} = 0.742\mathring{A}$ is displayed in Figure 4.6. The optimized circuit prepares the Hartree-Fock state (M0), then applies one double excitation gate with $\theta = 0.23$ (rounded here, thus must be the same as for VQE), and measures the expectation of the Hamiltonian at the end. The two double excitations with parameter zero do not change anything, so they are effectively equivalent to not applying any gate. Importantly, this optimized circuit corresponds exactly to the one used in the VQE and produces the same ground state energy of $E_{min,ADAPT-VQE} = -1.13726$.



```
0: ─╭BasisState(M0)─╭G²(0.23)─╭G²(0.00)─╭G²(0.00)─┤ ╭<𝓗>
1: ─├BasisState(M0)─├G²(0.23)─├G²(0.00)─├G²(0.00)─┤ ├<𝓗>
2: ─├BasisState(M0)─├G²(0.23)─├G²(0.00)─├G²(0.00)─┤ ├<𝓗>
3: ─╰BasisState(M0)─╰G²(0.23)─╰G²(0.00)─╰G²(0.00)─┤ ╰<𝓗>
M0 =
[1 1 0 0]
```

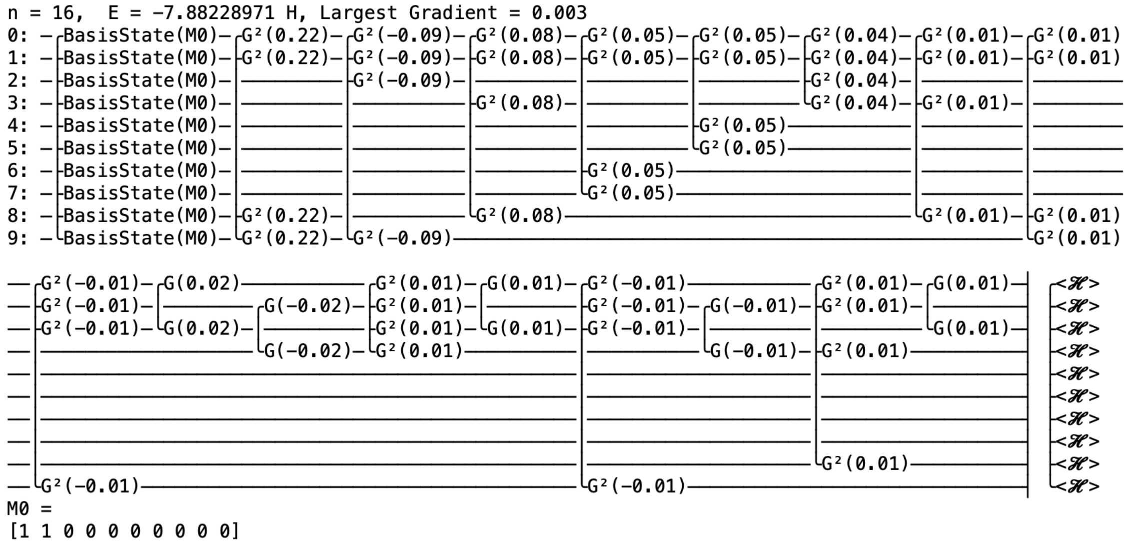
Figure 4.6: With ADAPT-VQE found optimal circuit for the ground state preparation of the hydrogen molecule for $r_{H-H} = 0.742\mathring{A}$.

In the next section, we will use a similar approach to the ADAPT-VQE as shown in Figure 4.5 for the other molecules to compute their ground state energies at different internuclear distances and different internuclear angles (only for H_2O). However, there are a few differences that need to be highlighted here. We will use the geometries that were used to generate the Hamiltonians in Section 3.2.

Each molecule requires a different number of qubits, as mentioned in Section 3.2, and has a different number of electrons, resulting in different Hartree-Fock states. For example, LiH requires 12 qubits and has 4 electrons, but we neglect the 2 in the inner 1s shell of lithium, so we are left with 10 qubits and 2 active electrons. Thus, the Hartree-Fock state is $|1,1,0,0,0,0,0,0,0,0>$ with a Hartree-Fock energy of $E_{HF} = -7.86269Ha$ at an internuclear distance of $r_{Li-H} = 1.57\mathring{A}$. Similarly, for BeH_2 with 12 qubits and 4 active electrons, the Hartree-Fock state is $|1,1,1,1,0,0,0,0,0,0,0,0>$ with an energy of $E_{HF} = -15.56010Ha$ at distance $r_{Be-H} = 1.33\mathring{A}$. For H_2O, which also needs 12 qubits but has 8 active electrons, the Hartree-Fock state is $|1,1,1,1,1,1,1,1,0,0,0,0>$ with an energy of $E_{HF} = -74.96305Ha$ at distance $r_{H-O} = 0.958\mathring{A}$ and angle 104.5°.

Furthermore, the UCCSD Ansatz for those molecules contains many more single and double excitations because we need to account for excitations acting on all possible qubits. This means that the operator pool contains many more gates, making the programs resource-intensive. To still be able to compute the ground states for multiple geometries in a reasonable time, we therefore terminate the procedure earlier than for H_2. For LiH and BeH_2, we stop at an energy gradient of $< 3 \cdot 10^{-3}$, and for H_2O, we stop at a gradient of $< 1 \cdot 10^{-2}$, which proves to be sufficient.

The optimized circuits for preparing the ground states of the molecules LiH, BeH_2, and H_2O can be found in Figures 4.7, 4.8, and 4.9, respectively. These circuits are shown for the mentioned geometries. "M0" represents the initial state, which is the Hartree-Fock state, "n" is the number of iterations needed until the gradient is small enough, and "Largest Gradient" is the gradient of the gate contributing the most to the energy change. You can see that these gradients satisfy our termination criterion. Furthermore, the ground state energies found are shown, and they all lie below the Hartree-Fock energies, as expected. It's evident that the more electrons a molecule has, the more gates need to be applied to reach the ground state. Additionally, you can observe that for all three of these molecules, a variety of single and double excitations, acting on different qubits with different optimized parameters, are applied.



```
n = 16,  E = -7.88228971 H, Largest Gradient = 0.003
0: ─╭BasisState(M0)─╭G²(0.22)─╭G²(-0.09)─╭G²(0.08)─╭G²(0.05)─╭G²(0.05)─╭G²(0.04)─╭G²(0.01)─╭G²(0.01)
1: ─├BasisState(M0)─├G²(0.22)─├G²(-0.09)─├G²(0.08)─├G²(0.05)─├G²(0.05)─├G²(0.04)─├G²(0.01)─├G²(0.01)
2: ─├BasisState(M0)─│─────────├G²(-0.09)─│─────────│─────────│─────────├G²(0.04)─│─────────│────────
3: ─├BasisState(M0)─│─────────│──────────├G²(0.08)─│─────────│─────────╰G²(0.04)─├G²(0.01)─│────────
4: ─├BasisState(M0)─│─────────│──────────│─────────│─────────├G²(0.05)───────────│─────────│────────
5: ─├BasisState(M0)─│─────────│──────────│─────────│─────────╰G²(0.05)───────────│─────────│────────
6: ─├BasisState(M0)─│─────────│──────────│─────────├G²(0.05)─────────────────────│─────────│────────
7: ─├BasisState(M0)─│─────────│──────────│─────────╰G²(0.05)─────────────────────│─────────│────────
8: ─├BasisState(M0)─├G²(0.22)─│──────────╰G²(0.08)───────────────────────────────╰G²(0.01)─├G²(0.01)
9: ─╰BasisState(M0)─╰G²(0.22)─╰G²(-0.09)───────────────────────────────────────────────────╰G²(0.01)

──╭G²(-0.01)─╭G(0.02)───────────╭G²(0.01)─╭G(0.01)─╭G²(-0.01)───────────╭G²(0.01)─╭G(0.01)─┤ ╭<ℋ>
──├G²(-0.01)─│─────────╭G(-0.02)─├G²(0.01)─│────────├G²(-0.01)─╭G(-0.01)─├G²(0.01)─│────────┤ ├<ℋ>
──├G²(-0.01)─╰G(0.02)─│─────────├G²(0.01)─╰G(0.01)─├G²(-0.01)─│─────────│─────────╰G(0.01)─┤ ├<ℋ>
──│──────────────────╰G(-0.02)─╰G²(0.01)───────────│──────────╰G(-0.01)─├G²(0.01)──────────┤ ├<ℋ>
──│───────────────────────────────────────────────│───────────────────│───────────────────┤ ├<ℋ>
──│───────────────────────────────────────────────│───────────────────│───────────────────┤ ├<ℋ>
──│───────────────────────────────────────────────│───────────────────│───────────────────┤ ├<ℋ>
──│───────────────────────────────────────────────│───────────────────│───────────────────┤ ├<ℋ>
──│───────────────────────────────────────────────│───────────────────╰G²(0.01)──────────┤ ├<ℋ>
──╰G²(-0.01)──────────────────────────────────────╰G²(-0.01)───────────────────────────────┤ ╰<ℋ>
M0 =
[1 1 0 0 0 0 0 0 0 0]
```

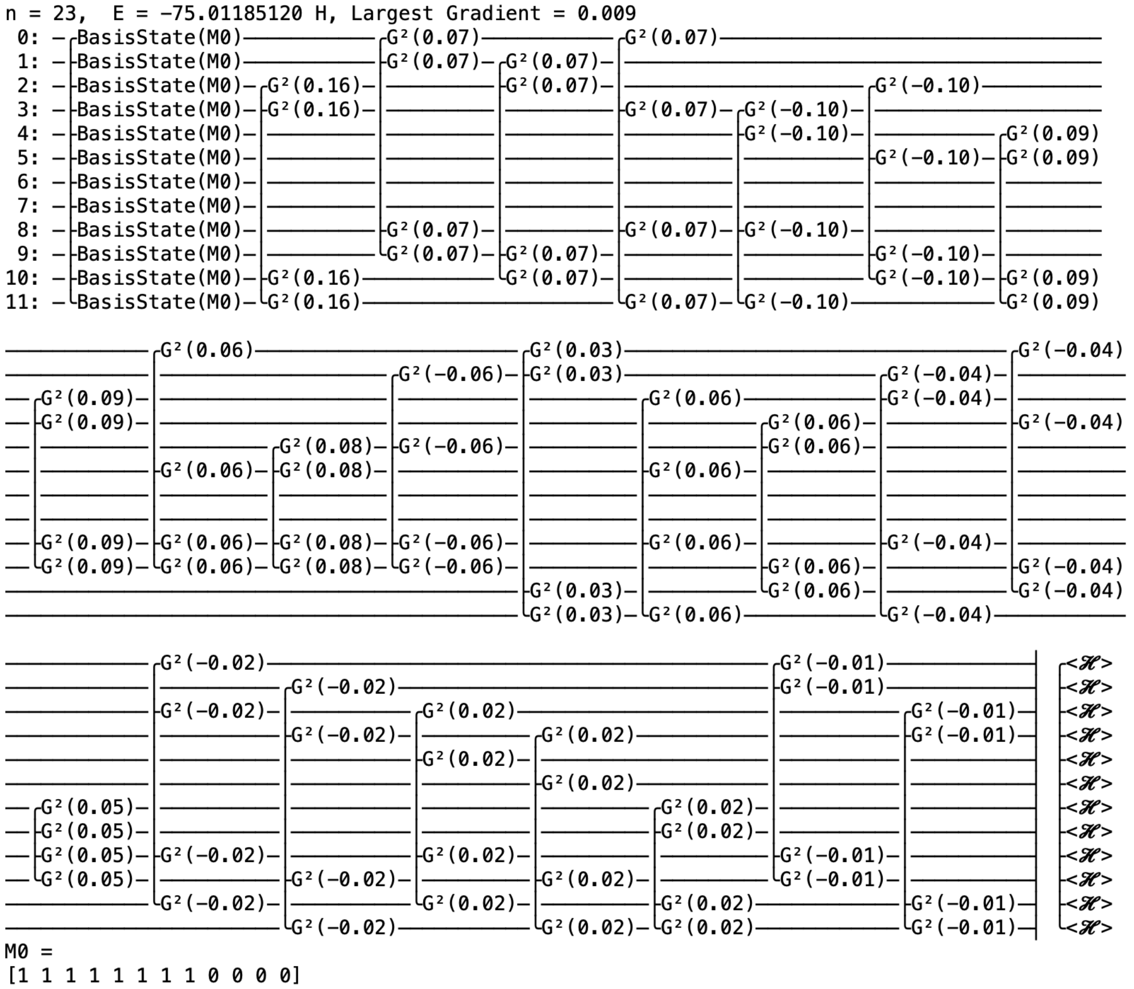
Figure 4.7: With ADAPT-VQE found optimal circuit for the ground state preparation of LiH for $r_{Li-H} = 1.57\mathring{A}$.

For completeness, we furthermore tested how the ADAPT-VQE would work in the case of LiH if we would use all 12 qubits, instead of neglecting the first 2. The output circuit is depicted in Figure 4.10. You can see that the ADAPT-VQE requires almost double as many iterations, and the circuits are obviously not the same. Nevertheless, most of the gates here do not involve the first two qubits, which we neglected previously. The gates not involving the first two qubits also mostly align with the ones in the circuit in Figure 4.7. The resulting energy has a difference in the 4th digit, which is a good trade-off between accuracy and efficiency. This underlines that neglecting these two qubits does not affect our calculations too

```
n = 22,  E = -15.59437221 H, Largest Gradient = 0.003
 0: ─╭BasisState(M0)───────────╭G²(0.10)────────────────────╭G²(0.12)────────────╭G²(-0.08)
 1: ─├BasisState(M0)───────────│──────────╭G²(0.10)──────────├G²(0.12)─╭G²(-0.08)─│─────────
 2: ─├BasisState(M0)─╭G²(0.14)─│──────────├G²(0.10)─╭G²(0.08)─│─────────├G²(-0.08)─│─────────
 3: ─├BasisState(M0)─├G²(0.14)─├G²(0.10)─│─────────├G²(0.08)─│─────────│──────────├G²(-0.08)
 4: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│─────────│──────────│─────────
 5: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│─────────│──────────│─────────
 6: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│─────────│──────────│─────────
 7: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│─────────│──────────│─────────
 8: ─├BasisState(M0)─├G²(0.14)─├G²(0.10)─│─────────│─────────├G²(0.12)─├G²(-0.08)─│─────────
 9: ─├BasisState(M0)─╰G²(0.14)─│─────────├G²(0.10)─│─────────╰G²(0.12)─│──────────├G²(-0.08)
10: ─├BasisState(M0)───────────│─────────╰G²(0.10)─├G²(0.08)────────────│──────────╰G²(-0.08)
11: ─╰BasisState(M0)───────────╰G²(0.10)───────────╰G²(0.08)────────────╰G²(-0.08)───────────

──╭G²(0.06)─╭G²(0.10)─╭G²(0.10)─╭G²(-0.01)─────────────────────────────────────────╭G(0.02)─╭G²(0.01)
──├G²(0.06)─├G²(0.10)─├G²(0.10)─│──────────╭G²(-0.01)────────────╭G(-0.02)─│────────├G²(0.01)
──│─────────│─────────│─────────├G²(-0.01)─│──────────╭G²(0.01)─│─────────│────────│────────
──│─────────│─────────│─────────│──────────├G²(-0.01)─├G²(0.01)─│─────────│────────│────────
──│─────────│─────────├G²(0.10)─│──────────│──────────│─────────│─────────│────────├G²(0.01)
──│─────────│─────────╰G²(0.10)─│──────────│──────────│─────────│─────────│────────╰G²(0.01)
──│─────────├G²(0.10)───────────│──────────│──────────│─────────│─────────│─────────────────
──│─────────╰G²(0.10)───────────│──────────│──────────│─────────│─────────│─────────────────
──│─────────────────────────────├G²(-0.01)─│──────────├G²(0.01)─│─────────╰G(0.02)──────────
──│─────────────────────────────│──────────├G²(-0.01)─╰G²(0.01)─╰G(-0.02)──────────────────
──├G²(0.06)─────────────────────╰G²(-0.01)─│────────────────────────────────────────────────
──╰G²(0.06)────────────────────────────────╰G²(-0.01)───────────────────────────────────────

───────────────────────────────────╭G²(0.01)──────────╭G²(-0.00)────────────┤ ╭<𝓗>
───────────╭G²(-0.01)──────────────├G²(0.01)──────────│──────────╭G²(-0.00)─┤ ├<𝓗>
──╭G²(0.00)─├G²(-0.01)─╭G(-0.01)─│───────────────────│──────────├G²(-0.00)─┤ ├<𝓗>
──├G²(0.00)─│──────────│─────────│─────────╭G(0.01)─├G²(-0.00)─│──────────┤ ├<𝓗>
──│─────────│──────────│─────────│─────────│────────│──────────│──────────┤ ├<𝓗>
──│─────────│──────────│─────────│─────────│────────│──────────│──────────┤ ├<𝓗>
──│─────────│──────────│─────────├G²(0.01)─│────────│──────────│──────────┤ ├<𝓗>
──│─────────│──────────│─────────╰G²(0.01)─│────────│──────────│──────────┤ ├<𝓗>
──│─────────├G²(-0.01)─│───────────────────│────────│──────────│──────────┤ ├<𝓗>
──│─────────│──────────│───────────────────│────────├G²(-0.00)─├G²(-0.00)─┤ ├<𝓗>
──├G²(0.00)─│──────────╰G(-0.01)───────────│────────╰G²(-0.00)─╰G²(-0.00)─┤ ├<𝓗>
──╰G²(0.00)─╰G²(-0.01)─────────────────────╰G(0.01)────────────────────────┤ ╰<𝓗>
M0 = 
[1 1 1 1 0 0 0 0 0 0 0 0]
```

Figure 4.8: With ADAPT-VQE found optimal circuit for the ground state preparation of BeH_2 for $r_{Be-H} = 1.33\mathring{A}$.

much, but it reduces computational costs.



```
n = 23,  E = -75.01185120 H, Largest Gradient = 0.009
 0: ─╭BasisState(M0)───────────╭G²(0.07)───────────╭G²(0.07)───────────────────────────────────
 1: ─├BasisState(M0)───────────├G²(0.07)─╭G²(0.07)─│──────────────────────────────────────────
 2: ─├BasisState(M0)─╭G²(0.16)─│─────────├G²(0.07)─│─────────────────────╭G²(-0.10)────────────
 3: ─├BasisState(M0)─├G²(0.16)─│─────────│─────────├G²(0.07)─╭G²(-0.10)─│───────────────────
 4: ─├BasisState(M0)─│─────────│─────────│─────────│─────────├G²(-0.10)─│──────────╭G²(0.09)
 5: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│──────────├G²(-0.10)─├G²(0.09)
 6: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│──────────│──────────│────────
 7: ─├BasisState(M0)─│─────────│─────────│─────────│─────────│──────────│──────────│────────
 8: ─├BasisState(M0)─│─────────├G²(0.07)─│─────────├G²(0.07)─├G²(-0.10)─│──────────│────────
 9: ─├BasisState(M0)─│─────────╰G²(0.07)─├G²(0.07)─│─────────│──────────├G²(-0.10)─│────────
10: ─├BasisState(M0)─├G²(0.16)───────────╰G²(0.07)─│─────────│──────────╰G²(-0.10)─├G²(0.09)
11: ─╰BasisState(M0)─╰G²(0.16)─────────────────────╰G²(0.07)─╰G²(-0.10)────────────╰G²(0.09)

────────────╭G²(0.06)─────────────────────╭G²(0.03)───────────────────────────────╭G²(-0.04)
────────────│───────────────────╭G²(-0.06)─├G²(0.03)─────────────────────╭G²(-0.04)─│─────────
──╭G²(0.09)─│───────────────────│──────────│─────────╭G²(0.06)───────────├G²(-0.04)─│─────────
──├G²(0.09)─│───────────────────│──────────│─────────│─────────╭G²(0.06)─│──────────├G²(-0.04)
──│─────────│─────────╭G²(0.08)─├G²(-0.06)─│─────────│─────────├G²(0.06)─│──────────│─────────
──│─────────├G²(0.06)─├G²(0.08)─│──────────│─────────├G²(0.06)─│─────────│──────────│─────────
──│─────────│─────────│─────────│──────────│─────────│─────────│─────────│──────────│─────────
──│─────────│─────────│─────────│──────────│─────────│─────────│─────────│──────────│─────────
──├G²(0.09)─├G²(0.06)─├G²(0.08)─├G²(-0.06)─│─────────├G²(0.06)─│─────────├G²(-0.04)─│─────────
──╰G²(0.09)─╰G²(0.06)─╰G²(0.08)─╰G²(-0.06)─│─────────│─────────├G²(0.06)─│──────────├G²(-0.04)
───────────────────────────────────────────├G²(0.03)─│─────────╰G²(0.06)─│──────────╰G²(-0.04)
───────────────────────────────────────────╰G²(0.03)─╰G²(0.06)───────────╰G²(-0.04)───────────

────────────╭G²(-0.02)─────────────────────────────────────────────────╭G²(-0.01)────────────┤ ╭<𝓗>
────────────│──────────╭G²(-0.02)──────────────────────────────────────├G²(-0.01)────────────┤ ├<𝓗>
────────────├G²(-0.02)─│──────────╭G²(0.02)────────────────────────────│──────────╭G²(-0.01)─┤ ├<𝓗>
────────────│──────────├G²(-0.02)─│─────────╭G²(0.02)──────────────────│──────────├G²(-0.01)─┤ ├<𝓗>
────────────│──────────│──────────├G²(0.02)─│───────────────────────────│──────────│──────────┤ ├<𝓗>
────────────│──────────│──────────│─────────├G²(0.02)───────────────────│──────────│──────────┤ ├<𝓗>
──╭G²(0.05)─│──────────│──────────│─────────│─────────╭G²(0.02)─│──────────│──────────┤ ├<𝓗>
──├G²(0.05)─│──────────│──────────│─────────│─────────├G²(0.02)─│──────────│──────────┤ ├<𝓗>
──├G²(0.05)─├G²(-0.02)─│──────────├G²(0.02)─│─────────│─────────├G²(-0.01)─│──────────┤ ├<𝓗>
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M0 =
[1 1 1 1 1 1 1 1 0 0 0 0]
```
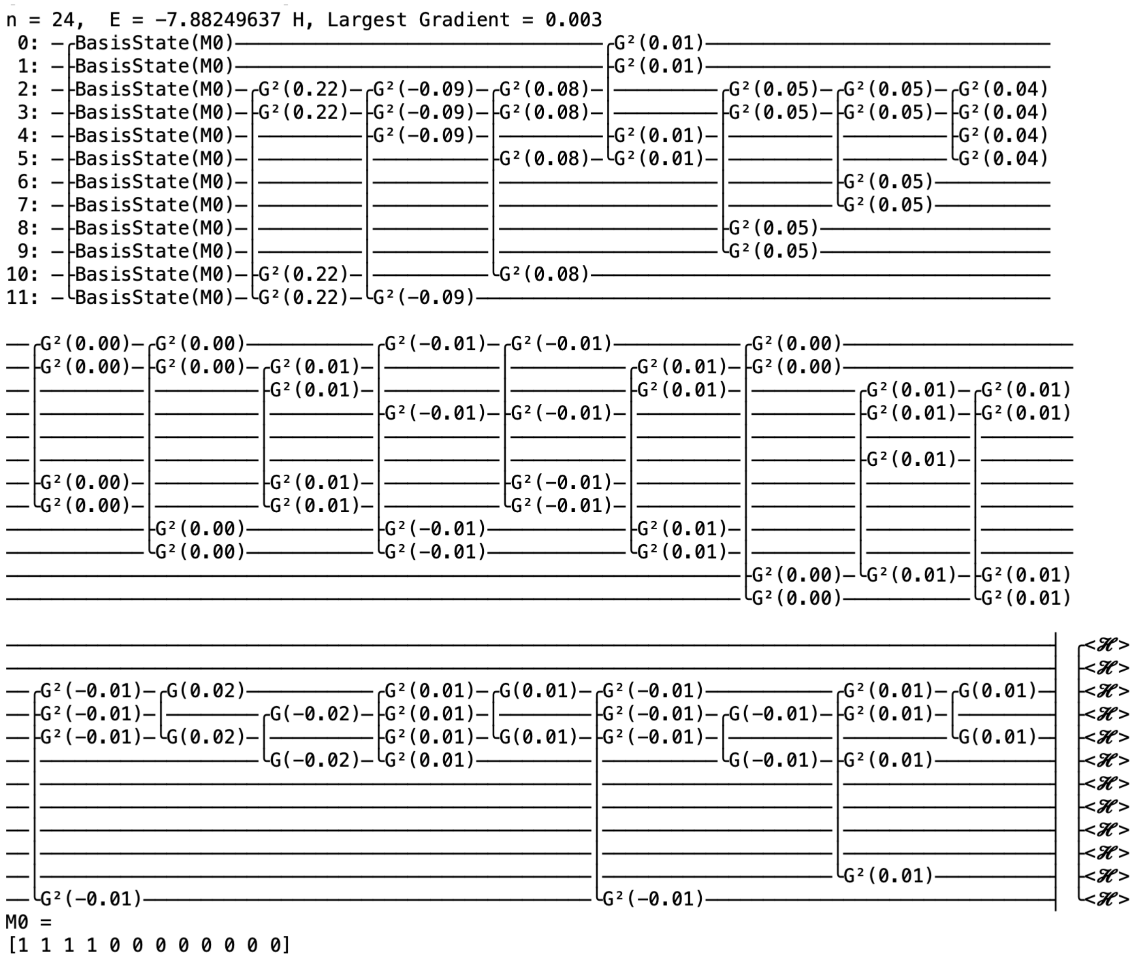

Figure 4.9: With ADAPT-VQE found optimal circuit for the ground state preparation of H_2O for $r_{H-O} = 0.958\mathring{A}$ and angle 104.5°.



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n = 24,  E = -7.88249637 H, Largest Gradient = 0.003
 0: ─╭BasisState(M0)────────────────────────────────╭G²(0.01)──────────────────────────────
 1: ─├BasisState(M0)────────────────────────────────├G²(0.01)──────────────────────────────
 2: ─├BasisState(M0)─╭G²(0.22)─╭G²(-0.09)─╭G²(0.08)─│─────────╭G²(0.05)─╭G²(0.05)─╭G²(0.04)
 3: ─├BasisState(M0)─├G²(0.22)─├G²(-0.09)─├G²(0.08)─│─────────├G²(0.05)─├G²(0.05)─├G²(0.04)
 4: ─├BasisState(M0)─│─────────├G²(-0.09)─│─────────├G²(0.01)─│─────────│─────────├G²(0.04)
 5: ─├BasisState(M0)─│─────────│──────────├G²(0.08)─╰G²(0.01)─│─────────│─────────╰G²(0.04)
 6: ─├BasisState(M0)─│─────────│──────────│───────────────────│─────────├G²(0.05)──────────
 7: ─├BasisState(M0)─│─────────│──────────│───────────────────│─────────╰G²(0.05)──────────
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 9: ─├BasisState(M0)─│─────────│──────────│───────────────────╰G²(0.05)────────────────────
10: ─├BasisState(M0)─├G²(0.22)─│──────────╰G²(0.08)────────────────────────────────────────
11: ─╰BasisState(M0)─╰G²(0.22)─╰G²(-0.09)──────────────────────────────────────────────────

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──│─────────│─────────│─────────├G²(-0.01)─├G²(-0.01)─│─────────│─────────├G²(0.01)─├G²(0.01)
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──╰G²(-0.01)───────────────────────────────────────╰G²(-0.01)──────────────────────────────┤ ╰<𝓗>
M0 =
[1 1 1 1 0 0 0 0 0 0 0 0]
```

Figure 4.10: With ADAPT-VQE found optimal circuit for the ground state preparation of LiH for $r_{Li-H} = 1.57\mathring{A}$ using 12 qubits.

4.2 Energy surfaces of different molecules

Finally, we want to present the energy surfaces of our molecules, created with the VQE, and determine the ground state geometries by identifying the configurations with minimal energy. To ensure the reliability of our algorithm, we will compare three methods. The primary focus will be on the energies calculated with the VQE (labeled as "my VQE energies" and colored purple). These will be compared to the energies obtained by the VQE without applying any excitation gate, representing the Hartree-Fock state ("Hamiltonian expval in HF-state," colored orange), and to the lowest eigenvalue of the Hamiltonians, which is determined through diagonalization using Givens-Rotations ("lowest eigval of diagonalized Hamiltonian", colored green).

At the end of each section, we will also compare our results with the existing literature. In our plots, we will mark the equilibrium positions, which correspond to the locations of minimal energies, for both the VQE energies and the Hartree-Fock energies.

4.2.1 Hydrogen molecule - H_2

The energy surface for the hydrogen molecule is depicted in Figure 4.11. We calculated the energies for internuclear distances ranging from $0.2\mathring{A}$ to $4\mathring{A}$. The found equilibrium distance is $r_{H-H} = 0.7356\mathring{A}$, corresponding to an energy of $-1.13731Ha$, as described in section 4.1.

The curve behaves as expected: For small internuclear distances, the energy diverges, indicating that pressing the atoms together requires energy, and it is not possible to bring them closer easily after a certain internuclear distance is reached. This is logical because bringing two atoms closer after a certain point means that the nuclei are pressed together. Since we neglected any nuclear forces in our model (which are important for fusion) and only included Coulomb forces, the repulsive force due to their positive charge becomes extremely strong as nuclei get closer to each other, following Coulomb's law. This force cannot be overcome. Furthermore minimum is present in the curve, defining the equilibrium.

The energy converges for large internuclear distances, meaning that by tearing the two H atoms apart, the entanglement between them decreases until they form two separate systems. The energy is then just the sum of both atomic ground state energies, which does not change as the nuclei are further torn apart.

It is evident that our claim that the Hartree-Fock energy is a good approximation for the equilibrium distance holds true. The Hartree-Fock energies and the VQE energies in this figure match quite well around equilibrium. However, for larger internuclear distances, they diverge. This reflects the fact that Hartree-Fock is not a good approximation for large distances because it assumes that the two electrons occupy two different spin orbitals due to the Pauli principle. For large distances, the Pauli principle does not hold, as the two atoms form two separate systems, each with one electron, which can then occupy the lowest atomic spin-orbital in both.

Nevertheless, the Hartree-Fock and VQE energies also don't match exactly around equilibrium. This is better visible in Figure 4.12, which is a zoomed-in version of Figure 4.11 around equilibrium. The Hartree-Fock energies are consistently higher, as they should be because they represent an upper limit. Furthermore, the equilibrium distance found with the Hartree-Fock energies is shifted to the left compared to the equilibrium found with the VQE, indicating a slightly stronger bond.

However, the exact energies match perfectly with the VQE energies, underlining the success of our VQE.

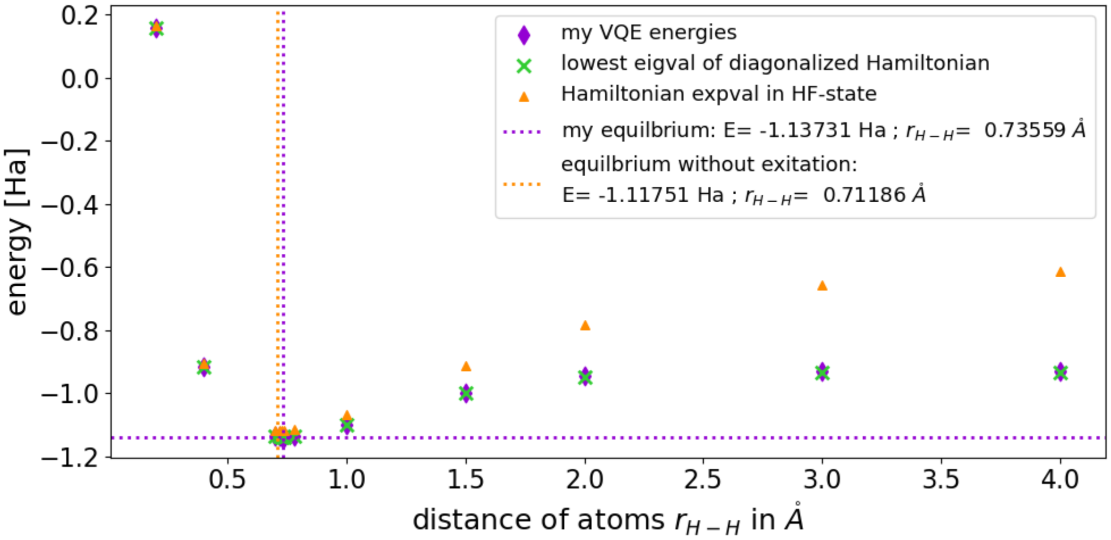

Figure 4.11: VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance for H_2. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 4 qubits.

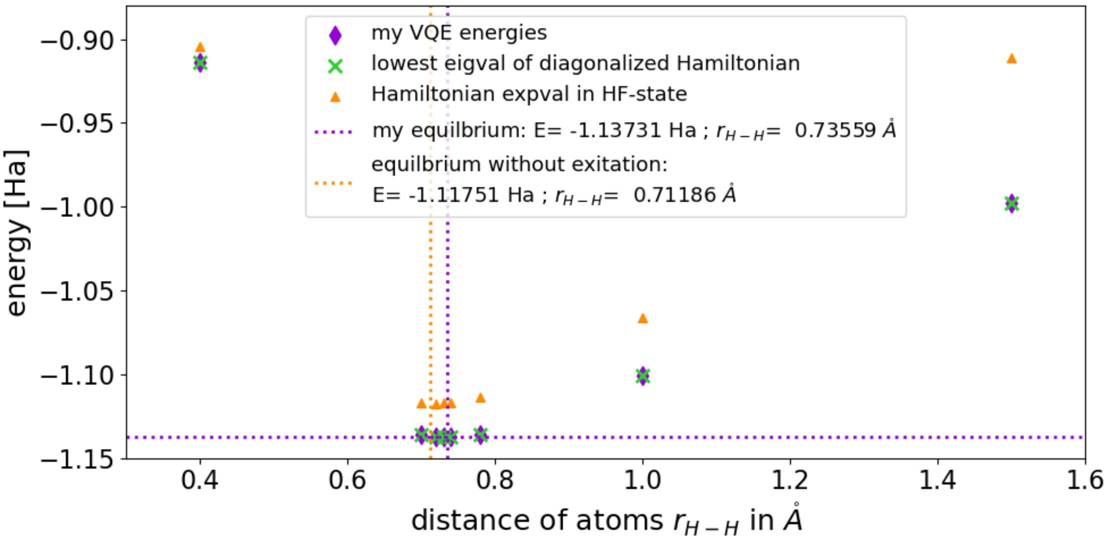

Figure 4.12: zoomed version of Figure 4.11. VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance for H_2 around the Equilibrium. The Equilibrium distance corresponds to the minimal energy. The Equilibrium distance corresponds to the minimal energy.

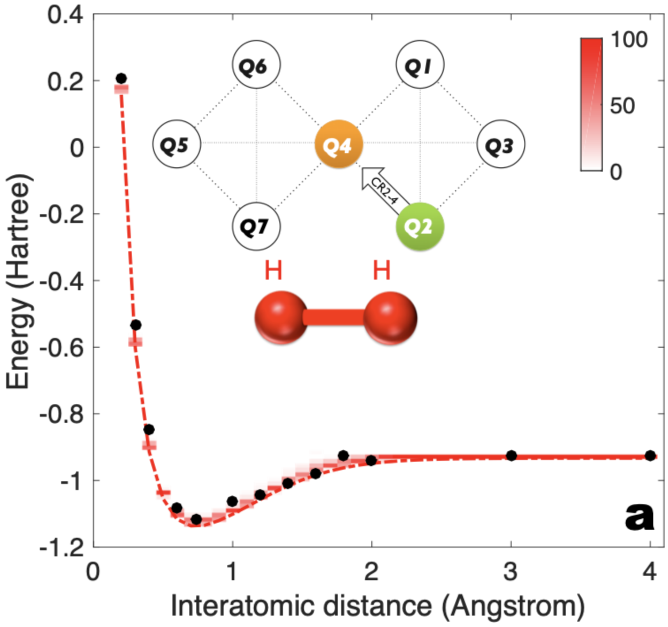

Figure 4.13: Energy surface of H_2 taken from IBM paper: Experimental results (black circles), exact energy surfaces (dotted lines) and density plots of outcomes from numerical simulations, for a number of interatomic distances. The top insets highlight the qubits used for the experiment. The bottom insets of each figure are representations of the molecular geometry, not drawn to scale. (source: [22])

A similar plot, created by IBM and presented in the paper [22], is shown in Figure 4.13. IBM used only two qubits for this simulation and also shows exact and experimental values. The exact values were simulated classically, while the experimental ones were obtained using real quantum hardware. This is in contrast to our approach, which relies on a simulator. The dashed curve represents a classical simulation of quantum hardware, which aligns with our methodology. Similar to our approach, IBM also employed the STO-3G approximation for modeling atomic orbitals. Comparing this energy surface to ours shows that all the curves match. The equilibrium for both, IBM's and our results, lies around $0.7\AA$, with an energy of approximately -1.1 Ha, and the energy starts to converge at a distance of about $2\AA$ to a value between -0.8 Ha and -1 Ha.

4.2.2 Lithium hydride - LiH

The same plots were created for LiH. Figure 4.14 displays the full version, while Figure 4.15 provides a zoomed-in view around the equilibrium point. We observe here the same trends as we did for H_2: The curve behaves as expected, and the Hartree-Fock and VQE energies are closely matching around the equilibrium and diverging for larger distances. Furthermore, the exact energies align with the VQE energies.

The determined equilibrium distance is $1.56\AA$ with an energy of $-7.8824 Ha$.

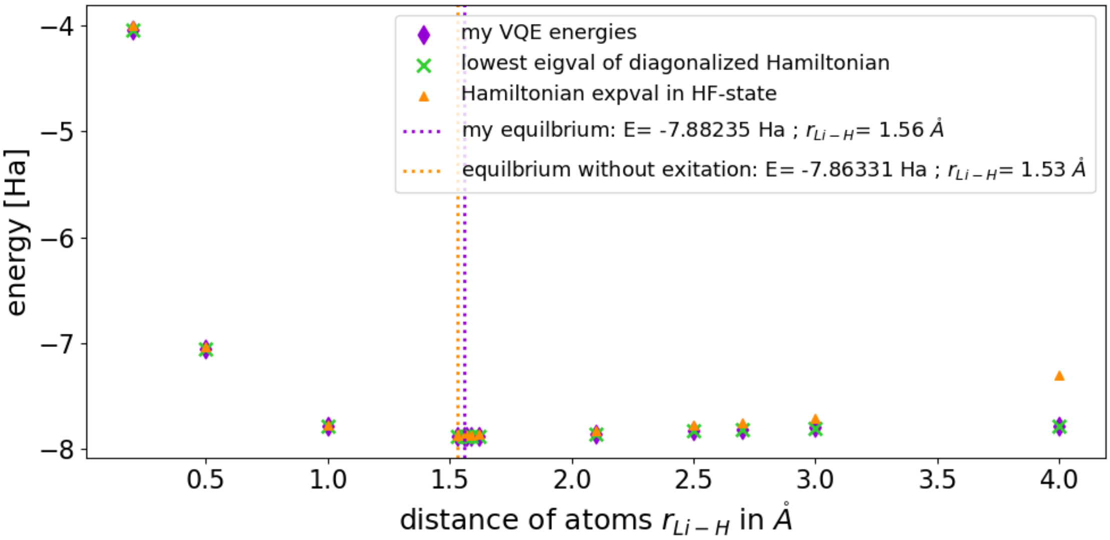

Figure 4.14: VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance for LiH. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 10 qubits.

We can compare these figures with Figure 4.16 from IBM (source: [22]). For LiH, IBM used 4 qubits and shows exact and experimental values. The exact and experimental values of LiH by IBM don't align perfectly, but the simulator values and the experimental ones do. One interesting and unexpected feature is that a bump appears at a distance of around $2.8\AA$. After investigating Figure 4.13 once more, it becomes clear that the bump is also present but much smaller in the H_2 energy surface. Furthermore, the experimental data (black dots) are consistently above the exact values.

An explanation for the bumps is given by Artur Izmaylov in [23]. He claims that it is a result of symmetry breaking. Since we do not reproduce this unwanted bump, we will not explain it further.

Comparing the exact energy surface to ours shows that the curves match much better than the experimental and exact curve of IBM. Our equilibrium with a distance of $1.56\AA$ and an energy of $-7.8824 Ha$ matches the minimum of the exact curve, while the minimum of IBM's experimental data is shifted to the right and the energy is observably higher. Furthermore, the convergence of our energies for

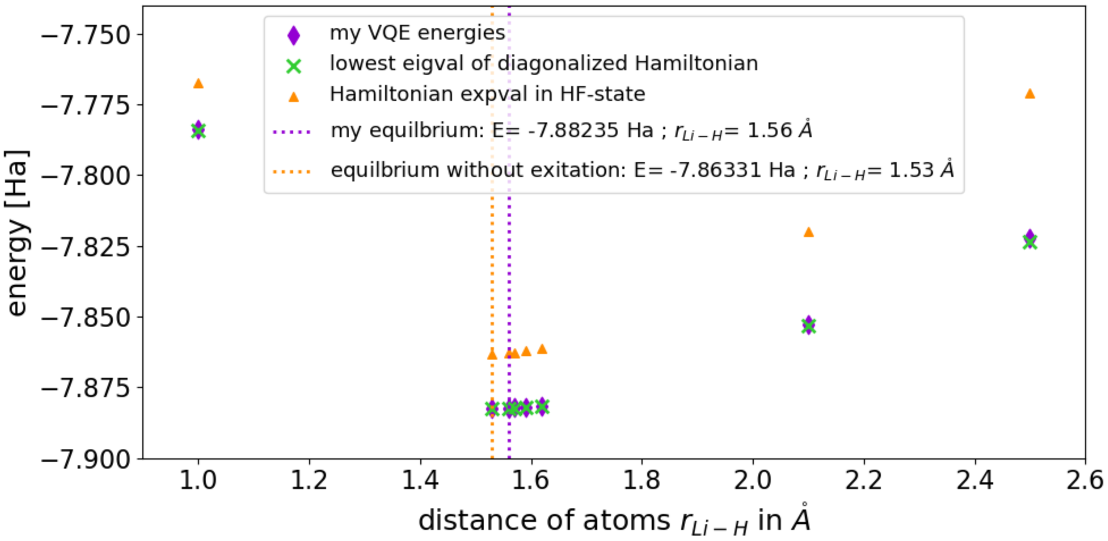

Figure 4.15: zoomed version of Figure 4.14. VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance for LiH around the Equilibrium. The Equilibrium distance corresponds to the minimal energy. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 10 qubits.

large internuclear distances matches with that of IBM's exact values.

The fact that IBM's experimental data (black dots) are consistently above the exact values could result from the fact that their state preparation circuit does not have enough gates, meaning that their VQE iterations were not sufficient. Thus, we could produce a more precise energy surface.

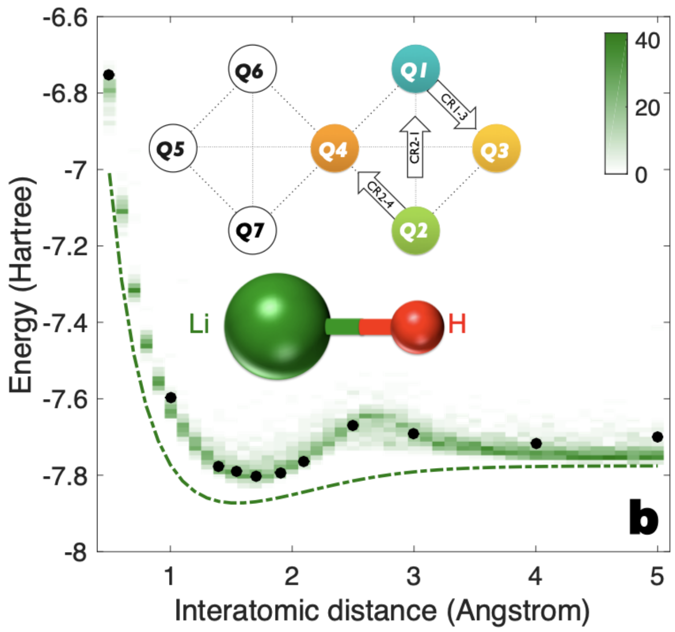

Figure 4.16: Energy surface of LiH taken from IBM paper: Experimental results (black circles), exact energy surfaces (dotted lines) and density plots of outcomes from numerical simulations, for a number of interatomic distances. The top insets highlight the qubits used for the experiment. The bottom insets of each figure are representations of the molecular geometry, not drawn to scale.(source: [22])

4.2.3 Beryllium hydride - BeH_2 - 1 dimensional

The full BeH_2 energy surface plots for internnuclear distances from $0.5\mathring{A}$ to $4\mathring{A}$ can be found in Figure 4.17, with a zoomed-in version shown in Figure 4.18. As expected, all the energies behave as anticipated. The VQE energies and the exact energies align well for distances up to $2.5\mathring{A}$, while the Hartree-Fock energies behave similarly to those for H_2 and LiH, being close to the VQE energies for distances near equilibrium and diverging for larger ones. A significant difference here is that the VQE and exact energies no longer align well for distances greater than $2.5\mathring{A}$ to $3\mathring{A}$. This results in the VQE energies not converging for large distances anymore, which contradicts the physical intuition that the three atoms should become independent of each other for large distances. Given that the exact and VQE energies only differ significantly for large distances, it appears that there is a distance-dependent issue occuring.

A notable observation is that for the internuclear distance of $4\mathring{A}$, the difference between the exact energy and the Hartree-Fock energy for H_2 and LiH was at most $0.5Ha$, while for BeH_2, the difference is more than double that amount. As the Hartree-Fock approximation becomes a less accurate guess for larger distances, this might be the source of the problem. It's possible that our initial state is too far from the actual ground state in the case of BeH_2, causing our algorithm to converge to a local minimum. The initial state was adequate for the distance of $3\mathring{A}$ and for the other molecules, but it seems to be problematic for BeH_2 at larger distances.

Further investigation could involve exploring the dependency of the VQE energy for BeH_2 at $4\mathring{A}$ on the initial state. Unfortunately, due to time constraints, we were unable to pursue this investigation in this thesis. Nonetheless, it presents an intriguing problem worthy of exploration.

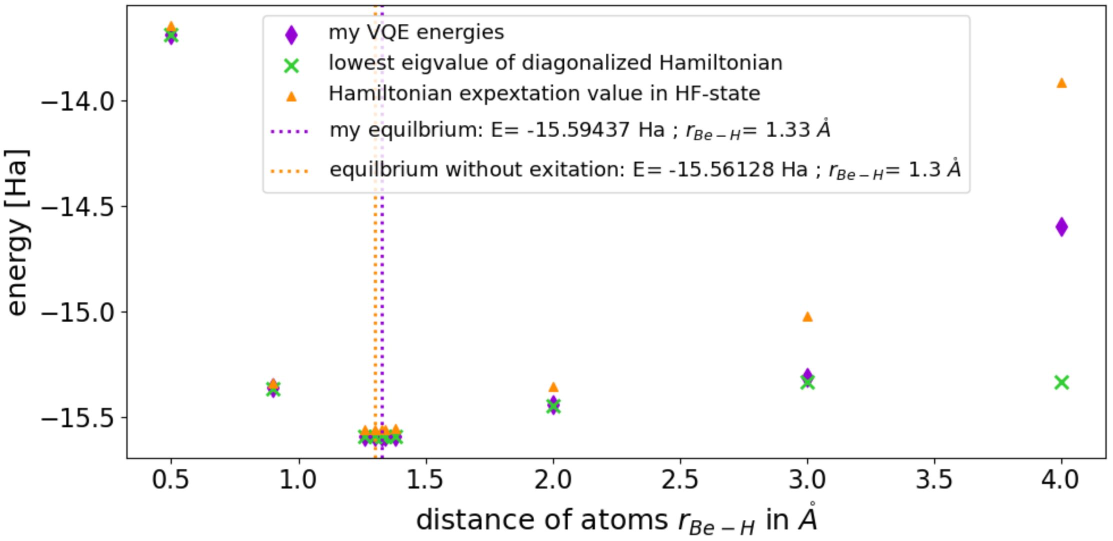

Figure 4.17: VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance for BeH_2. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 12 qubits.

This issue does not seem to be present in IBM's energy surface. IBM employed six qubits for the BeH_2 molecule and provided once again a figure with both exact and experimental values, which do not align perfectly (Figure 4.19). However, considering the single discrepancy in our energies, specifically the VQE energy for the internuclear distance of $4\mathring{A}$, we will omit this point and focus on comparing the remaining data to that of IBM's, as it remains unaffected by that point.

Our equilibrium corresponds to an internuclear distance of $1.33\mathring{A}$ and an energy of $-15.5944Ha$. Remarkably, IBM's exact data aligns with ours, affirming the accuracy of our data when disregarding large distances.

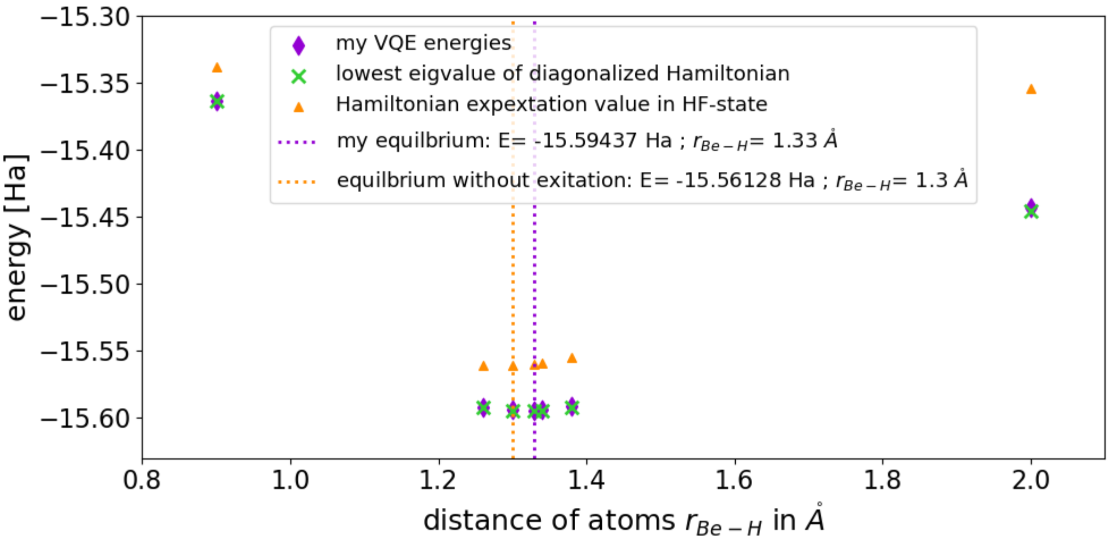

Figure 4.18: zoomed version of Figure 4.17. VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance for BeH_2 around the Equilibrium. The Equilibrium distance corresponds to the minimal energy. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 12 qubits.

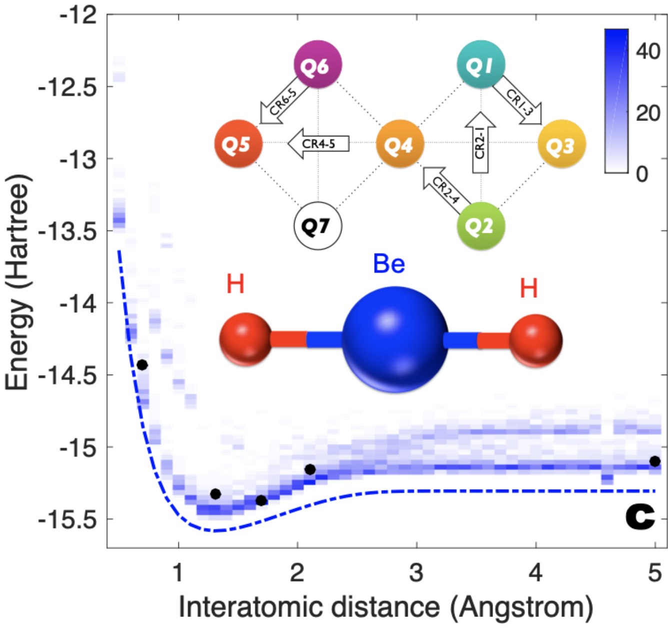

Figure 4.19: Energy surface of BeH_2 taken from IBM paper: Experimental results (black circles), exact energy surfaces (dotted lines) and density plots of outcomes from numerical simulations, for a number of interatomic distances. The top insets highlight the qubits used for the experiment. The bottom insets of each figure are representations of the molecular geometry, not drawn to scale.(source: [22])

4.2.4 Water molecule - H_2O - 2 dimensional

The last molecule we aim to investigate is the water molecule (H_2O). As previously mentioned, the equilibrium geometry of water includes an angle between the three atoms. Our goal is to verify that this angle represents the equilibrium geometry and determine the equilibrium distance between the hydrogen and oxygen atoms.

Figure 4.20 displays the full plot illustrating the dependency of VQE energies on the internuclear distance (r_{H-O}) and the angle between the three atoms (ϕ) for the water molecule. Similar to previous molecules, we've plotted the VQE energies, exact energies, and Hartree-Fock energies. This was done for internuclear distances from $0.2\mathring{A}$ to $4\mathring{A}$ and for the three angles 80°, 104.5°, and 120°. Additionally, we've marked the equilibrium determined by the VQE energies and the equilibrium determined by the Hartree-Fock energies. To facilitate a more detailed examination of this plot, we've provided an alternative view in Figure 4.21 and a zoomed-in version in Figure 4.23.

The alternative view in Figure 4.21 focuses solely on the internuclear distance dependency of the energies. Similar to the behavior observed for BeH_2, the VQE energies align closely with the exact values up to a distance of $3\mathring{A}$. However, at a distance of $4\mathring{A}$, the exact and VQE energies begin to deviate. As mentioned earlier, this issue likely stems from the same distant-dependent problem that was encountered with BeH_2.

Figure 4.22 depicts the dependence of ground state energies for H_2O on internuclear distance, as calculated in paper [24]. In this paper, the energies were computed using the QCC (Qubit Coupled Cluster) Ansatz, which is similar to the UCC (Unitary Coupled Cluster) Ansatz, but acting directly in the qubit space, reducing the required gate count. Since UCC and QCC are not directly comparable, our focus will be on comparing them with the Exact curve and the QMF (Quantum Mean Field) curve, which corresponds to the Hartree-Fock energies.

Upon comparing the internuclear distance dependence of our VQE energies to the exact energies shown in Figure 4.13, we observe that the equilibrium distance aligns closely, approximately at $1\mathring{A}$. Comparing Figure 4.22 to Figure 4.23, we furthermore see that the Hartree-Fock energies rise more rapidly than the VQE energies at distances around $1\mathring{A}$ for both. It's worth noting that the paper introduced an additional symmetry constraint to ensure that the Hartree-Fock energies do not break symmetries, which was not necessary in our approach.

In Figure 4.23, the energy landscape is depicted more clearly. It becomes evident that the equilibrium determined by the VQE energies corresponds to the actual lowest point in the energy landscape. On the other hand, the equilibrium defined by the Hartree-Fock energies may be the lowest for those energies but does not represent the true equilibrium of the system. Within the depicted distance range, the exact energies and VQE energies closely match, while the Hartree-Fock energies consistently register as higher. The equilibrium geometry we discover is defined by an internuclear distance of $r_{H-O} = 1.02\mathring{A}$ and an angle of $\phi = 104.5°$.

Therefore, we have successfully demonstrated that H_2O indeed favors a bent configuration of its constituent atoms.

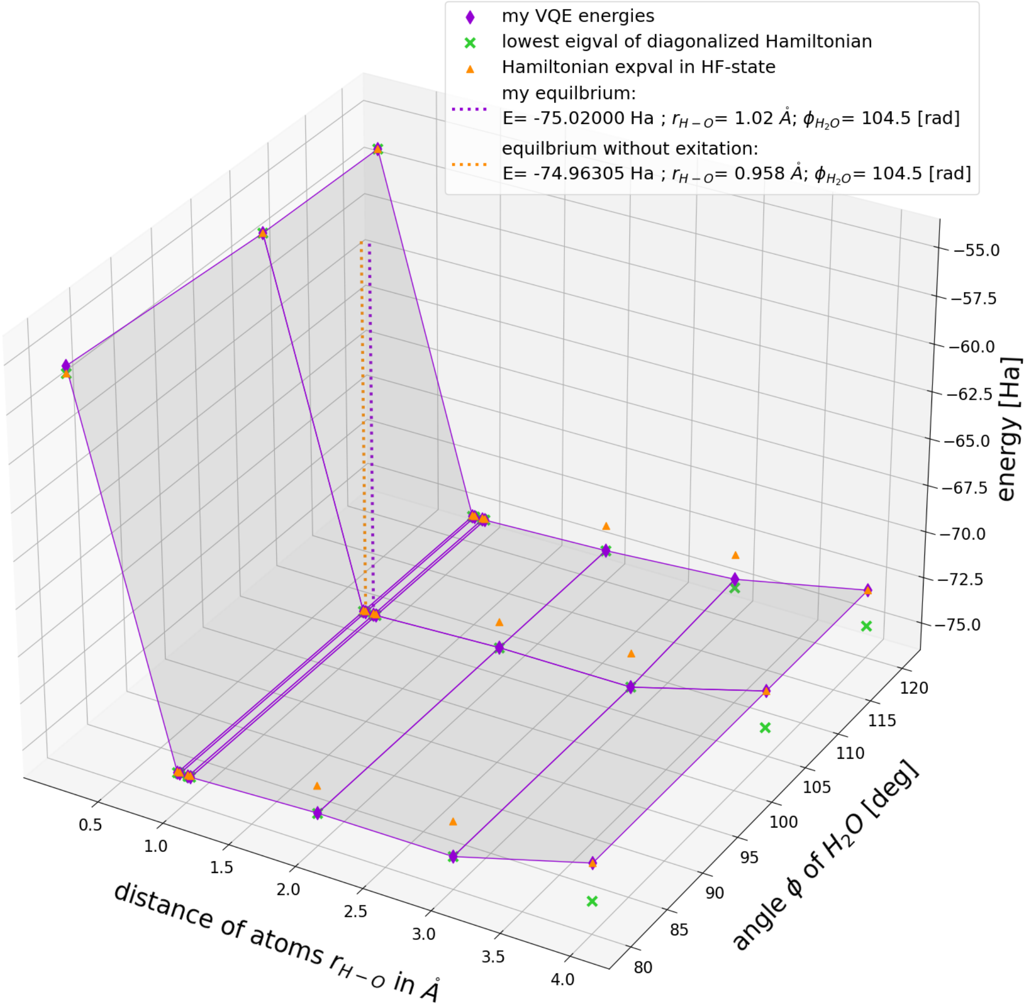

Figure 4.20: VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance and angle for H_2. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 12 qubits.

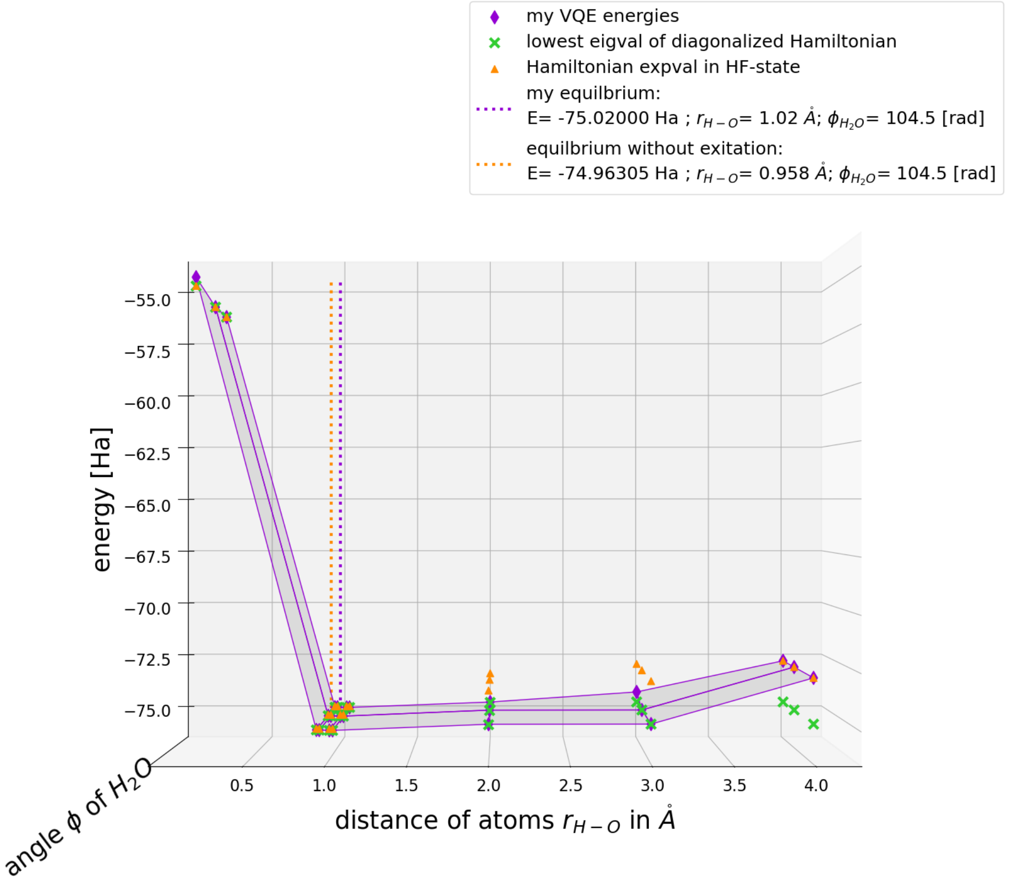

Figure 4.21: VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance and angle for H_2. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 12 qubits.

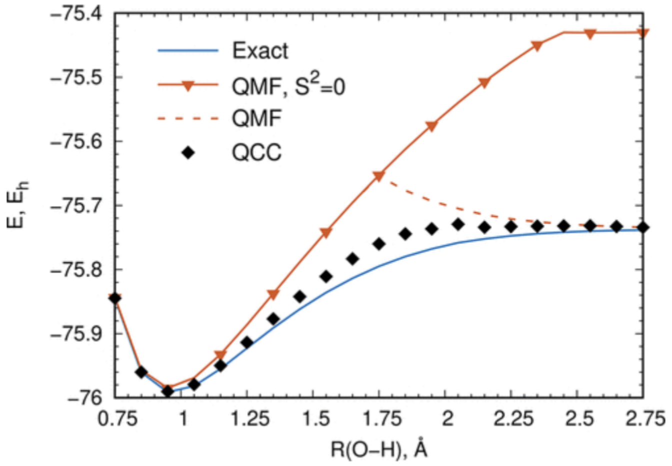

Figure 4.22: Potential energy curves for the symmetric stretch of the water molecule (source: [**H2O˙referece**]).

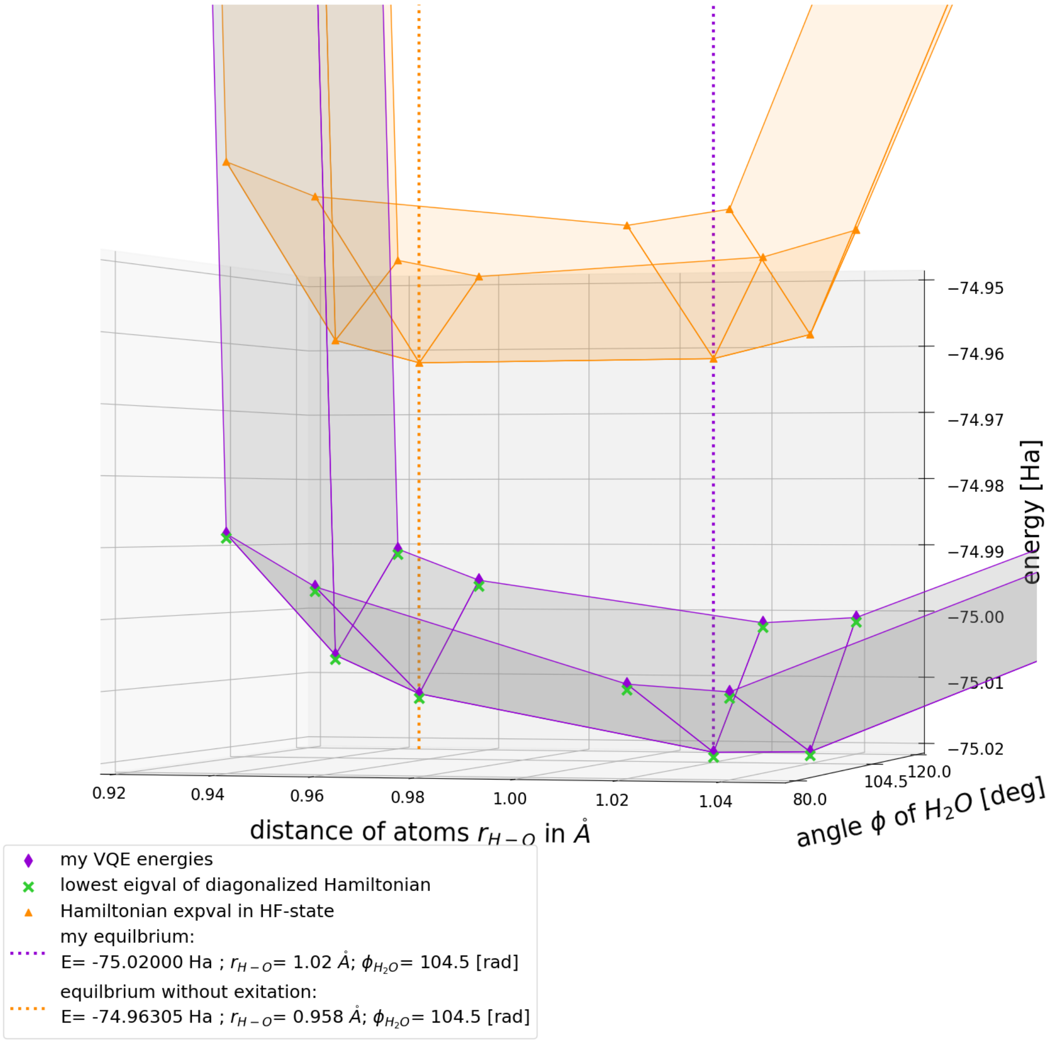

Figure 4.23: zoomed version of Figure 4.20. VQE Ground State Energy, lowest Hamiltonian eigenvalue, and HF-energy vs. Internuclear Distance and angle for H_2O around the Equilibrium. The Equilibrium distance corresponds to the minimal energy. The Equilibrium distance corresponds to the minimal energy. The simulation was made with 12 qubits.

5 Conclusion

In this thesis, we've explored the capabilities of Quantum Variational Eigensolver (VQE) algorithms in the domain of quantum chemistry. Our primary focus was on understanding the ground state properties and energy landscapes of several molecules, including H_2, LiH, BeH_2, and H_2O.

Starting with the simplest molecule, H_2, VQE demonstrated its effectiveness in reproducing the molecule's equilibrium distance and associated energy. Our comparisons with IBM's simulations, which used real quantum hardware instead of a simulator, validated the reliability of our VQE-based approach.

Moving on to more complex molecules, we successfully applied VQE to LiH, BeH_2, and H_2O. Despite the added complexity, we accurately determined their equilibrium geometries and energies, contributing to our understanding of these molecules' behavior.

However, we also noticed discrepancies in the VQE energy surfaces for BeH_2 and H_2O at larger internuclear distances, raising questions about the choice of initial states for large internuclear distances in our approach.

In conclusion, this thesis highlights the potential of VQE in modeling molecular structures and energy landscapes. While VQE proved effective in capturing ground states for various molecules, challenges remain, particularly concerning big internuclear distances. This work offers insights into the evolving capabilities of quantum technologies and their applications in understanding molecular systems.

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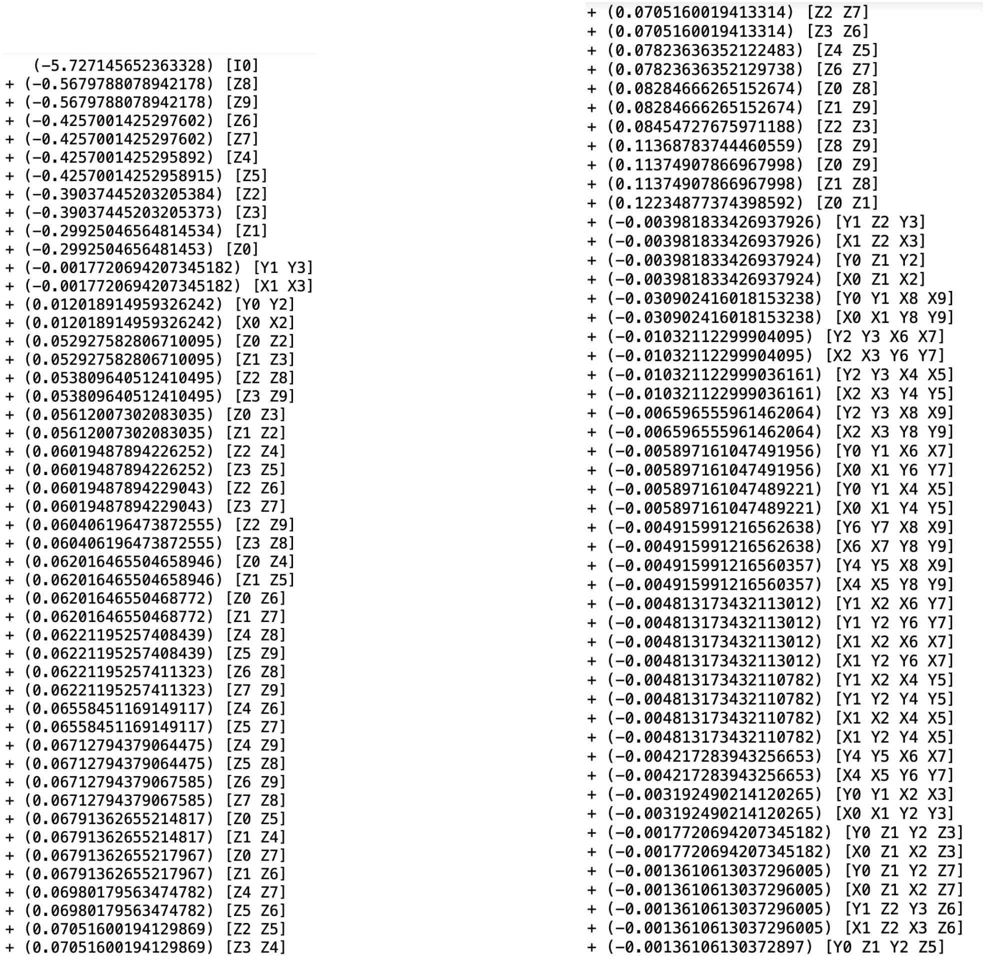
A Qubit Hamiltonians

The qubit numbering in the output of our program uses a convention that is shifted by one. This means that, for example, qubit 0 here corresponds to qubit 1 in the thesis.

A.1 *LiH*



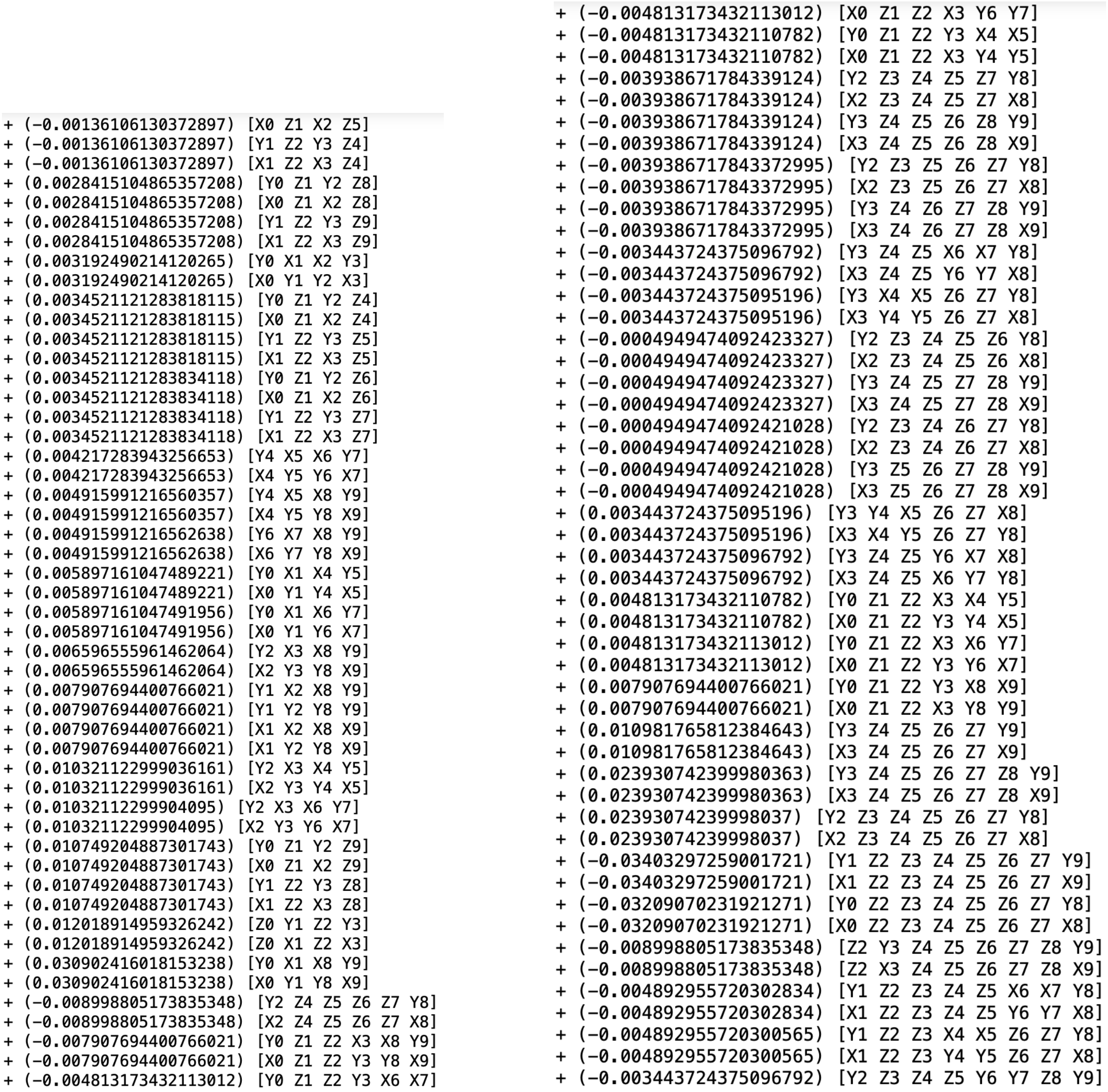
```
  (-5.727145652363328) [I0]
+ (-0.5679788078942178) [Z8]
+ (-0.5679788078942178) [Z9]
+ (-0.4257001425297602) [Z6]
+ (-0.4257001425297602) [Z7]
+ (-0.4257001425295892) [Z4]
+ (-0.42570014252958915) [Z5]
+ (-0.39037445203205384) [Z2]
+ (-0.39037445203205373) [Z3]
+ (-0.29925046564814534) [Z1]
+ (-0.2992504656481453) [Z0]
+ (-0.0017720694207345182) [Y1 Y3]
+ (-0.0017720694207345182) [X1 X3]
+ (0.012018914959326242) [Y0 Y2]
+ (0.012018914959326242) [X0 X2]
+ (0.052927582806710095) [Z0 Z2]
+ (0.052927582806710095) [Z1 Z3]
+ (0.053809640512410495) [Z2 Z8]
+ (0.053809640512410495) [Z3 Z9]
+ (0.05612007302083035) [Z0 Z3]
+ (0.05612007302083035) [Z1 Z2]
+ (0.06019487894226252) [Z2 Z4]
+ (0.06019487894226252) [Z3 Z5]
+ (0.06019487894229043) [Z2 Z6]
+ (0.06019487894229043) [Z3 Z7]
+ (0.060406196473872555) [Z2 Z9]
+ (0.060406196473872555) [Z3 Z8]
+ (0.062016465504658946) [Z0 Z4]
+ (0.062016465504658946) [Z1 Z5]
+ (0.06201646550468772) [Z0 Z6]
+ (0.06201646550468772) [Z1 Z7]
+ (0.06221195257408439) [Z4 Z8]
+ (0.06221195257408439) [Z5 Z9]
+ (0.06221195257411323) [Z6 Z8]
+ (0.06221195257411323) [Z7 Z9]
+ (0.06558451169149117) [Z4 Z6]
+ (0.06558451169149117) [Z5 Z7]
+ (0.06712794379064475) [Z4 Z9]
+ (0.06712794379064475) [Z5 Z8]
+ (0.06712794379067585) [Z6 Z9]
+ (0.06712794379067585) [Z7 Z8]
+ (0.06791362655214817) [Z0 Z5]
+ (0.06791362655214817) [Z1 Z4]
+ (0.06791362655217967) [Z0 Z7]
+ (0.06791362655217967) [Z1 Z6]
+ (0.06980179563474782) [Z4 Z7]
+ (0.06980179563474782) [Z5 Z6]
+ (0.07051600194129869) [Z2 Z5]
+ (0.07051600194129869) [Z3 Z4]
```

(a)

```
+ (0.0705160019413314) [Z2 Z7]
+ (0.0705160019413314) [Z3 Z6]
+ (0.07823636352122483) [Z4 Z5]
+ (0.07823636352129738) [Z6 Z7]
+ (0.08284666265152674) [Z0 Z8]
+ (0.08284666265152674) [Z1 Z9]
+ (0.08454727675971188) [Z2 Z3]
+ (0.11368783744460559) [Z8 Z9]
+ (0.11374907866967998) [Z0 Z9]
+ (0.11374907866967998) [Z1 Z8]
+ (0.12234877374398592) [Z0 Z1]
+ (-0.003981833426937926) [Y1 Z2 Y3]
+ (-0.003981833426937926) [X1 Z2 X3]
+ (-0.003981833426937924) [Y0 Z1 Y2]
+ (-0.003981833426937924) [X0 Z1 X2]
+ (-0.030902416018153238) [Y0 Y1 X8 X9]
+ (-0.030902416018153238) [X0 X1 Y8 Y9]
+ (-0.01032112299904095) [Y2 Y3 X6 X7]
+ (-0.01032112299904095) [X2 X3 Y6 Y7]
+ (-0.010321122999036161) [Y2 Y3 X4 X5]
+ (-0.010321122999036161) [X2 X3 Y4 Y5]
+ (-0.006596555961462064) [Y2 Y3 X8 X9]
+ (-0.006596555961462064) [X2 X3 Y8 Y9]
+ (-0.005897161047491956) [Y0 Y1 X6 X7]
+ (-0.005897161047491956) [X0 X1 Y6 Y7]
+ (-0.005897161047489221) [Y0 Y1 X4 X5]
+ (-0.005897161047489221) [X0 X1 Y4 Y5]
+ (-0.004915991216562638) [Y6 Y7 X8 X9]
+ (-0.004915991216562638) [X6 X7 Y8 Y9]
+ (-0.004915991216560357) [Y4 Y5 X8 X9]
+ (-0.004915991216560357) [X4 X5 Y8 Y9]
+ (-0.004813173432113012) [Y1 X2 X6 Y7]
+ (-0.004813173432113012) [Y1 Y2 Y6 Y7]
+ (-0.004813173432113012) [X1 X2 X6 X7]
+ (-0.004813173432113012) [X1 Y2 Y6 X7]
+ (-0.004813173432110782) [Y1 X2 X4 Y5]
+ (-0.004813173432110782) [Y1 Y2 Y4 Y5]
+ (-0.004813173432110782) [X1 X2 X4 X5]
+ (-0.004813173432110782) [X1 Y2 Y4 X5]
+ (-0.004217283943256653) [Y4 Y5 X6 X7]
+ (-0.004217283943256653) [X4 X5 Y6 Y7]
+ (-0.003192490214120265) [Y0 Y1 X2 X3]
+ (-0.003192490214120265) [X0 X1 Y2 Y3]
+ (-0.0017720694207345182) [Y0 Z1 Y2 Z3]
+ (-0.0017720694207345182) [X0 Z1 X2 Z3]
+ (-0.0013610613037296005) [Y0 Z1 Y2 Z7]
+ (-0.0013610613037296005) [X0 Z1 X2 Z7]
+ (-0.0013610613037296005) [Y1 Z2 Y3 Z6]
+ (-0.0013610613037296005) [X1 Z2 X3 Z6]
+ (-0.00136106130372897) [Y0 Z1 Y2 Z5]
```

(b)

Figure A.1: qubit Hamiltonian of LiH for $r_{Li-H} = 1.57\mathring{A}$. Part 1



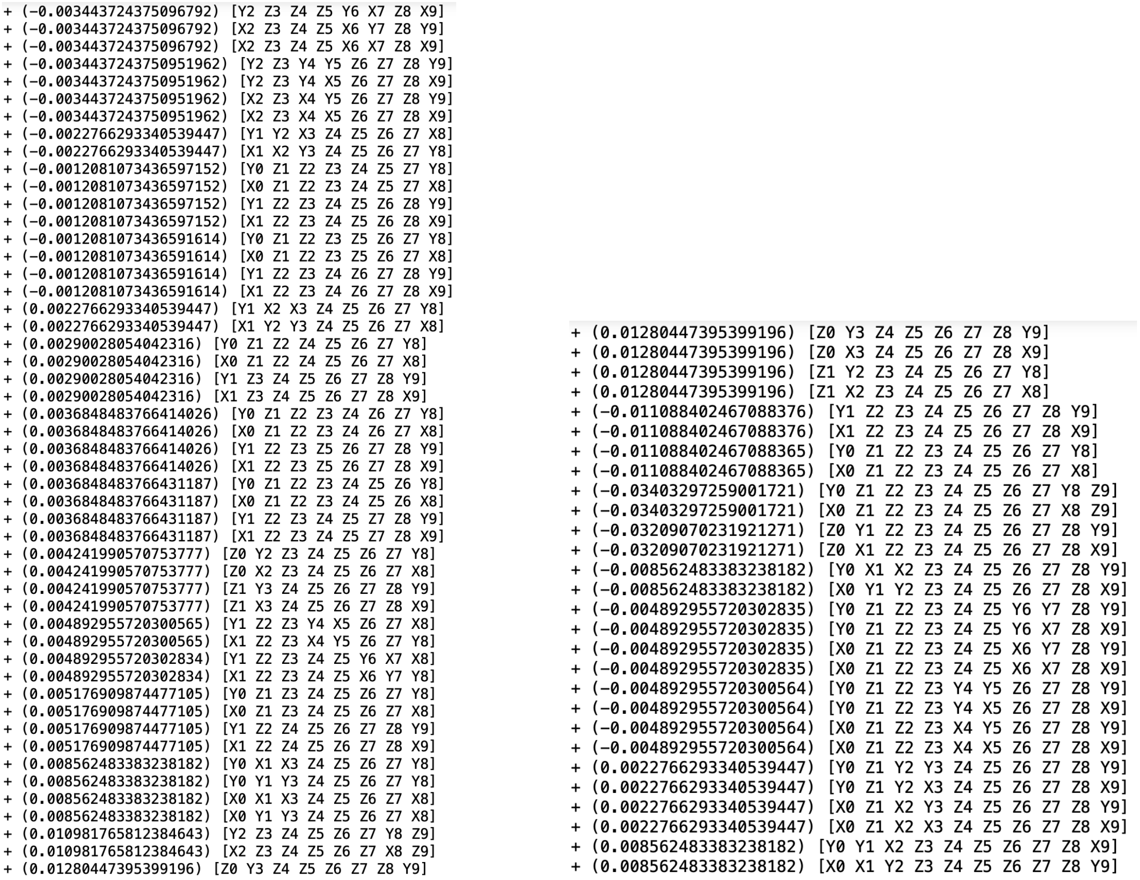
```
+ (-0.00136106130372897) [X0 Z1 X2 Z5]
+ (-0.00136106130372897) [Y1 Z2 Y3 Z4]
+ (-0.00136106130372897) [X1 Z2 X3 Z4]
+ (0.0028415104865357208) [Y0 Z1 Y2 Z8]
+ (0.0028415104865357208) [X0 Z1 X2 Z8]
+ (0.0028415104865357208) [Y1 Z2 Y3 Z9]
+ (0.0028415104865357208) [X1 Z2 X3 Z9]
+ (0.003192490214120265) [Y0 X1 X2 Y3]
+ (0.003192490214120265) [X0 Y1 Y2 X3]
+ (0.0034521121283818115) [Y0 Z1 Y2 Z4]
+ (0.0034521121283818115) [X0 Z1 X2 Z4]
+ (0.0034521121283818115) [Y1 Z2 Y3 Z5]
+ (0.0034521121283818115) [X1 Z2 X3 Z5]
+ (0.0034521121283834118) [Y0 Z1 Y2 Z6]
+ (0.0034521121283834118) [X0 Z1 X2 Z6]
+ (0.0034521121283834118) [Y1 Z2 Y3 Z7]
+ (0.0034521121283834118) [X1 Z2 X3 Z7]
+ (0.004217283943256653) [Y4 X5 X6 Y7]
+ (0.004217283943256653) [X4 Y5 Y6 X7]
+ (0.004915991216560357) [Y4 X5 X8 Y9]
+ (0.004915991216560357) [X4 Y5 Y8 X9]
+ (0.004915991216562638) [Y6 X7 X8 Y9]
+ (0.004915991216562638) [X6 Y7 Y8 X9]
+ (0.005897161047489221) [Y0 X1 X4 Y5]
+ (0.005897161047489221) [X0 Y1 Y4 X5]
+ (0.005897161047491956) [Y0 X1 X6 Y7]
+ (0.005897161047491956) [X0 Y1 Y6 X7]
+ (0.006596555961462064) [Y2 X3 X8 Y9]
+ (0.006596555961462064) [X2 Y3 Y8 X9]
+ (0.007907694400766021) [Y1 X2 X8 Y9]
+ (0.007907694400766021) [Y1 Y2 Y8 Y9]
+ (0.007907694400766021) [X1 X2 X8 X9]
+ (0.007907694400766021) [X1 Y2 Y8 X9]
+ (0.010321122999036161) [Y2 X3 X4 Y5]
+ (0.010321122999036161) [X2 Y3 Y4 X5]
+ (0.01032112299904095) [Y2 X3 X6 Y7]
+ (0.01032112299904095) [X2 Y3 Y6 X7]
+ (0.010749204887301743) [Y0 Z1 Y2 Z9]
+ (0.010749204887301743) [X0 Z1 X2 Z9]
+ (0.010749204887301743) [Y1 Z2 Y3 Z8]
+ (0.010749204887301743) [X1 Z2 X3 Z8]
+ (0.012018914959326242) [Z0 Y1 Z2 Y3]
+ (0.012018914959326242) [Z0 X1 Z2 X3]
+ (0.030902416018153238) [Y0 X1 X8 Y9]
+ (0.030902416018153238) [X0 Y1 Y8 X9]
+ (-0.008998805173835348) [Y2 Z4 Z5 Z6 Z7 Y8]
+ (-0.008998805173835348) [X2 Z4 Z5 Z6 Z7 X8]
+ (-0.007907694400766021) [Y0 Z1 Z2 X3 X8 Y9]
+ (-0.007907694400766021) [X0 Z1 Z2 Y3 Y8 X9]
+ (-0.004813173432113012) [Y0 Z1 Z2 Y3 X6 X7]
```

(a)

```
+ (-0.004813173432113012) [X0 Z1 Z2 X3 Y6 Y7]
+ (-0.004813173432110782) [Y0 Z1 Z2 Y3 X4 X5]
+ (-0.004813173432110782) [X0 Z1 Z2 X3 Y4 Y5]
+ (-0.003938671784339124) [Y2 Z3 Z4 Z5 Z7 Y8]
+ (-0.003938671784339124) [X2 Z3 Z4 Z5 Z7 X8]
+ (-0.003938671784339124) [Y3 Z4 Z5 Z6 Z8 Y9]
+ (-0.003938671784339124) [X3 Z4 Z5 Z6 Z8 X9]
+ (-0.0039386717843372995) [Y2 Z3 Z5 Z6 Z7 Y8]
+ (-0.0039386717843372995) [X2 Z3 Z5 Z6 Z7 X8]
+ (-0.0039386717843372995) [Y3 Z4 Z6 Z7 Z8 Y9]
+ (-0.0039386717843372995) [X3 Z4 Z6 Z7 Z8 X9]
+ (-0.003443724375096792) [Y3 Z4 Z5 X6 X7 Y8]
+ (-0.003443724375096792) [X3 Z4 Z5 Y6 Y7 X8]
+ (-0.003443724375095196) [Y3 X4 X5 Z6 Z7 Y8]
+ (-0.003443724375095196) [X3 Y4 Y5 Z6 Z7 X8]
+ (-0.0004949474092423327) [Y2 Z3 Z4 Z5 Z6 Y8]
+ (-0.0004949474092423327) [X2 Z3 Z4 Z5 Z6 X8]
+ (-0.0004949474092423327) [Y3 Z4 Z5 Z7 Z8 Y9]
+ (-0.0004949474092423327) [X3 Z4 Z5 Z7 Z8 X9]
+ (-0.0004949474092421028) [Y2 Z3 Z4 Z6 Z7 Y8]
+ (-0.0004949474092421028) [X2 Z3 Z4 Z6 Z7 X8]
+ (-0.0004949474092421028) [Y3 Z5 Z6 Z7 Z8 Y9]
+ (-0.0004949474092421028) [X3 Z5 Z6 Z7 Z8 X9]
+ (0.003443724375095196) [Y3 Y4 X5 Z6 Z7 X8]
+ (0.003443724375095196) [X3 X4 Y5 Z6 Z7 Y8]
+ (0.003443724375096792) [Y3 Z4 Z5 Y6 X7 X8]
+ (0.003443724375096792) [X3 Z4 Z5 X6 Y7 Y8]
+ (0.004813173432110782) [Y0 Z1 Z2 X3 X4 Y5]
+ (0.004813173432110782) [X0 Z1 Z2 Y3 Y4 X5]
+ (0.004813173432113012) [Y0 Z1 Z2 X3 X6 Y7]
+ (0.004813173432113012) [X0 Z1 Z2 Y3 Y6 X7]
+ (0.007907694400766021) [Y0 Z1 Z2 Y3 X8 X9]
+ (0.007907694400766021) [X0 Z1 Z2 X3 Y8 Y9]
+ (0.010981765812384643) [Y3 Z4 Z5 Z6 Z7 Y9]
+ (0.010981765812384643) [X3 Z4 Z5 Z6 Z7 X9]
+ (0.023930742399980363) [Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.023930742399980363) [X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.02393074239998037) [Y2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (0.02393074239998037) [X2 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.03403297259001721) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Y9]
+ (-0.03403297259001721) [X1 Z2 Z3 Z4 Z5 Z6 Z7 X9]
+ (-0.03209070231921271) [Y0 Z2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (-0.03209070231921271) [X0 Z2 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.008998805173835348) [Z2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.008998805173835348) [Z2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.004892955720302834) [Y1 Z2 Z3 Z4 Z5 X6 X7 Y8]
+ (-0.004892955720302834) [X1 Z2 Z3 Z4 Z5 Y6 Y7 X8]
+ (-0.004892955720300565) [Y1 Z2 Z3 X4 X5 Z6 Z7 Y8]
+ (-0.004892955720300565) [X1 Z2 Z3 Y4 Y5 Z6 Z7 X8]
+ (-0.003443724375096792) [Y2 Z3 Z4 Z5 Y6 Y7 Z8 Y9]
```

(b)

Figure A.2: qubit Hamiltonian of LiH for $r_{Li-H} = 1.57 \mathring{A}$. Part 2



```
+ (-0.003443724375096792) [Y2 Z3 Z4 Z5 Y6 X7 Z8 X9]
+ (-0.003443724375096792) [X2 Z3 Z4 Z5 X6 Y7 Z8 Y9]
+ (-0.003443724375096792) [X2 Z3 Z4 Z5 X6 X7 Z8 X9]
+ (-0.0034437243750951962) [Y2 Z3 Y4 Y5 Z6 Z7 Z8 Y9]
+ (-0.0034437243750951962) [Y2 Z3 Y4 X5 Z6 Z7 Z8 X9]
+ (-0.0034437243750951962) [X2 Z3 X4 Y5 Z6 Z7 Z8 Y9]
+ (-0.0034437243750951962) [X2 Z3 X4 X5 Z6 Z7 Z8 X9]
+ (-0.0022766293340539447) [Y1 Y2 X3 Z4 Z5 Z6 Z7 X8]
+ (-0.0022766293340539447) [X1 X2 Y3 Z4 Z5 Z6 Z7 Y8]
+ (-0.0012081073436597152) [Y0 Z1 Z2 Z3 Z4 Z5 Z7 Y8]
+ (-0.0012081073436597152) [X0 Z1 Z2 Z3 Z4 Z5 Z7 X8]
+ (-0.0012081073436597152) [Y1 Z2 Z3 Z4 Z5 Z6 Z8 Y9]
+ (-0.0012081073436597152) [X1 Z2 Z3 Z4 Z5 Z6 Z8 X9]
+ (-0.0012081073436591614) [Y0 Z1 Z2 Z3 Z5 Z6 Z7 Y8]
+ (-0.0012081073436591614) [X0 Z1 Z2 Z3 Z5 Z6 Z7 X8]
+ (-0.0012081073436591614) [Y1 Z2 Z3 Z4 Z6 Z7 Z8 Y9]
+ (-0.0012081073436591614) [X1 Z2 Z3 Z4 Z6 Z7 Z8 X9]
+ (0.0022766293340539447) [Y1 X2 X3 Z4 Z5 Z6 Z7 Y8]
+ (0.0022766293340539447) [X1 Y2 Y3 Z4 Z5 Z6 Z7 X8]
+ (0.00290028054042316) [Y0 Z1 Z2 Z4 Z5 Z6 Z7 Y8]
+ (0.00290028054042316) [X0 Z1 Z2 Z4 Z5 Z6 Z7 X8]
+ (0.00290028054042316) [Y1 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.00290028054042316) [X1 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.0036848483766414026) [Y0 Z1 Z2 Z3 Z4 Z6 Z7 Y8]
+ (0.0036848483766414026) [X0 Z1 Z2 Z3 Z4 Z6 Z7 X8]
+ (0.0036848483766414026) [Y1 Z2 Z3 Z5 Z6 Z7 Z8 Y9]
+ (0.0036848483766414026) [X1 Z2 Z3 Z5 Z6 Z7 Z8 X9]
+ (0.0036848483766431187) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Y8]
+ (0.0036848483766431187) [X0 Z1 Z2 Z3 Z4 Z5 Z6 X8]
+ (0.0036848483766431187) [Y1 Z2 Z3 Z4 Z5 Z7 Z8 Y9]
+ (0.0036848483766431187) [X1 Z2 Z3 Z4 Z5 Z7 Z8 X9]
+ (0.004241990570753777) [Z0 Y2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (0.004241990570753777) [Z0 X2 Z3 Z4 Z5 Z6 Z7 X8]
+ (0.004241990570753777) [Z1 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.004241990570753777) [Z1 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.004892955720300565) [Y1 Z2 Z3 Y4 X5 Z6 Z7 X8]
+ (0.004892955720300565) [X1 Z2 Z3 X4 Y5 Z6 Z7 Y8]
+ (0.004892955720302834) [Y1 Z2 Z3 Z4 Z5 Y6 X7 X8]
+ (0.004892955720302834) [X1 Z2 Z3 Z4 Z5 X6 Y7 Y8]
+ (0.005176909874477105) [Y0 Z1 Z3 Z4 Z5 Z6 Z7 Y8]
+ (0.005176909874477105) [X0 Z1 Z3 Z4 Z5 Z6 Z7 X8]
+ (0.005176909874477105) [Y1 Z2 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.005176909874477105) [X1 Z2 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.008562483383238182) [Y0 X1 X3 Z4 Z5 Z6 Z7 Y8]
+ (0.008562483383238182) [Y0 Y1 Y3 Z4 Z5 Z6 Z7 Y8]
+ (0.008562483383238182) [X0 X1 X3 Z4 Z5 Z6 Z7 X8]
+ (0.008562483383238182) [X0 Y1 Y3 Z4 Z5 Z6 Z7 X8]
+ (0.010981765812384643) [Y2 Z3 Z4 Z5 Z6 Z7 Y8 Z9]
+ (0.010981765812384643) [X2 Z3 Z4 Z5 Z6 Z7 X8 Z9]
+ (0.01280447395399196) [Z0 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
```

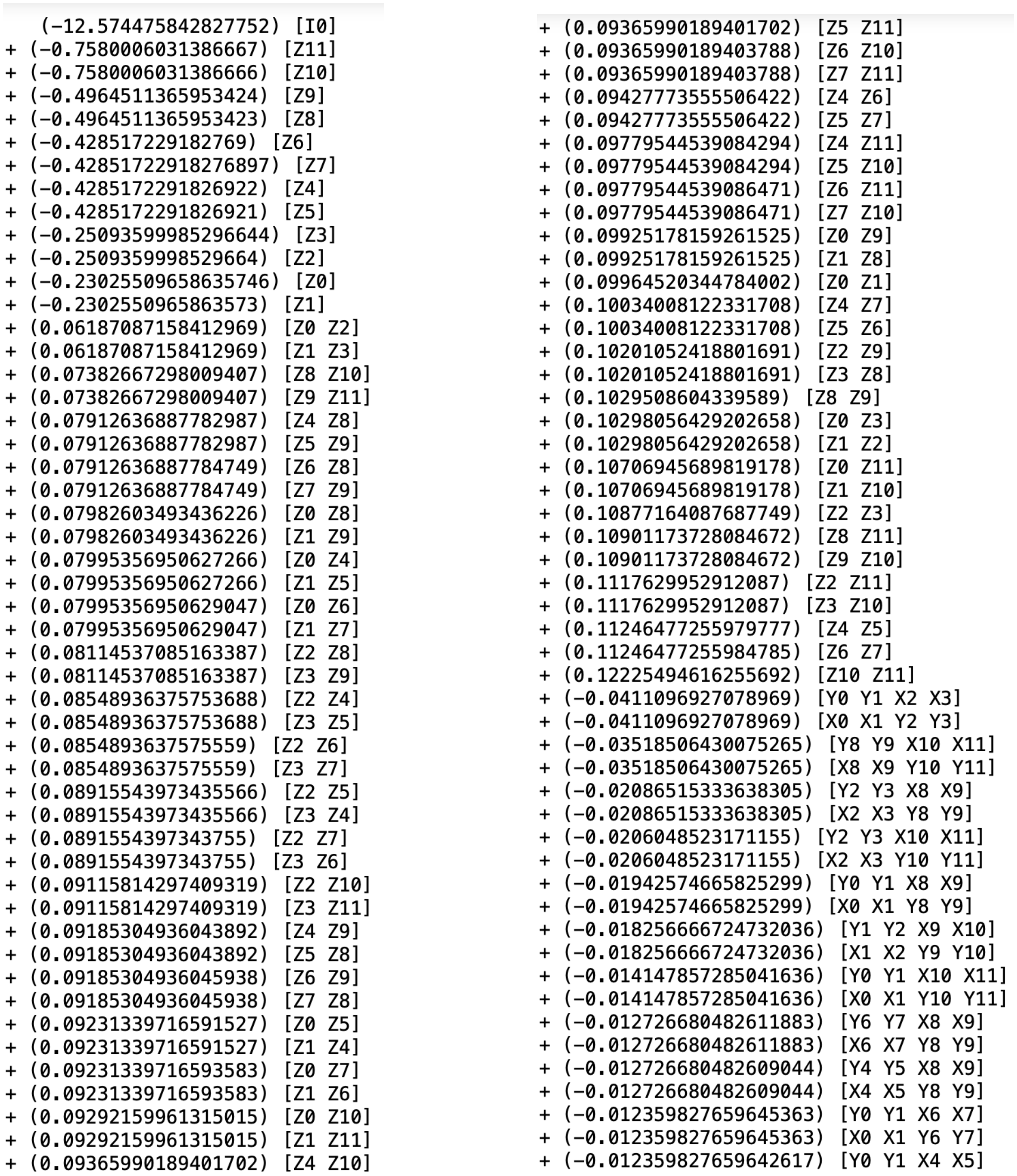
(a)

```
+ (0.01280447395399196) [Z0 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.01280447395399196) [Z0 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.01280447395399196) [Z1 Y2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (0.01280447395399196) [Z1 X2 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.011088402467088376) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.011088402467088376) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.011088402467088365) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (-0.011088402467088365) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.03403297259001721) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z9]
+ (-0.03403297259001721) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z9]
+ (-0.03209070231921271) [Z0 Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.03209070231921271) [Z0 X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.008562483383238182) [Y0 X1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.008562483383238182) [X0 Y1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.004892955720302835) [Y0 Z1 Z2 Z3 Z4 Z5 Y6 Y7 Z8 Y9]
+ (-0.004892955720302835) [Y0 Z1 Z2 Z3 Z4 Z5 Y6 X7 Z8 X9]
+ (-0.004892955720302835) [X0 Z1 Z2 Z3 Z4 Z5 X6 Y7 Z8 Y9]
+ (-0.004892955720302835) [X0 Z1 Z2 Z3 Z4 Z5 X6 X7 Z8 X9]
+ (-0.004892955720300564) [Y0 Z1 Z2 Z3 Y4 Y5 Z6 Z7 Z8 Y9]
+ (-0.004892955720300564) [Y0 Z1 Z2 Z3 Y4 X5 Z6 Z7 Z8 X9]
+ (-0.004892955720300564) [X0 Z1 Z2 Z3 X4 Y5 Z6 Z7 Z8 Y9]
+ (-0.004892955720300564) [X0 Z1 Z2 Z3 X4 X5 Z6 Z7 Z8 X9]
+ (0.0022766293340539447) [Y0 Z1 Y2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.0022766293340539447) [Y0 Z1 Y2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.0022766293340539447) [X0 Z1 X2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.0022766293340539447) [X0 Z1 X2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.008562483383238182) [Y0 Y1 X2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.008562483383238182) [X0 X1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
```

(b)

Figure A.3: qubit Hamiltonian of LiH for $r_{Li-H} = 1.57\mathring{A}$. Part 3

A.2 BeH_2



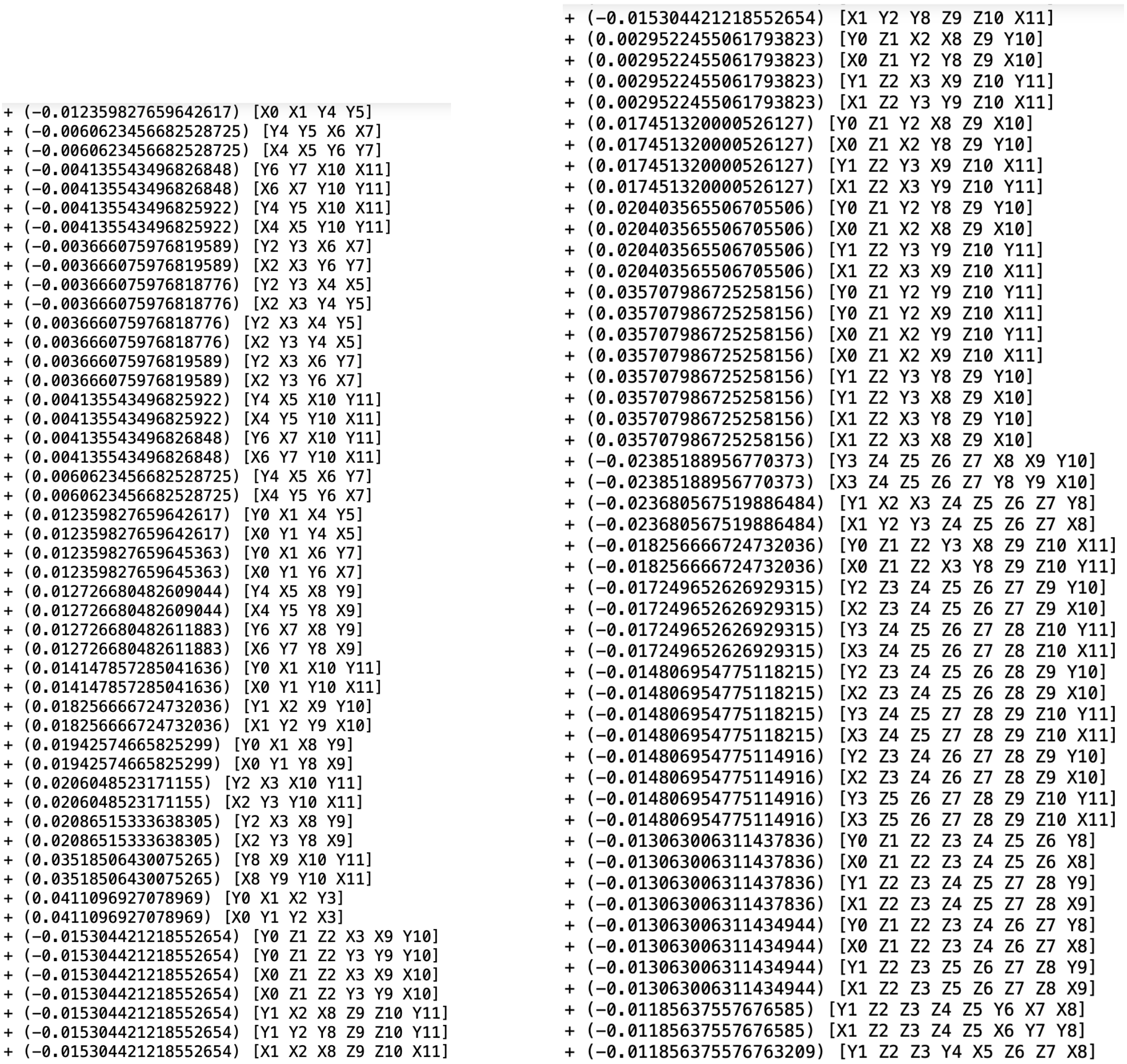
```
  (-12.574475842827752) [I0]
+ (-0.7580006031386667) [Z11]
+ (-0.758000603138666) [Z10]
+ (-0.4964511365953424) [Z9]
+ (-0.4964511365953423) [Z8]
+ (-0.428517229182769) [Z6]
+ (-0.42851722918276897) [Z7]
+ (-0.4285172291826922) [Z4]
+ (-0.4285172291826921) [Z5]
+ (-0.25093599985296644) [Z3]
+ (-0.2509359998529664) [Z2]
+ (-0.23025509658635746) [Z0]
+ (-0.2302550965863573) [Z1]
+ (0.06187087158412969) [Z0 Z2]
+ (0.06187087158412969) [Z1 Z3]
+ (0.07382667298009407) [Z8 Z10]
+ (0.07382667298009407) [Z9 Z11]
+ (0.07912636887782987) [Z4 Z8]
+ (0.07912636887782987) [Z5 Z9]
+ (0.07912636887784749) [Z6 Z8]
+ (0.07912636887784749) [Z7 Z9]
+ (0.07982603493436226) [Z0 Z8]
+ (0.07982603493436226) [Z1 Z9]
+ (0.07995356950627266) [Z0 Z4]
+ (0.07995356950627266) [Z1 Z5]
+ (0.07995356950629047) [Z0 Z6]
+ (0.07995356950629047) [Z1 Z7]
+ (0.08114537085163387) [Z2 Z8]
+ (0.08114537085163387) [Z3 Z9]
+ (0.08548936375753688) [Z2 Z4]
+ (0.08548936375753688) [Z3 Z5]
+ (0.0854893637575559) [Z2 Z6]
+ (0.0854893637575559) [Z3 Z7]
+ (0.08915543973435566) [Z2 Z5]
+ (0.08915543973435566) [Z3 Z4]
+ (0.0891554397343755) [Z2 Z7]
+ (0.0891554397343755) [Z3 Z6]
+ (0.09115814297409319) [Z2 Z10]
+ (0.09115814297409319) [Z3 Z11]
+ (0.09185304936043892) [Z4 Z9]
+ (0.09185304936043892) [Z5 Z8]
+ (0.09185304936045938) [Z6 Z9]
+ (0.09185304936045938) [Z7 Z8]
+ (0.09231339716591527) [Z0 Z5]
+ (0.09231339716591527) [Z1 Z4]
+ (0.09231339716593583) [Z0 Z7]
+ (0.09231339716593583) [Z1 Z6]
+ (0.09292159961315015) [Z0 Z10]
+ (0.09292159961315015) [Z1 Z11]
+ (0.09365990189401702) [Z4 Z10]
```

(a)

```
+ (0.09365990189401702) [Z5 Z11]
+ (0.09365990189403788) [Z6 Z10]
+ (0.09365990189403788) [Z7 Z11]
+ (0.0942777355506422) [Z4 Z6]
+ (0.0942777355506422) [Z5 Z7]
+ (0.09779544539084294) [Z4 Z11]
+ (0.09779544539084294) [Z5 Z10]
+ (0.09779544539086471) [Z6 Z11]
+ (0.09779544539086471) [Z7 Z10]
+ (0.09925178159261525) [Z0 Z9]
+ (0.09925178159261525) [Z1 Z8]
+ (0.09964520344784002) [Z0 Z1]
+ (0.10034008122331708) [Z4 Z7]
+ (0.10034008122331708) [Z5 Z6]
+ (0.10201052418801691) [Z2 Z9]
+ (0.10201052418801691) [Z3 Z8]
+ (0.1029508604339589) [Z8 Z9]
+ (0.10298056429202658) [Z0 Z3]
+ (0.10298056429202658) [Z1 Z2]
+ (0.10706945689819178) [Z0 Z11]
+ (0.10706945689819178) [Z1 Z10]
+ (0.10877164087687749) [Z2 Z3]
+ (0.10901173728084672) [Z8 Z11]
+ (0.10901173728084672) [Z9 Z10]
+ (0.1117629952912087) [Z2 Z11]
+ (0.1117629952912087) [Z3 Z10]
+ (0.11246477255979777) [Z4 Z5]
+ (0.11246477255984785) [Z6 Z7]
+ (0.12225494616255692) [Z10 Z11]
+ (-0.0411096927078969) [Y0 Y1 X2 X3]
+ (-0.0411096927078969) [X0 X1 Y2 Y3]
+ (-0.03518506430075265) [Y8 Y9 X10 X11]
+ (-0.03518506430075265) [X8 X9 Y10 Y11]
+ (-0.02086515333638305) [Y2 Y3 X8 X9]
+ (-0.02086515333638305) [X2 X3 Y8 Y9]
+ (-0.0206048523171155) [Y2 Y3 X10 X11]
+ (-0.0206048523171155) [X2 X3 Y10 Y11]
+ (-0.01942574665825299) [Y0 Y1 X8 X9]
+ (-0.01942574665825299) [X0 X1 Y8 Y9]
+ (-0.018256666724732036) [Y1 Y2 X9 X10]
+ (-0.018256666724732036) [X1 X2 Y9 Y10]
+ (-0.014147857285041636) [Y0 Y1 X10 X11]
+ (-0.014147857285041636) [X0 X1 Y10 Y11]
+ (-0.012726680482611883) [Y6 Y7 X8 X9]
+ (-0.012726680482611883) [X6 X7 Y8 Y9]
+ (-0.012726680482609044) [Y4 Y5 X8 X9]
+ (-0.012726680482609044) [X4 X5 Y8 Y9]
+ (-0.012359827659645363) [Y0 Y1 X6 X7]
+ (-0.012359827659645363) [X0 X1 Y6 Y7]
+ (-0.012359827659642617) [Y0 Y1 X4 X5]
```

(b)

Figure A.4: qubit Hamiltonian of BeH_2 for $r_{Be-H} = 1.33\mathring{A}$. Part 1



```
+ (-0.012359827659642617) [X0 X1 Y4 Y5]
+ (-0.0060623456682528725) [Y4 Y5 X6 X7]
+ (-0.0060623456682528725) [X4 X5 Y6 Y7]
+ (-0.004135543496826848) [Y6 Y7 X10 X11]
+ (-0.004135543496826848) [X6 X7 Y10 Y11]
+ (-0.004135543496825922) [Y4 Y5 X10 X11]
+ (-0.004135543496825922) [X4 X5 Y10 Y11]
+ (-0.003666075976819589) [Y2 Y3 X6 X7]
+ (-0.003666075976819589) [X2 X3 Y6 Y7]
+ (-0.003666075976818776) [Y2 Y3 X4 X5]
+ (-0.003666075976818776) [X2 X3 Y4 Y5]
+ (0.003666075976818776) [Y2 X3 X4 Y5]
+ (0.003666075976818776) [X2 Y3 Y4 X5]
+ (0.003666075976819589) [Y2 X3 X6 Y7]
+ (0.003666075976819589) [X2 Y3 Y6 X7]
+ (0.004135543496825922) [Y4 X5 X10 Y11]
+ (0.004135543496825922) [X4 Y5 Y10 X11]
+ (0.004135543496826848) [Y6 X7 X10 Y11]
+ (0.004135543496826848) [X6 Y7 Y10 X11]
+ (0.0060623456682528725) [Y4 X5 X6 Y7]
+ (0.0060623456682528725) [X4 Y5 Y6 X7]
+ (0.012359827659642617) [Y0 X1 X4 Y5]
+ (0.012359827659642617) [X0 Y1 Y4 X5]
+ (0.012359827659645363) [Y0 X1 X6 Y7]
+ (0.012359827659645363) [X0 Y1 Y6 X7]
+ (0.012726680482609044) [Y4 X5 X8 Y9]
+ (0.012726680482609044) [X4 Y5 Y8 X9]
+ (0.012726680482611883) [Y6 X7 X8 Y9]
+ (0.012726680482611883) [X6 Y7 Y8 X9]
+ (0.014147857285041636) [Y0 X1 X10 Y11]
+ (0.014147857285041636) [X0 Y1 Y10 X11]
+ (0.018256666724732036) [Y1 X2 X9 Y10]
+ (0.018256666724732036) [X1 Y2 Y9 X10]
+ (0.01942574665825299) [Y0 X1 X8 Y9]
+ (0.01942574665825299) [X0 Y1 Y8 X9]
+ (0.0206048523171155) [Y2 X3 X10 Y11]
+ (0.0206048523171155) [X2 Y3 Y10 X11]
+ (0.02086515333638305) [Y2 X3 X8 Y9]
+ (0.02086515333638305) [X2 Y3 Y8 X9]
+ (0.03518506430075265) [Y8 X9 X10 Y11]
+ (0.03518506430075265) [X8 Y9 Y10 X11]
+ (0.0411096927078969) [Y0 X1 X2 Y3]
+ (0.0411096927078969) [X0 Y1 Y2 X3]
+ (-0.015304421218552654) [Y0 Z1 Z2 X3 X9 Y10]
+ (-0.015304421218552654) [Y0 Z1 Z2 Y3 Y9 Y10]
+ (-0.015304421218552654) [X0 Z1 Z2 X3 X9 X10]
+ (-0.015304421218552654) [X0 Z1 Z2 Y3 Y9 X10]
+ (-0.015304421218552654) [Y1 X2 X8 Z9 Z10 Y11]
+ (-0.015304421218552654) [Y1 Y2 Y8 Z9 Z10 Y11]
+ (-0.015304421218552654) [X1 X2 X8 Z9 Z10 X11]
```

(a)

```
+ (-0.015304421218552654) [X1 Y2 Y8 Z9 Z10 X11]
+ (0.0029522455061793823) [Y0 Z1 X2 X8 Z9 Y10]
+ (0.0029522455061793823) [X0 Z1 Y2 Y8 Z9 X10]
+ (0.0029522455061793823) [Y1 Z2 X3 X9 Z10 Y11]
+ (0.0029522455061793823) [X1 Z2 Y3 Y9 Z10 X11]
+ (0.017451320000526127) [Y0 Z1 Y2 X8 Z9 X10]
+ (0.017451320000526127) [X0 Z1 X2 Y8 Z9 Y10]
+ (0.017451320000526127) [Y1 Z2 Y3 X9 Z10 X11]
+ (0.017451320000526127) [X1 Z2 X3 Y9 Z10 Y11]
+ (0.020403565506705506) [Y0 Z1 Y2 Y8 Z9 Y10]
+ (0.020403565506705506) [X0 Z1 X2 X8 Z9 X10]
+ (0.020403565506705506) [Y1 Z2 Y3 Y9 Z10 Y11]
+ (0.020403565506705506) [X1 Z2 X3 X9 Z10 X11]
+ (0.035707986725258156) [Y0 Z1 Y2 Y9 Z10 Y11]
+ (0.035707986725258156) [Y0 Z1 Y2 X9 Z10 X11]
+ (0.035707986725258156) [X0 Z1 X2 Y9 Z10 Y11]
+ (0.035707986725258156) [X0 Z1 X2 X9 Z10 X11]
+ (0.035707986725258156) [Y1 Z2 Y3 Y8 Z9 Y10]
+ (0.035707986725258156) [Y1 Z2 Y3 X8 Z9 X10]
+ (0.035707986725258156) [X1 Z2 X3 Y8 Z9 Y10]
+ (0.035707986725258156) [X1 Z2 X3 X8 Z9 X10]
+ (-0.02385188956770373) [Y3 Z4 Z5 Z6 Z7 X8 X9 Y10]
+ (-0.02385188956770373) [X3 Z4 Z5 Z6 Z7 Y8 Y9 X10]
+ (-0.023680567519886484) [Y1 X2 X3 Z4 Z5 Z6 Z7 Y8]
+ (-0.023680567519886484) [X1 Y2 Y3 Z4 Z5 Z6 Z7 X8]
+ (-0.018256666724732036) [Y0 Z1 Z2 Y3 X8 Z9 Z10 X11]
+ (-0.018256666724732036) [X0 Z1 Z2 X3 Y8 Z9 Z10 Y11]
+ (-0.017249652626929315) [Y2 Z3 Z4 Z5 Z6 Z7 Z9 Y10]
+ (-0.017249652626929315) [X2 Z3 Z4 Z5 Z6 Z7 Z9 X10]
+ (-0.017249652626929315) [Y3 Z4 Z5 Z6 Z7 Z8 Z10 Y11]
+ (-0.017249652626929315) [X3 Z4 Z5 Z6 Z7 Z8 Z10 X11]
+ (-0.014806954775118215) [Y2 Z3 Z4 Z5 Z6 Z8 Z9 Y10]
+ (-0.014806954775118215) [X2 Z3 Z4 Z5 Z6 Z8 Z9 X10]
+ (-0.014806954775118215) [Y3 Z4 Z5 Z7 Z8 Z9 Z10 Y11]
+ (-0.014806954775118215) [X3 Z4 Z5 Z7 Z8 Z9 Z10 X11]
+ (-0.014806954775114916) [Y2 Z3 Z4 Z6 Z7 Z8 Z9 Y10]
+ (-0.014806954775114916) [X2 Z3 Z4 Z6 Z7 Z8 Z9 X10]
+ (-0.014806954775114916) [Y3 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.014806954775114916) [X3 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.013063006311437836) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Y8]
+ (-0.013063006311437836) [X0 Z1 Z2 Z3 Z4 Z5 Z6 X8]
+ (-0.013063006311437836) [Y1 Z2 Z3 Z4 Z5 Z7 Z8 Y9]
+ (-0.013063006311437836) [X1 Z2 Z3 Z4 Z5 Z7 Z8 X9]
+ (-0.013063006311434944) [Y0 Z1 Z2 Z3 Z4 Z6 Z7 Y8]
+ (-0.013063006311434944) [X0 Z1 Z2 Z3 Z4 Z6 Z7 X8]
+ (-0.013063006311434944) [Y1 Z2 Z3 Z5 Z6 Z7 Z8 Y9]
+ (-0.013063006311434944) [X1 Z2 Z3 Z5 Z6 Z7 Z8 X9]
+ (-0.01185637557676585) [Y1 Z2 Z3 Z4 Z5 Y6 X7 X8]
+ (-0.01185637557676585) [X1 Z2 Z3 Z4 Z5 X6 Y7 Y8]
+ (-0.011856375576763209) [Y1 Z2 Z3 Y4 X5 Z6 Z7 X8]
```

(b)

Figure A.5: qubit Hamiltonian of BeH_2 for $r_{Be-H} = 1.33\mathring{A}$. Part 2

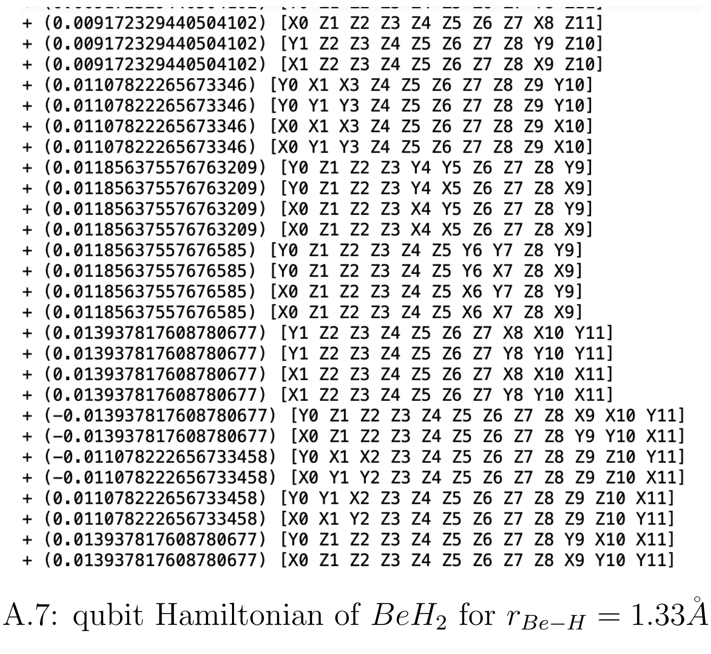
```
+ (-0.011856375576763209) [X1 Z2 Z3 X4 Y5 Z6 Z7 Y8]
+ (-0.011760339478224933) [Y0 Z1 Z3 Z4 Z5 Z6 Z7 Y8]
+ (-0.011760339478224933) [X0 Z1 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.011760339478224933) [Y1 Z2 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.011760339478224933) [X1 Z2 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.011364644346492758) [Y2 Z3 Z4 Z5 Z7 Z8 Z9 Y10]
+ (-0.011364644346492758) [X2 Z3 Z4 Z5 Z7 Z8 Z9 X10]
+ (-0.011364644346492758) [Y3 Z4 Z5 Z6 Z8 Z9 Z10 Y11]
+ (-0.011364644346492758) [X3 Z4 Z5 Z6 Z8 Z9 Z10 X11]
+ (-0.011364644346490227) [Y2 Z3 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.011364644346490227) [X2 Z3 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.011364644346490227) [Y3 Z4 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.011364644346490227) [X3 Z4 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.003442310428625455) [Y3 Z4 Z5 Y6 X7 Z8 Z9 X10]
+ (-0.003442310428625455) [X3 Z4 Z5 X6 Y7 Z8 Z9 Y10]
+ (-0.0034423104286246888) [Y3 Y4 X5 Z6 Z7 Z8 Z9 X10]
+ (-0.0034423104286246888) [X3 X4 Y5 Z6 Z7 Z8 Z9 Y10]
+ (-0.0012066307346719862) [Y0 Z1 Z2 Z3 Z4 Z5 Z7 Y8]
+ (-0.0012066307346719862) [X0 Z1 Z2 Z3 Z4 Z5 Z7 X8]
+ (-0.0012066307346719862) [Y1 Z2 Z3 Z4 Z5 Z6 Z8 Y9]
+ (-0.0012066307346719862) [X1 Z2 Z3 Z4 Z5 Z6 Z8 X9]
+ (-0.0012066307346717325) [Y0 Z1 Z2 Z3 Z5 Z6 Z7 Y8]
+ (-0.0012066307346717325) [X0 Z1 Z2 Z3 Z5 Z6 Z7 X8]
+ (-0.0012066307346717325) [Y1 Z2 Z3 Z4 Z6 Z7 Z8 Y9]
+ (-0.0012066307346717325) [X1 Z2 Z3 Z4 Z6 Z7 Z8 X9]
+ (0.0027752432295770624) [Y3 Z4 Z5 Z6 Z7 Z8 Z9 Y11]
+ (0.0027752432295770624) [X3 Z4 Z5 Z6 Z7 Z8 Z9 X11]
+ (0.0034423104286246888) [Y3 X4 X5 Z6 Z7 Z8 Z9 Y10]
+ (0.0034423104286246888) [X3 Y4 Y5 Z6 Z7 Z8 Z9 X10]
+ (0.003442310428625455) [Y3 Z4 Z5 X6 X7 Z8 Z9 Y10]
+ (0.003442310428625455) [X3 Z4 Z5 Y6 Y7 Z8 Z9 X10]
+ (0.005275077217148104) [Y2 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (0.005275077217148104) [X2 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (0.00617460621740243) [Y0 Z2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (0.00617460621740243) [X0 Z2 Z3 Z4 Z5 Z6 Z7 X8]
+ (0.006602236940774411) [Y2 Z3 Z4 Z5 Z6 Z7 Z8 Y10]
+ (0.006602236940774411) [X2 Z3 Z4 Z5 Z6 Z7 Z8 X10]
+ (0.006602236940774411) [Y3 Z4 Z5 Z6 Z7 Z9 Z10 Y11]
+ (0.006602236940774411) [X3 Z4 Z5 Z6 Z7 Z9 Z10 X11]
+ (0.008731968988525754) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Y9]
+ (0.008731968988525754) [X1 Z2 Z3 Z4 Z5 Z6 Z7 X9]
+ (0.011856375576763209) [Y1 Z2 Z3 X4 X5 Z6 Z7 Y8]
+ (0.011856375576763209) [X1 Z2 Z3 Y4 Y5 Z6 Z7 X8]
+ (0.01185637557676585) [Y1 Z2 Z3 Z4 Z5 X6 X7 Y8]
+ (0.01185637557676585) [X1 Z2 Z3 Z4 Z5 Y6 Y7 X8]
+ (0.011920228041661552) [Y0 Z1 Z2 Z4 Z5 Z6 Z7 Y8]
+ (0.011920228041661552) [X0 Z1 Z2 Z4 Z5 Z6 Z7 X8]
+ (0.011920228041661552) [Y1 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.011920228041661552) [X1 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.018256666724732036) [Y0 Z1 Z2 X3 X8 Z9 Z10 Y11]
```

(a)

```
+ (0.018256666724732036) [X0 Z1 Z2 Y3 Y8 Z9 Z10 X11]
+ (0.023680567519886484) [Y1 Y2 X3 Z4 Z5 Z6 Z7 X8]
+ (0.023680567519886484) [X1 X2 Y3 Z4 Z5 Z6 Z7 Y8]
+ (0.02385188956770373) [Y3 Z4 Z5 Z6 Z7 Y8 X9 X10]
+ (0.02385188956770373) [X3 Z4 Z5 Z6 Z7 X8 Y9 Y10]
+ (0.021734958492682446) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (0.021734958492682446) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8]
+ (0.021734958492682456) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.021734958492682456) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.057334496865382736) [Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.057334496865382736) [X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.05733449686538275) [Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (0.05733449686538275) [X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.02385188956770373) [Y2 Z3 Z4 Z5 Z6 Z7 Y8 Y9 Z10 Y11]
+ (-0.02385188956770373) [Y2 Z3 Z4 Z5 Z6 Z7 Y8 X9 Z10 X11]
+ (-0.02385188956770373) [X2 Z3 Z4 Z5 Z6 Z7 X8 Y9 Z10 Y11]
+ (-0.02385188956770373) [X2 Z3 Z4 Z5 Z6 Z7 X8 X9 Z10 X11]
+ (-0.023680567519886484) [Y0 Z1 Y2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.023680567519886484) [Y0 Z1 Y2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.023680567519886484) [X0 Z1 X2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.023680567519886484) [X0 Z1 X2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.009617086913811433) [Z0 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.009617086913811433) [Z0 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.009617086913811433) [Z1 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.009617086913811433) [Z1 X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.004765488168276582) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z10]
+ (-0.004765488168276582) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z10]
+ (-0.004765488168276582) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 Z11]
+ (-0.004765488168276582) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 Z11]
+ (0.0014611357429220274) [Z0 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.0014611357429220274) [Z0 X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.0014611357429220274) [Z1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (0.0014611357429220274) [Z1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (0.0027752432295770624) [Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10 Z11]
+ (0.0027752432295770624) [X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10 Z11]
+ (0.0034423104286246888) [Y2 Z3 Y4 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.0034423104286246888) [Y2 Z3 Y4 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.0034423104286246888) [X2 Z3 X4 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.0034423104286246888) [X2 Z3 X4 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.003442310428625455) [Y2 Z3 Z4 Z5 Y6 Y7 Z8 Z9 Z10 Y11]
+ (0.003442310428625455) [Y2 Z3 Z4 Z5 Y6 X7 Z8 Z9 Z10 X11]
+ (0.003442310428625455) [X2 Z3 Z4 Z5 X6 Y7 Z8 Z9 Z10 Y11]
+ (0.003442310428625455) [X2 Z3 Z4 Z5 X6 X7 Z8 Z9 Z10 X11]
+ (0.005275077217148104) [Z2 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.005275077217148104) [Z2 X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.00617460621740243) [Z0 Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (0.00617460621740243) [Z0 X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (0.008731968988525754) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z9]
+ (0.008731968988525754) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z9]
+ (0.009172329440504102) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z11]
```

(b)

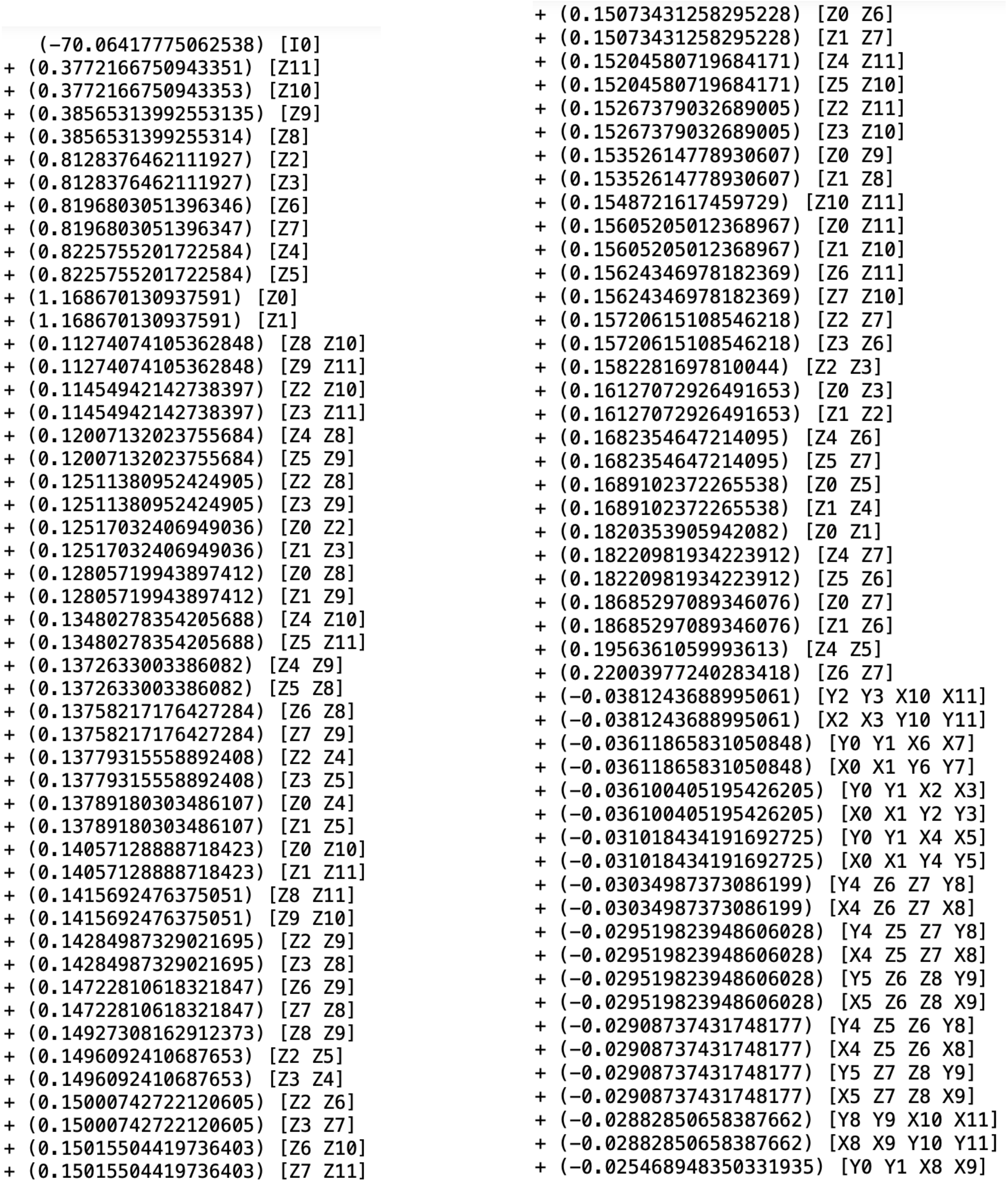
Figure A.6: qubit Hamiltonian of BeH_2 for $r_{Be-H} = 1.33\mathring{A}$. Part 3



```
+ (0.009172329440504102) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z11]
+ (0.009172329440504102) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 Z10]
+ (0.009172329440504102) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 Z10]
+ (0.01107822265673346) [Y0 X1 X3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (0.01107822265673346) [Y0 Y1 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (0.01107822265673346) [X0 X1 X3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (0.01107822265673346) [X0 Y1 Y3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (0.011856375576763209) [Y0 Z1 Z2 Z3 Y4 Y5 Z6 Z7 Z8 Y9]
+ (0.011856375576763209) [Y0 Z1 Z2 Z3 Y4 X5 Z6 Z7 Z8 X9]
+ (0.011856375576763209) [X0 Z1 Z2 Z3 X4 Y5 Z6 Z7 Z8 Y9]
+ (0.011856375576763209) [X0 Z1 Z2 Z3 X4 X5 Z6 Z7 Z8 X9]
+ (0.01185637557676585) [Y0 Z1 Z2 Z3 Z4 Z5 Y6 Y7 Z8 Y9]
+ (0.01185637557676585) [Y0 Z1 Z2 Z3 Z4 Z5 Y6 X7 Z8 X9]
+ (0.01185637557676585) [X0 Z1 Z2 Z3 Z4 Z5 X6 Y7 Z8 Y9]
+ (0.01185637557676585) [X0 Z1 Z2 Z3 Z4 Z5 X6 X7 Z8 X9]
+ (0.013937817608780677) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 X8 X10 Y11]
+ (0.013937817608780677) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Y10 Y11]
+ (0.013937817608780677) [X1 Z2 Z3 Z4 Z5 Z6 Z7 X8 X10 X11]
+ (0.013937817608780677) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Y10 X11]
+ (-0.013937817608780677) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 X10 Y11]
+ (-0.013937817608780677) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 Y10 X11]
+ (-0.011078222656733458) [Y0 X1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.011078222656733458) [X0 Y1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.011078222656733458) [Y0 Y1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.011078222656733458) [X0 X1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.013937817608780677) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 X10 X11]
+ (0.013937817608780677) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 Y10 Y11]
```

Figure A.7: qubit Hamiltonian of BeH_2 for $r_{Be-H} = 1.33\mathring{A}$. Part 4

A.3 H_2O



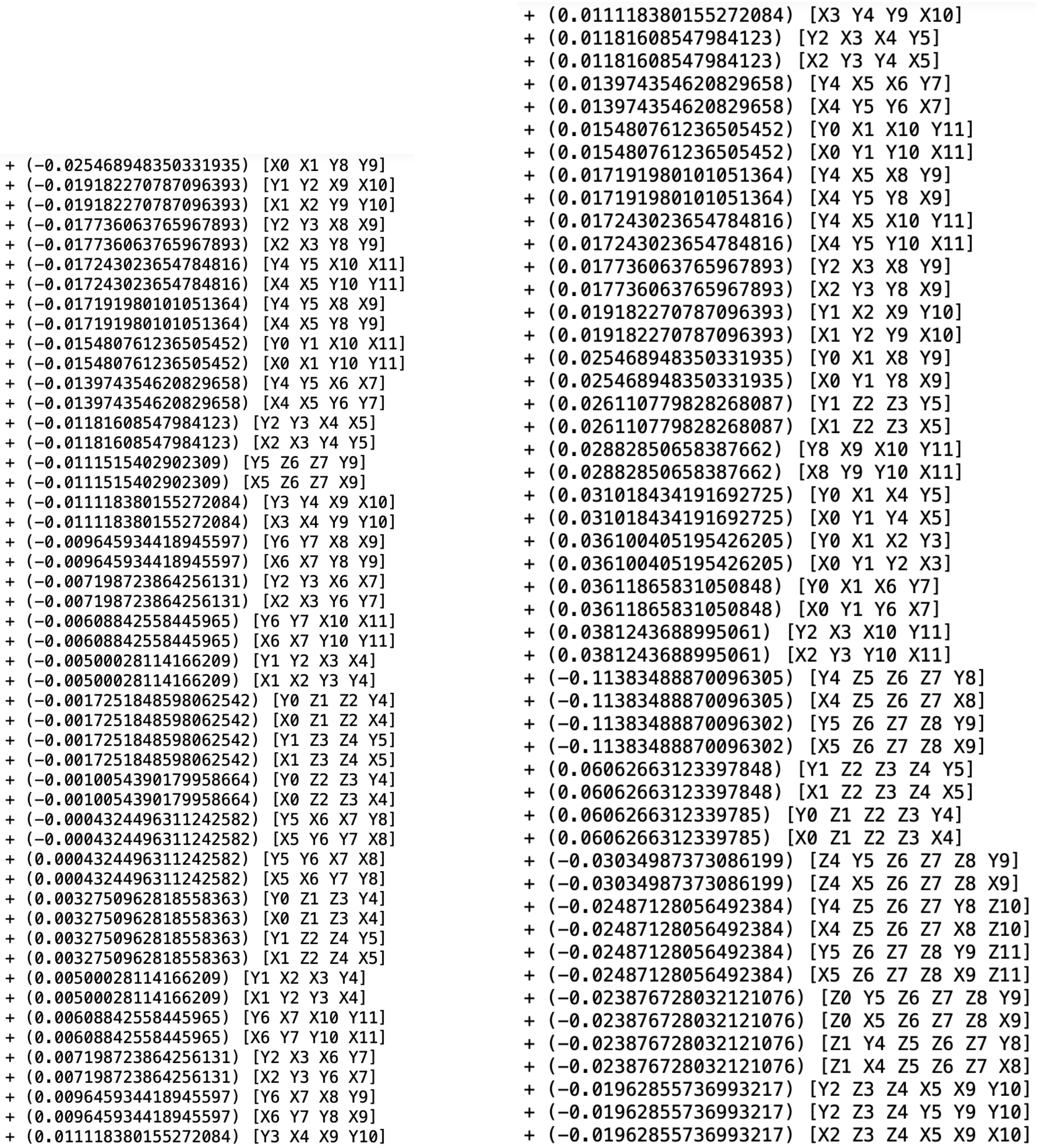
```
  (-70.06417775062538) [I0]
+ (0.3772166750943351) [Z11]
+ (0.3772166750943353) [Z10]
+ (0.38565313992553135) [Z9]
+ (0.3856531399255314) [Z8]
+ (0.8128376462111927) [Z2]
+ (0.8128376462111927) [Z3]
+ (0.8196803051396346) [Z6]
+ (0.8196803051396347) [Z7]
+ (0.8225755201722584) [Z4]
+ (0.8225755201722584) [Z5]
+ (1.168670130937591) [Z0]
+ (1.168670130937591) [Z1]
+ (0.11274074105362848) [Z8 Z10]
+ (0.11274074105362848) [Z9 Z11]
+ (0.11454942142738397) [Z2 Z10]
+ (0.11454942142738397) [Z3 Z11]
+ (0.12007132023755684) [Z4 Z8]
+ (0.12007132023755684) [Z5 Z9]
+ (0.12511380952424905) [Z2 Z8]
+ (0.12511380952424905) [Z3 Z9]
+ (0.12517032406949036) [Z0 Z2]
+ (0.12517032406949036) [Z1 Z3]
+ (0.12805719943897412) [Z0 Z8]
+ (0.12805719943897412) [Z1 Z9]
+ (0.13480278354205688) [Z4 Z10]
+ (0.13480278354205688) [Z5 Z11]
+ (0.1372633003386082) [Z4 Z9]
+ (0.1372633003386082) [Z5 Z8]
+ (0.13758217176427284) [Z6 Z8]
+ (0.13758217176427284) [Z7 Z9]
+ (0.13779315558892408) [Z2 Z4]
+ (0.13779315558892408) [Z3 Z5]
+ (0.13789180303486107) [Z0 Z4]
+ (0.13789180303486107) [Z1 Z5]
+ (0.14057128888718423) [Z0 Z10]
+ (0.14057128888718423) [Z1 Z11]
+ (0.1415692476375051) [Z8 Z11]
+ (0.1415692476375051) [Z9 Z10]
+ (0.14284987329021695) [Z2 Z9]
+ (0.14284987329021695) [Z3 Z8]
+ (0.14722810618321847) [Z6 Z9]
+ (0.14722810618321847) [Z7 Z8]
+ (0.14927308162912373) [Z8 Z9]
+ (0.1496092410687653) [Z2 Z5]
+ (0.1496092410687653) [Z3 Z4]
+ (0.15000742722120605) [Z2 Z6]
+ (0.15000742722120605) [Z3 Z7]
+ (0.15015504419736403) [Z6 Z10]
+ (0.15015504419736403) [Z7 Z11]
```

(a)

```
+ (0.15073431258295228) [Z0 Z6]
+ (0.15073431258295228) [Z1 Z7]
+ (0.15204580719684171) [Z4 Z11]
+ (0.15204580719684171) [Z5 Z10]
+ (0.15267379032689005) [Z2 Z11]
+ (0.15267379032689005) [Z3 Z10]
+ (0.15352614778930607) [Z0 Z9]
+ (0.15352614778930607) [Z1 Z8]
+ (0.154872161745 9729) [Z10 Z11]
+ (0.15605205012368967) [Z0 Z11]
+ (0.15605205012368967) [Z1 Z10]
+ (0.15624346978182369) [Z6 Z11]
+ (0.15624346978182369) [Z7 Z10]
+ (0.15720615108546218) [Z2 Z7]
+ (0.15720615108546218) [Z3 Z6]
+ (0.158228169781004 4) [Z2 Z3]
+ (0.16127072926491653) [Z0 Z3]
+ (0.16127072926491653) [Z1 Z2]
+ (0.1682354647214095) [Z4 Z6]
+ (0.1682354647214095) [Z5 Z7]
+ (0.1689102372265538) [Z0 Z5]
+ (0.1689102372265538) [Z1 Z4]
+ (0.1820353905942082) [Z0 Z1]
+ (0.18220981934223912) [Z4 Z7]
+ (0.18220981934223912) [Z5 Z6]
+ (0.18685297089346076) [Z0 Z7]
+ (0.18685297089346076) [Z1 Z6]
+ (0.1956361059993613) [Z4 Z5]
+ (0.22003977240283418) [Z6 Z7]
+ (-0.0381243688995061) [Y2 Y3 X10 X11]
+ (-0.0381243688995061) [X2 X3 Y10 Y11]
+ (-0.03611865831050848) [Y0 Y1 X6 X7]
+ (-0.03611865831050848) [X0 X1 Y6 Y7]
+ (-0.036100405195426205) [Y0 Y1 X2 X3]
+ (-0.036100405195426205) [X0 X1 Y2 Y3]
+ (-0.031018434191692725) [Y0 Y1 X4 X5]
+ (-0.031018434191692725) [X0 X1 Y4 Y5]
+ (-0.03034987373086199) [Y4 Z6 Z7 Y8]
+ (-0.03034987373086199) [X4 Z6 Z7 X8]
+ (-0.029519823948606028) [Y4 Z5 Z7 Y8]
+ (-0.029519823948606028) [X4 Z5 Z7 X8]
+ (-0.029519823948606028) [Y5 Z6 Z8 Y9]
+ (-0.029519823948606028) [X5 Z6 Z8 X9]
+ (-0.02908737431748177) [Y4 Z5 Z6 Y8]
+ (-0.02908737431748177) [X4 Z5 Z6 X8]
+ (-0.02908737431748177) [Y5 Z7 Z8 Y9]
+ (-0.02908737431748177) [X5 Z7 Z8 X9]
+ (-0.02882850658387662) [Y8 Y9 X10 X11]
+ (-0.02882850658387662) [X8 X9 Y10 Y11]
+ (-0.025468948350331935) [Y0 Y1 X8 X9]
```

(b)

Figure A.8: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958 \AA$ and $\phi = 104.5°$. Part 1



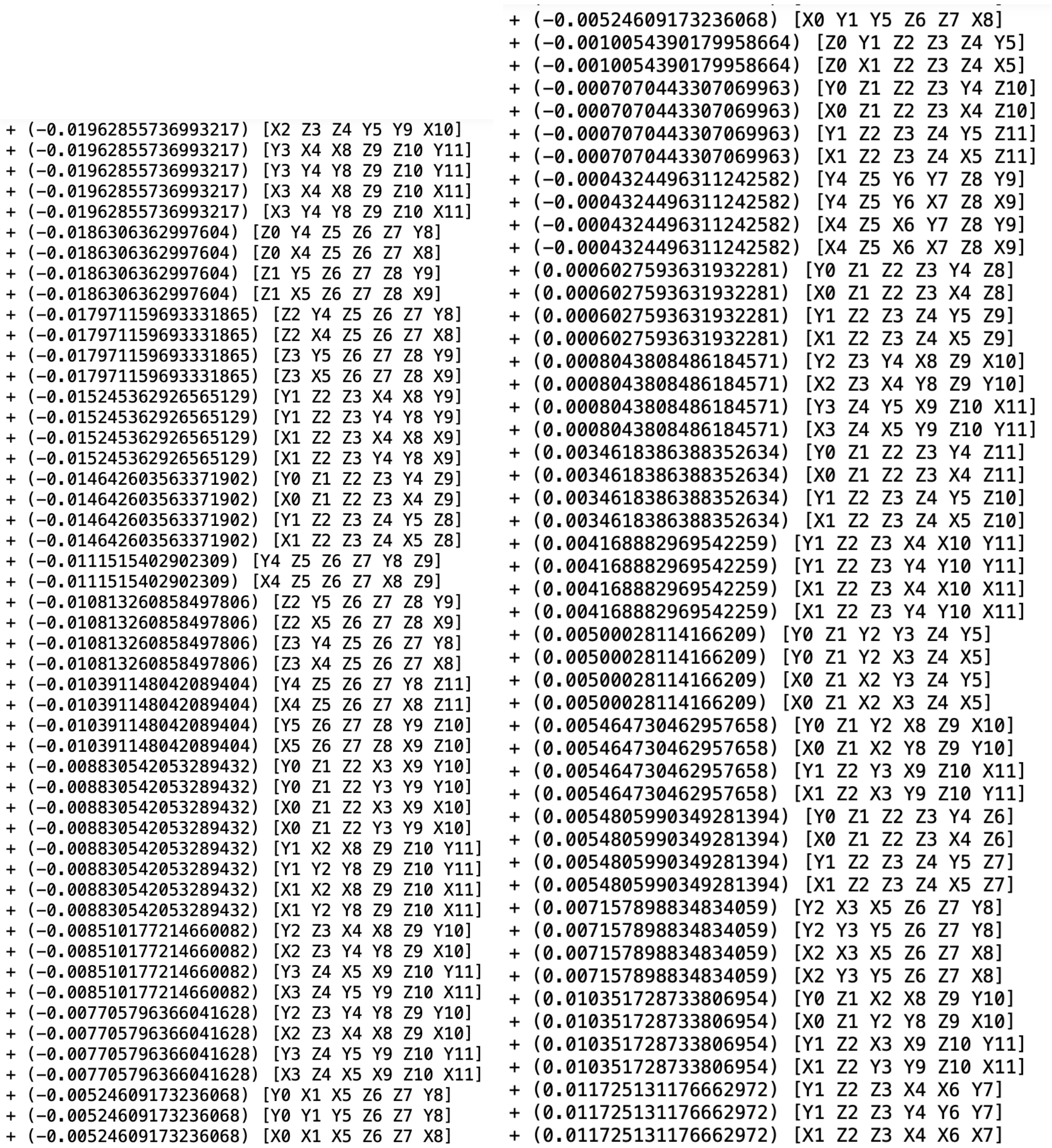
```
+ (-0.025468948350331935) [X0 X1 Y8 Y9]
+ (-0.019182270787096393) [Y1 Y2 X9 X10]
+ (-0.019182270787096393) [X1 X2 Y9 Y10]
+ (-0.017736063765967893) [Y2 Y3 X8 X9]
+ (-0.017736063765967893) [X2 X3 Y8 Y9]
+ (-0.017243023654784816) [Y4 Y5 X10 X11]
+ (-0.017243023654784816) [X4 X5 Y10 Y11]
+ (-0.017191980101051364) [Y4 Y5 X8 X9]
+ (-0.017191980101051364) [X4 X5 Y8 Y9]
+ (-0.015480761236505452) [Y0 Y1 X10 X11]
+ (-0.015480761236505452) [X0 X1 Y10 Y11]
+ (-0.013974354620829658) [Y4 Y5 X6 X7]
+ (-0.013974354620829658) [X4 X5 Y6 Y7]
+ (-0.01181608547984123) [Y2 Y3 X4 X5]
+ (-0.01181608547984123) [X2 X3 Y4 Y5]
+ (-0.0111515402902309) [Y5 Z6 Z7 Y9]
+ (-0.0111515402902309) [X5 Z6 Z7 X9]
+ (-0.011118380155272084) [Y3 Y4 X9 X10]
+ (-0.011118380155272084) [X3 X4 Y9 Y10]
+ (-0.009645934418945597) [Y6 Y7 X8 X9]
+ (-0.009645934418945597) [X6 X7 Y8 Y9]
+ (-0.007198723864256131) [Y2 Y3 X6 X7]
+ (-0.007198723864256131) [X2 X3 Y6 Y7]
+ (-0.00608842558445965) [Y6 Y7 X10 X11]
+ (-0.00608842558445965) [X6 X7 Y10 Y11]
+ (-0.00500028114166209) [Y1 Y2 X3 X4]
+ (-0.00500028114166209) [X1 X2 Y3 Y4]
+ (-0.0017251848598062542) [Y0 Z1 Z2 Y4]
+ (-0.0017251848598062542) [X0 Z1 Z2 X4]
+ (-0.0017251848598062542) [Y1 Z3 Z4 Y5]
+ (-0.0017251848598062542) [X1 Z3 Z4 X5]
+ (-0.0010054390179958664) [Y0 Z2 Z3 Y4]
+ (-0.0010054390179958664) [X0 Z2 Z3 X4]
+ (-0.0004324496311242582) [Y5 X6 X7 Y8]
+ (-0.0004324496311242582) [X5 Y6 Y7 X8]
+ (0.0004324496311242582) [Y5 Y6 X7 X8]
+ (0.0004324496311242582) [X5 X6 Y7 Y8]
+ (0.0032750962818558363) [Y0 Z1 Z3 Y4]
+ (0.0032750962818558363) [X0 Z1 Z3 X4]
+ (0.0032750962818558363) [Y1 Z2 Z4 Y5]
+ (0.0032750962818558363) [X1 Z2 Z4 X5]
+ (0.00500028114166209) [Y1 X2 X3 Y4]
+ (0.00500028114166209) [X1 Y2 Y3 X4]
+ (0.00608842558445965) [Y6 X7 X10 Y11]
+ (0.00608842558445965) [X6 Y7 Y10 X11]
+ (0.007198723864256131) [Y2 X3 X6 Y7]
+ (0.007198723864256131) [X2 Y3 Y6 X7]
+ (0.009645934418945597) [Y6 X7 X8 Y9]
+ (0.009645934418945597) [X6 Y7 Y8 X9]
+ (0.011118380155272084) [Y3 X4 X9 Y10]
```

(a)

```
+ (0.011118380155272084) [X3 Y4 Y9 X10]
+ (0.01181608547984123) [Y2 X3 X4 Y5]
+ (0.01181608547984123) [X2 Y3 Y4 X5]
+ (0.013974354620829658) [Y4 X5 X6 Y7]
+ (0.013974354620829658) [X4 Y5 Y6 X7]
+ (0.015480761236505452) [Y0 X1 X10 Y11]
+ (0.015480761236505452) [X0 Y1 Y10 X11]
+ (0.017191980101051364) [Y4 X5 X8 Y9]
+ (0.017191980101051364) [X4 Y5 Y8 X9]
+ (0.017243023654784816) [Y4 X5 X10 Y11]
+ (0.017243023654784816) [X4 Y5 Y10 X11]
+ (0.017736063765967893) [Y2 X3 X8 Y9]
+ (0.017736063765967893) [X2 Y3 Y8 X9]
+ (0.019182270787096393) [Y1 X2 X9 Y10]
+ (0.019182270787096393) [X1 Y2 Y9 X10]
+ (0.025468948350331935) [Y0 X1 X8 Y9]
+ (0.025468948350331935) [X0 Y1 Y8 X9]
+ (0.026110779828268087) [Y1 Z2 Z3 Y5]
+ (0.026110779828268087) [X1 Z2 Z3 X5]
+ (0.02882850658387662) [Y8 X9 X10 Y11]
+ (0.02882850658387662) [X8 Y9 Y10 X11]
+ (0.031018434191692725) [Y0 X1 X4 Y5]
+ (0.031018434191692725) [X0 Y1 Y4 X5]
+ (0.036100405195426205) [Y0 X1 X2 Y3]
+ (0.036100405195426205) [X0 Y1 Y2 X3]
+ (0.03611865831050848) [Y0 X1 X6 Y7]
+ (0.03611865831050848) [X0 Y1 Y6 X7]
+ (0.0381243688995061) [Y2 X3 X10 Y11]
+ (0.0381243688995061) [X2 Y3 Y10 X11]
+ (-0.11383488870096305) [Y4 Z5 Z6 Z7 Y8]
+ (-0.11383488870096305) [X4 Z5 Z6 Z7 X8]
+ (-0.11383488870096302) [Y5 Z6 Z7 Z8 Y9]
+ (-0.11383488870096302) [X5 Z6 Z7 Z8 X9]
+ (0.06062663123397848) [Y1 Z2 Z3 Z4 Y5]
+ (0.06062663123397848) [X1 Z2 Z3 Z4 X5]
+ (0.0606266312339785) [Y0 Z1 Z2 Z3 Y4]
+ (0.0606266312339785) [X0 Z1 Z2 Z3 X4]
+ (-0.03034987373086199) [Z4 Y5 Z6 Z7 Z8 Y9]
+ (-0.03034987373086199) [Z4 X5 Z6 Z7 Z8 X9]
+ (-0.02487128056492384) [Y4 Z5 Z6 Z7 Y8 Z10]
+ (-0.02487128056492384) [X4 Z5 Z6 Z7 X8 Z10]
+ (-0.02487128056492384) [Y5 Z6 Z7 Z8 Y9 Z11]
+ (-0.02487128056492384) [X5 Z6 Z7 Z8 X9 Z11]
+ (-0.023876728032121076) [Z0 Y5 Z6 Z7 Z8 Y9]
+ (-0.023876728032121076) [Z0 X5 Z6 Z7 Z8 X9]
+ (-0.023876728032121076) [Z1 Y4 Z5 Z6 Z7 Y8]
+ (-0.023876728032121076) [Z1 X4 Z5 Z6 Z7 X8]
+ (-0.01962855736993217) [Y2 Z3 Z4 X5 X9 Y10]
+ (-0.01962855736993217) [Y2 Z3 Z4 Y5 Y9 Y10]
+ (-0.01962855736993217) [X2 Z3 Z4 X5 X9 X10]
```

(b)

Figure A.9: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$. Part 2



```
+ (-0.01962855736993217) [X2 Z3 Z4 Y5 Y9 X10]
+ (-0.01962855736993217) [Y3 X4 X8 Z9 Z10 Y11]
+ (-0.01962855736993217) [Y3 Y4 Y8 Z9 Z10 Y11]
+ (-0.01962855736993217) [X3 X4 X8 Z9 Z10 X11]
+ (-0.01962855736993217) [X3 Y4 Y8 Z9 Z10 X11]
+ (-0.0186306362997604) [Z0 Y4 Z5 Z6 Z7 Y8]
+ (-0.0186306362997604) [Z0 X4 Z5 Z6 Z7 X8]
+ (-0.0186306362997604) [Z1 Y5 Z6 Z7 Z8 Y9]
+ (-0.0186306362997604) [Z1 X5 Z6 Z7 Z8 X9]
+ (-0.017971159693331865) [Z2 Y4 Z5 Z6 Z7 Y8]
+ (-0.017971159693331865) [Z2 X4 Z5 Z6 Z7 X8]
+ (-0.017971159693331865) [Z3 Y5 Z6 Z7 Z8 Y9]
+ (-0.017971159693331865) [Z3 X5 Z6 Z7 Z8 X9]
+ (-0.015245362926565129) [Y1 Z2 Z3 X4 X8 Y9]
+ (-0.015245362926565129) [Y1 Z2 Z3 Y4 Y8 Y9]
+ (-0.015245362926565129) [X1 Z2 Z3 X4 X8 X9]
+ (-0.015245362926565129) [X1 Z2 Z3 Y4 Y8 X9]
+ (-0.014642603563371902) [Y0 Z1 Z2 Z3 Y4 Z9]
+ (-0.014642603563371902) [X0 Z1 Z2 Z3 X4 Z9]
+ (-0.014642603563371902) [Y1 Z2 Z3 Z4 Y5 Z8]
+ (-0.014642603563371902) [X1 Z2 Z3 Z4 X5 Z8]
+ (-0.0111515402902309) [Y4 Z5 Z6 Z7 Y8 Z9]
+ (-0.0111515402902309) [X4 Z5 Z6 Z7 X8 Z9]
+ (-0.010813260858497806) [Z2 Y5 Z6 Z7 Z8 Y9]
+ (-0.010813260858497806) [Z2 X5 Z6 Z7 Z8 X9]
+ (-0.010813260858497806) [Z3 Y4 Z5 Z6 Z7 Y8]
+ (-0.010813260858497806) [Z3 X4 Z5 Z6 Z7 X8]
+ (-0.010391148042089404) [Y4 Z5 Z6 Z7 Y8 Z11]
+ (-0.010391148042089404) [X4 Z5 Z6 Z7 X8 Z11]
+ (-0.010391148042089404) [Y5 Z6 Z7 Z8 Y9 Z10]
+ (-0.010391148042089404) [X5 Z6 Z7 Z8 X9 Z10]
+ (-0.008830542053289432) [Y0 Z1 Z2 X3 X9 Y10]
+ (-0.008830542053289432) [Y0 Z1 Z2 Y3 Y9 Y10]
+ (-0.008830542053289432) [X0 Z1 Z2 X3 X9 X10]
+ (-0.008830542053289432) [X0 Z1 Z2 Y3 Y9 X10]
+ (-0.008830542053289432) [Y1 X2 X8 Z9 Z10 Y11]
+ (-0.008830542053289432) [Y1 Y2 Y8 Z9 Z10 Y11]
+ (-0.008830542053289432) [X1 X2 X8 Z9 Z10 X11]
+ (-0.008830542053289432) [X1 Y2 Y8 Z9 Z10 X11]
+ (-0.008510177214660082) [Y2 Z3 X4 X8 Z9 Y10]
+ (-0.008510177214660082) [X2 Z3 Y4 Y8 Z9 X10]
+ (-0.008510177214660082) [Y3 Z4 X5 X9 Z10 Y11]
+ (-0.008510177214660082) [X3 Z4 Y5 Y9 Z10 X11]
+ (-0.007705796366041628) [Y2 Z3 Y4 Y8 Z9 Y10]
+ (-0.007705796366041628) [X2 Z3 X4 X8 Z9 X10]
+ (-0.007705796366041628) [Y3 Z4 Y5 Y9 Z10 Y11]
+ (-0.007705796366041628) [X3 Z4 X5 X9 Z10 X11]
+ (-0.00524609173236068) [Y0 X1 X5 Z6 Z7 Y8]
+ (-0.00524609173236068) [Y0 Y1 Y5 Z6 Z7 Y8]
+ (-0.00524609173236068) [X0 X1 X5 Z6 Z7 X8]
```

```
+ (-0.00524609173236068) [X0 Y1 Y5 Z6 Z7 X8]
+ (-0.0010054390179958664) [Z0 Y1 Z2 Z3 Z4 Y5]
+ (-0.0010054390179958664) [Z0 X1 Z2 Z3 Z4 X5]
+ (-0.0007070443307069963) [Y0 Z1 Z2 Z3 Y4 Z10]
+ (-0.0007070443307069963) [X0 Z1 Z2 Z3 X4 Z10]
+ (-0.0007070443307069963) [Y1 Z2 Z3 Z4 Y5 Z11]
+ (-0.0007070443307069963) [X1 Z2 Z3 Z4 X5 Z11]
+ (-0.0004324496311242582) [Y4 Z5 Y6 Y7 Z8 Y9]
+ (-0.0004324496311242582) [Y4 Z5 Y6 X7 Z8 X9]
+ (-0.0004324496311242582) [X4 Z5 X6 Y7 Z8 Y9]
+ (-0.0004324496311242582) [X4 Z5 X6 X7 Z8 X9]
+ (0.0006027593631932281) [Y0 Z1 Z2 Z3 Y4 Z8]
+ (0.0006027593631932281) [X0 Z1 Z2 Z3 X4 Z8]
+ (0.0006027593631932281) [Y1 Z2 Z3 Z4 Y5 Z9]
+ (0.0006027593631932281) [X1 Z2 Z3 Z4 X5 Z9]
+ (0.0008043808486184571) [Y2 Z3 Y4 X8 Z9 X10]
+ (0.0008043808486184571) [X2 Z3 X4 Y8 Z9 Y10]
+ (0.0008043808486184571) [Y3 Z4 Y5 X9 Z10 X11]
+ (0.0008043808486184571) [X3 Z4 X5 Y9 Z10 Y11]
+ (0.0034618386388352634) [Y0 Z1 Z2 Z3 Y4 Z11]
+ (0.0034618386388352634) [X0 Z1 Z2 Z3 X4 Z11]
+ (0.0034618386388352634) [Y1 Z2 Z3 Z4 Y5 Z10]
+ (0.0034618386388352634) [X1 Z2 Z3 Z4 X5 Z10]
+ (0.004168882969542259) [Y1 Z2 Z3 X4 X10 Y11]
+ (0.004168882969542259) [Y1 Z2 Z3 Y4 Y10 Y11]
+ (0.004168882969542259) [X1 Z2 Z3 X4 X10 X11]
+ (0.004168882969542259) [X1 Z2 Z3 Y4 Y10 X11]
+ (0.00500028114166209) [Y0 Z1 Y2 Y3 Z4 Y5]
+ (0.00500028114166209) [Y0 Z1 Y2 X3 Z4 X5]
+ (0.00500028114166209) [X0 Z1 X2 Y3 Z4 Y5]
+ (0.00500028114166209) [X0 Z1 X2 X3 Z4 X5]
+ (0.005464730462957658) [Y0 Z1 Y2 X8 Z9 X10]
+ (0.005464730462957658) [X0 Z1 X2 Y8 Z9 Y10]
+ (0.005464730462957658) [Y1 Z2 Y3 X9 Z10 X11]
+ (0.005464730462957658) [X1 Z2 X3 Y9 Z10 Y11]
+ (0.0054805990349281394) [Y0 Z1 Z2 Z3 Y4 Z6]
+ (0.0054805990349281394) [X0 Z1 Z2 Z3 X4 Z6]
+ (0.0054805990349281394) [Y1 Z2 Z3 Z4 Y5 Z7]
+ (0.0054805990349281394) [X1 Z2 Z3 Z4 X5 Z7]
+ (0.007157898834834059) [Y2 X3 X5 Z6 Z7 Y8]
+ (0.007157898834834059) [Y2 Y3 Y5 Z6 Z7 Y8]
+ (0.007157898834834059) [X2 X3 X5 Z6 Z7 X8]
+ (0.007157898834834059) [X2 Y3 Y5 Z6 Z7 X8]
+ (0.010351728733806954) [Y0 Z1 X2 X8 Z9 Y10]
+ (0.010351728733806954) [X0 Z1 Y2 Y8 Z9 X10]
+ (0.010351728733806954) [Y1 Z2 X3 X9 Z10 Y11]
+ (0.010351728733806954) [X1 Z2 Y3 Y9 Z10 X11]
+ (0.011725131176662972) [Y1 Z2 Z3 X4 X6 Y7]
+ (0.011725131176662972) [Y1 Z2 Z3 Y4 Y6 Y7]
+ (0.011725131176662972) [X1 Z2 Z3 X4 X6 X7]
```

(a) (b)

Figure A.10: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$. Part 3

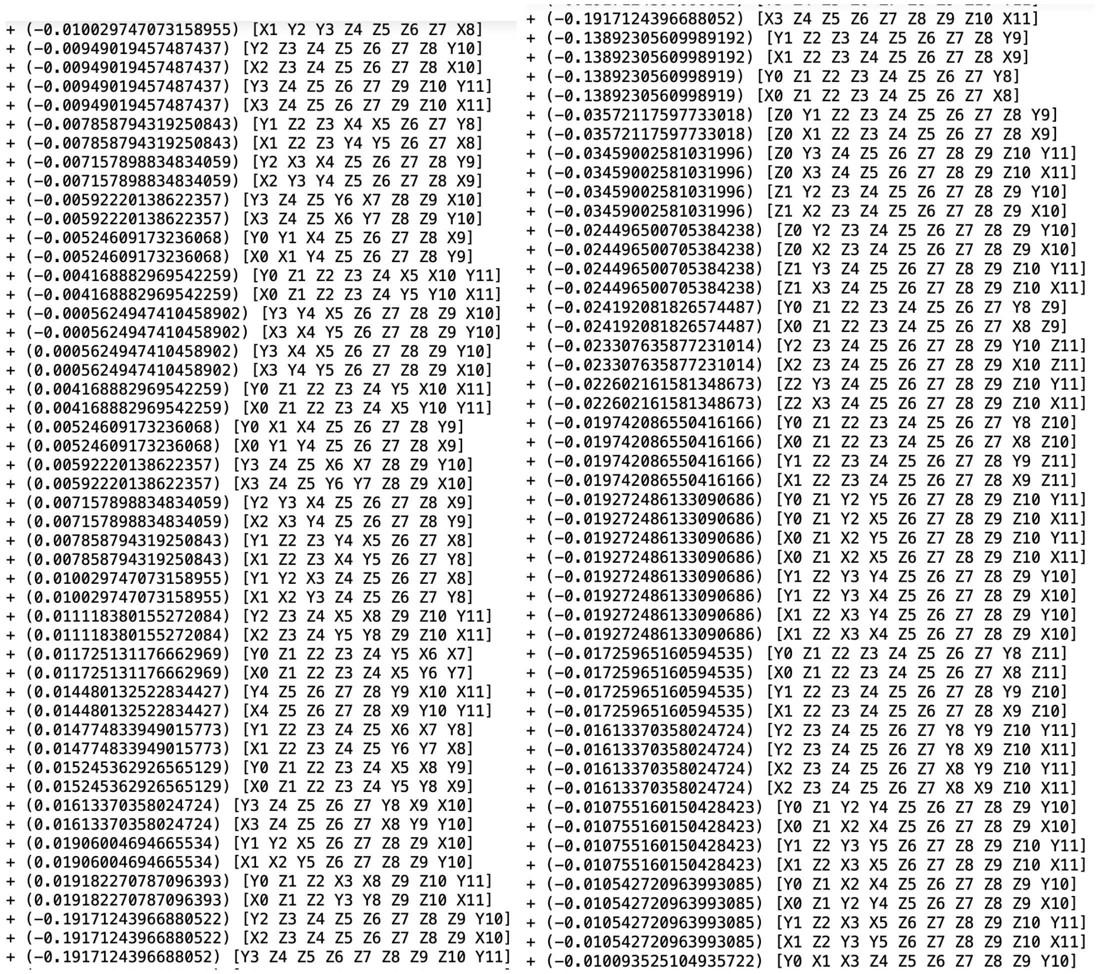
```
+ (0.011725131176662972) [X1 Z2 Z3 Y4 Y6 X7]
+ (0.011922761003890543) [Y2 Z3 Y4 Y9 Z10 Y11]
+ (0.011922761003890543) [Y2 Z3 Y4 X9 Z10 X11]
+ (0.011922761003890543) [X2 Z3 X4 Y9 Z10 Y11]
+ (0.011922761003890543) [X2 Z3 X4 X9 Z10 X11]
+ (0.011922761003890543) [Y3 Z4 Y5 Y8 Z9 Y10]
+ (0.011922761003890543) [Y3 Z4 Y5 X8 Z9 X10]
+ (0.011922761003890543) [X3 Z4 X5 Y8 Z9 Y10]
+ (0.011922761003890543) [X3 Z4 X5 X8 Z9 X10]
+ (0.01448013252283442 7) [Y5 Z6 Z7 X8 X10 Y11]
+ (0.014480132522834427) [Y5 Z6 Z7 Y8 Y10 Y11]
+ (0.014480132522834427) [X5 Z6 Z7 X8 X10 X11]
+ (0.014480132522834427) [X5 Z6 Z7 Y8 Y10 X11]
+ (0.015816459196764627) [Y0 Z1 Y2 Y8 Z9 Y10]
+ (0.015816459196764627) [X0 Z1 X2 X8 Z9 X10]
+ (0.015816459196764627) [Y1 Z2 Y3 Y9 Z10 Y11]
+ (0.015816459196764627) [X1 Z2 X3 X9 Z10 X11]
+ (0.01720573021159111) [Y0 Z1 Z2 Z3 Y4 Z7]
+ (0.01720573021159111) [X0 Z1 Z2 Z3 X4 Z7]
+ (0.01720573021159111) [Y1 Z2 Z3 Z4 Y5 Z6]
+ (0.01720573021159111) [X1 Z2 Z3 Z4 X5 Z6]
+ (0.024647001250054052) [Y0 Z1 Y2 Y9 Z10 Y11]
+ (0.024647001250054052) [Y0 Z1 Y2 X9 Z10 X11]
+ (0.024647001250054052) [X0 Z1 X2 Y9 Z10 Y11]
+ (0.024647001250054052) [X0 Z1 X2 X9 Z10 X11]
+ (0.024647001250054052) [Y1 Z2 Y3 Y8 Z9 Y10]
+ (0.024647001250054052) [Y1 Z2 Y3 X8 Z9 X10]
+ (0.024647001250054052) [X1 Z2 X3 Y8 Z9 Y10]
+ (0.024647001250054052) [X1 Z2 X3 X8 Z9 X10]
+ (0.026110779828268087) [Y0 Z1 Z2 Z3 Y4 Z5]
+ (0.026110779828268087) [X0 Z1 Z2 Z3 X4 Z5]
+ (-0.04746184628720327) [Y2 Z3 Z4 Z5 Z6 Z8 Z9 Y10]
+ (-0.04746184628720327) [X2 Z3 Z4 Z5 Z6 Z8 Z9 X10]
+ (-0.04746184628720327) [Y3 Z4 Z5 Z7 Z8 Z9 Z10 Y11]
+ (-0.04746184628720327) [X3 Z4 Z5 Z7 Z8 Z9 Z10 X11]
+ (-0.0415396449009797) [Y2 Z3 Z4 Z5 Z7 Z8 Z9 Y10]
+ (-0.0415396449009797) [X2 Z3 Z4 Z5 Z7 Z8 Z9 X10]
+ (-0.0415396449009797) [Y3 Z4 Z5 Z6 Z8 Z9 Z10 Y11]
+ (-0.0415396449009797) [X3 Z4 Z5 Z6 Z8 Z9 Z10 X11]
+ (-0.040003242085140216) [Y2 Z3 Z4 Z6 Z7 Z8 Z9 Y10]
+ (-0.040003242085140216) [X2 Z3 Z4 Z6 Z7 Z8 Z9 X10]
+ (-0.040003242085140216) [Y3 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.040003242085140216) [X3 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.039639044234569126) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Y8]
+ (-0.039639044234569126) [X0 Z1 Z2 Z3 Z4 Z5 Z6 X8]
+ (-0.039639044234569126) [Y1 Z2 Z3 Z4 Z5 Z7 Z8 Y9]
+ (-0.039639044234569126) [X1 Z2 Z3 Z4 Z5 Z7 Z8 X9]
+ (-0.03944074734409432) [Y2 Z3 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.03944074734409432) [X2 Z3 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.03944074734409432) [Y3 Z4 Z6 Z7 Z8 Z9 Z10 Y11]
```

(a)

```
+ (-0.03944074734409432) [X3 Z4 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.03572117597733019) [Y0 Z2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (-0.03572117597733019) [X0 Z2 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.029899223004069476) [Y0 Z1 Z2 Z3 Z5 Z6 Z7 Y8]
+ (-0.029899223004069476) [X0 Z1 Z2 Z3 Z5 Z6 Z7 X8]
+ (-0.029899223004069476) [Y1 Z2 Z3 Z4 Z6 Z7 Z8 Y9]
+ (-0.029899223004069476) [X1 Z2 Z3 Z4 Z6 Z7 Z8 X9]
+ (-0.028991270537916804) [Y0 Z1 Z3 Z4 Z5 Z6 Z7 Y8]
+ (-0.028991270537916804) [X0 Z1 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.028991270537916804) [Y1 Z2 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.028991270537916804) [X1 Z2 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.025623898155121602) [Y2 Z3 Z4 Z5 Z6 Z7 Z9 Y10]
+ (-0.025623898155121602) [X2 Z3 Z4 Z5 Z6 Z7 Z9 X10]
+ (-0.025623898155121602) [Y3 Z4 Z5 Z6 Z7 Z8 Z10 Y11]
+ (-0.025623898155121602) [X3 Z4 Z5 Z6 Z7 Z8 Z10 X11]
+ (-0.024864210285553356) [Y0 Z1 Z2 Z3 Z4 Z5 Z7 Y8]
+ (-0.024864210285553356) [X0 Z1 Z2 Z3 Z4 Z5 Z7 X8]
+ (-0.024864210285553356) [Y1 Z2 Z3 Z4 Z5 Z6 Z8 Y9]
+ (-0.024864210285553356) [X1 Z2 Z3 Z4 Z5 Z6 Z8 X9]
+ (-0.024192081826574487) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Y9]
+ (-0.024192081826574487) [X1 Z2 Z3 Z4 Z5 Z6 Z7 X9]
+ (-0.02330763587723101) [Y3 Z4 Z5 Z6 Z7 Z8 Z9 Y11]
+ (-0.02330763587723101) [X3 Z4 Z5 Z6 Z7 Z8 Z9 X11]
+ (-0.022602161581348673) [Y2 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.022602161581348673) [X2 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.02204042868481864) [Y0 Z1 Z2 Z3 Z4 Z6 Z7 Y8]
+ (-0.02204042868481864) [X0 Z1 Z2 Z3 Z4 Z6 Z7 X8]
+ (-0.02204042868481864) [Y1 Z2 Z3 Z5 Z6 Z7 Z8 Y9]
+ (-0.02204042868481864) [X1 Z2 Z3 Z5 Z6 Z7 Z8 X9]
+ (-0.019182270787096393) [Y0 Z1 Z2 Y3 X8 Z9 Z10 X11]
+ (-0.019182270787096393) [X0 Z1 Z2 X3 Y8 Z9 Z10 Y11]
+ (-0.01906004694665534) [Y1 X2 X5 Z6 Z7 Z8 Z9 Y10]
+ (-0.01906004694665534) [X1 Y2 Y5 Z6 Z7 Z8 Z9 X10]
+ (-0.018961523464757848) [Y0 Z1 Z2 Z4 Z5 Z6 Z7 Y8]
+ (-0.018961523464757848) [X0 Z1 Z2 Z4 Z5 Z6 Z7 X8]
+ (-0.018961523464757848) [Y1 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.018961523464757848) [X1 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.01613370358024724) [Y3 Z4 Z5 Z6 Z7 X8 X9 Y10]
+ (-0.01613370358024724) [X3 Z4 Z5 Z6 Z7 Y8 Y9 X10]
+ (-0.015245362926565129) [Y0 Z1 Z2 Z3 Z4 Y5 X8 X9]
+ (-0.015245362926565129) [X0 Z1 Z2 Z3 Z4 X5 Y8 Y9]
+ (-0.014774833949015773) [Y1 Z2 Z3 Z4 Z5 Y6 X7 X8]
+ (-0.014774833949015773) [X1 Z2 Z3 Z4 Z5 X6 Y7 Y8]
+ (-0.014480132522834427) [Y4 Z5 Z6 Z7 Z8 X9 X10 Y11]
+ (-0.014480132522834427) [X4 Z5 Z6 Z7 Z8 Y9 Y10 X11]
+ (-0.011725131176662969) [Y0 Z1 Z2 Z3 Z4 X5 X6 Y7]
+ (-0.011725131176662969) [X0 Z1 Z2 Z3 Z4 Y5 Y6 X7]
+ (-0.011118380155272084) [Y2 Z3 Z4 Y5 X8 Z9 Z10 X11]
+ (-0.011118380155272084) [X2 Z3 Z4 X5 Y8 Z9 Z10 Y11]
+ (-0.010029747073158955) [Y1 X2 X3 Z4 Z5 Z6 Z7 Y8]
```

(b)

Figure A.11: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$. Part 4



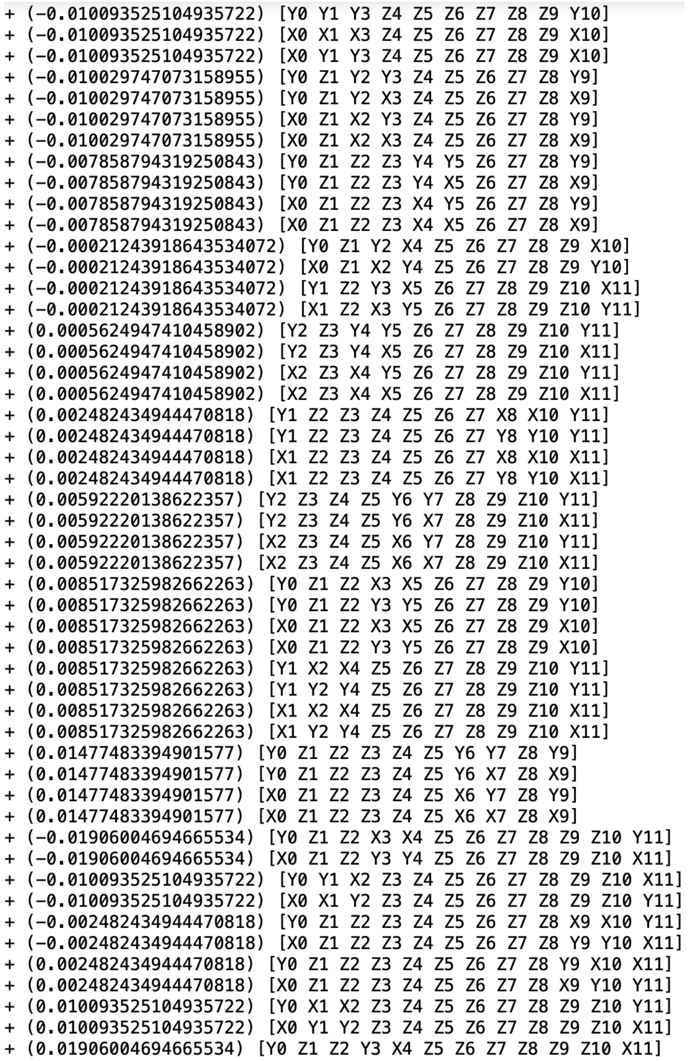
```
+ (-0.010029747073158955) [X1 Y2 Y3 Z4 Z5 Z6 Z7 X8]
+ (-0.00949019457487437) [Y2 Z3 Z4 Z5 Z6 Z7 Z8 Y10]
+ (-0.00949019457487437) [X2 Z3 Z4 Z5 Z6 Z7 Z8 X10]
+ (-0.00949019457487437) [Y3 Z4 Z5 Z6 Z7 Z9 Z10 Y11]
+ (-0.00949019457487437) [X3 Z4 Z5 Z6 Z7 Z9 Z10 X11]
+ (-0.007858794319250843) [Y1 Z2 Z3 X4 X5 Z6 Z7 Y8]
+ (-0.007858794319250843) [X1 Z2 Z3 Y4 Y5 Z6 Z7 X8]
+ (-0.007157898834834059) [Y2 X3 X4 Z5 Z6 Z7 Z8 Y9]
+ (-0.007157898834834059) [X2 Y3 Y4 Z5 Z6 Z7 Z8 X9]
+ (-0.00592220138622357) [Y3 Z4 Z5 Y6 X7 Z8 Z9 X10]
+ (-0.00592220138622357) [X3 Z4 Z5 X6 Y7 Z8 Z9 Y10]
+ (-0.00524609173236068) [Y0 Y1 X4 Z5 Z6 Z7 Z8 X9]
+ (-0.00524609173236068) [X0 X1 Y4 Z5 Z6 Z7 Z8 Y9]
+ (-0.004168882969542259) [Y0 Z1 Z2 Z3 Z4 X5 X10 Y11]
+ (-0.004168882969542259) [X0 Z1 Z2 Z3 Z4 Y5 Y10 X11]
+ (-0.0005624947410458902) [Y3 Y4 X5 Z6 Z7 Z8 Z9 X10]
+ (-0.0005624947410458902) [X3 X4 Y5 Z6 Z7 Z8 Z9 Y10]
+ (0.0005624947410458902) [Y3 X4 X5 Z6 Z7 Z8 Z9 Y10]
+ (0.0005624947410458902) [X3 Y4 Y5 Z6 Z7 Z8 Z9 X10]
+ (0.004168882969542259) [Y0 Z1 Z2 Z3 Z4 Y5 X10 X11]
+ (0.004168882969542259) [X0 Z1 Z2 Z3 Z4 X5 Y10 Y11]
+ (0.00524609173236068) [Y0 X1 X4 Z5 Z6 Z7 Z8 Y9]
+ (0.00524609173236068) [X0 Y1 Y4 Z5 Z6 Z7 Z8 X9]
+ (0.00592220138622357) [Y3 Z4 Z5 X6 X7 Z8 Z9 Y10]
+ (0.00592220138622357) [X3 Z4 Z5 Y6 Y7 Z8 Z9 X10]
+ (0.007157898834834059) [Y2 Y3 X4 Z5 Z6 Z7 Z8 X9]
+ (0.007157898834834059) [X2 X3 Y4 Z5 Z6 Z7 Z8 Y9]
+ (0.007858794319250843) [Y1 Z2 Z3 Y4 X5 Z6 Z7 X8]
+ (0.007858794319250843) [X1 Z2 Z3 X4 Y5 Z6 Z7 Y8]
+ (0.010029747073158955) [Y1 Y2 X3 Z4 Z5 Z6 Z7 X8]
+ (0.010029747073158955) [X1 X2 Y3 Z4 Z5 Z6 Z7 Y8]
+ (0.011118380155272084) [Y2 Z3 Z4 X5 X8 Z9 Z10 Y11]
+ (0.011118380155272084) [X2 Z3 Z4 Y5 Y8 Z9 Z10 X11]
+ (0.011725131176662969) [Y0 Z1 Z2 Z3 Z4 Y5 X6 X7]
+ (0.011725131176662969) [X0 Z1 Z2 Z3 Z4 X5 Y6 Y7]
+ (0.014480132522834427) [Y4 Z5 Z6 Z7 Z8 Y9 X10 X11]
+ (0.014480132522834427) [X4 Z5 Z6 Z7 Z8 X9 Y10 Y11]
+ (0.014774833949015773) [Y1 Z2 Z3 Z4 Z5 X6 X7 Y8]
+ (0.014774833949015773) [X1 Z2 Z3 Z4 Z5 Y6 Y7 X8]
+ (0.015245362926565129) [Y0 Z1 Z2 Z3 Z4 X5 X8 Y9]
+ (0.015245362926565129) [X0 Z1 Z2 Z3 Z4 Y5 Y8 X9]
+ (0.01613370358024724) [Y3 Z4 Z5 Z6 Z7 Y8 X9 X10]
+ (0.01613370358024724) [X3 Z4 Z5 Z6 Z7 X8 Y9 Y10]
+ (0.01906004694665534) [Y1 Y2 X5 Z6 Z7 Z8 Z9 X10]
+ (0.01906004694665534) [X1 X2 Y5 Z6 Z7 Z8 Z9 Y10]
+ (0.019182270787096393) [Y0 Z1 Z2 X3 X8 Z9 Z10 Y11]
+ (0.019182270787096393) [X0 Z1 Z2 Y3 Y8 Z9 Z10 X11]
+ (-0.19171243966880522) [Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.19171243966880522) [X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.1917124396688052) [Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
```

(a)

```
+ (-0.1917124396688052) [X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.13892305609989192) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.13892305609989192) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.1389230560998919) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8]
+ (-0.1389230560998919) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8]
+ (-0.03572117597733018) [Z0 Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.03572117597733018) [Z0 X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.03459002581031996) [Z0 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.03459002581031996) [Z0 X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.03459002581031996) [Z1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.03459002581031996) [Z1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.024496500705384238) [Z0 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.024496500705384238) [Z0 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.024496500705384238) [Z1 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.024496500705384238) [Z1 X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.024192081826574487) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z9]
+ (-0.024192081826574487) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z9]
+ (-0.023307635877231014) [Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Y10 Z11]
+ (-0.023307635877231014) [X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 X10 Z11]
+ (-0.022602161581348673) [Z2 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.022602161581348673) [Z2 X3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.019742086550416166) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z10]
+ (-0.019742086550416166) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z10]
+ (-0.019742086550416166) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 Z11]
+ (-0.019742086550416166) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 Z11]
+ (-0.019272486133090686) [Y0 Z1 Y2 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.019272486133090686) [Y0 Z1 Y2 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.019272486133090686) [X0 Z1 X2 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.019272486133090686) [X0 Z1 X2 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.019272486133090686) [Y1 Z2 Y3 Y4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.019272486133090686) [Y1 Z2 Y3 X4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.019272486133090686) [X1 Z2 X3 Y4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.019272486133090686) [X1 Z2 X3 X4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.01725965160594535) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Z11]
+ (-0.01725965160594535) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 X8 Z11]
+ (-0.01725965160594535) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 Z10]
+ (-0.01725965160594535) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 Z10]
+ (-0.01613370358024724) [Y2 Z3 Z4 Z5 Z6 Z7 Y8 Y9 Z10 Y11]
+ (-0.01613370358024724) [Y2 Z3 Z4 Z5 Z6 Z7 Y8 X9 Z10 X11]
+ (-0.01613370358024724) [X2 Z3 Z4 Z5 Z6 Z7 X8 Y9 Z10 Y11]
+ (-0.01613370358024724) [X2 Z3 Z4 Z5 Z6 Z7 X8 X9 Z10 X11]
+ (-0.010755160150428423) [Y0 Z1 Y2 Y4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.010755160150428423) [X0 Z1 X2 X4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.010755160150428423) [Y1 Z2 Y3 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.010755160150428423) [X1 Z2 X3 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.010542720963993085) [Y0 Z1 X2 X4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.010542720963993085) [X0 Z1 Y2 Y4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.010542720963993085) [Y1 Z2 X3 X5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.010542720963993085) [X1 Z2 Y3 Y5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.010093525104935722) [Y0 X1 X3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
```

(b)

Figure A.12: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$. Part 5



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+ (-0.010093525104935722) [Y0 Y1 Y3 Z4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.010093525104935722) [X0 X1 X3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.010093525104935722) [X0 Y1 Y3 Z4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.010029747073158955) [Y0 Z1 Y2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.010029747073158955) [Y0 Z1 Y2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.010029747073158955) [X0 Z1 X2 Y3 Z4 Z5 Z6 Z7 Z8 Y9]
+ (-0.010029747073158955) [X0 Z1 X2 X3 Z4 Z5 Z6 Z7 Z8 X9]
+ (-0.007858794319250843) [Y0 Z1 Z2 Z3 Y4 Y5 Z6 Z7 Z8 Y9]
+ (-0.007858794319250843) [Y0 Z1 Z2 Z3 Y4 X5 Z6 Z7 Z8 X9]
+ (-0.007858794319250843) [X0 Z1 Z2 Z3 X4 Y5 Z6 Z7 Z8 Y9]
+ (-0.007858794319250843) [X0 Z1 Z2 Z3 X4 X5 Z6 Z7 Z8 X9]
+ (-0.00021243918643534072) [Y0 Z1 Y2 X4 Z5 Z6 Z7 Z8 Z9 X10]
+ (-0.00021243918643534072) [X0 Z1 X2 Y4 Z5 Z6 Z7 Z8 Z9 Y10]
+ (-0.00021243918643534072) [Y1 Z2 Y3 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.00021243918643534072) [X1 Z2 X3 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.0005624947410458902) [Y2 Z3 Y4 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.0005624947410458902) [Y2 Z3 Y4 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.0005624947410458902) [X2 Z3 X4 Y5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.0005624947410458902) [X2 Z3 X4 X5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.002482434944470818) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 X8 X10 Y11]
+ (0.002482434944470818) [Y1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Y10 Y11]
+ (0.002482434944470818) [X1 Z2 Z3 Z4 Z5 Z6 Z7 X8 X10 X11]
+ (0.002482434944470818) [X1 Z2 Z3 Z4 Z5 Z6 Z7 Y8 Y10 X11]
+ (0.00592220138622357) [Y2 Z3 Z4 Z5 Y6 Y7 Z8 Z9 Z10 Y11]
+ (0.00592220138622357) [Y2 Z3 Z4 Z5 Y6 X7 Z8 Z9 Z10 X11]
+ (0.00592220138622357) [X2 Z3 Z4 Z5 X6 Y7 Z8 Z9 Z10 Y11]
+ (0.00592220138622357) [X2 Z3 Z4 Z5 X6 X7 Z8 Z9 Z10 X11]
+ (0.008517325982662263) [Y0 Z1 Z2 X3 X5 Z6 Z7 Z8 Z9 Y10]
+ (0.008517325982662263) [Y0 Z1 Z2 Y3 Y5 Z6 Z7 Z8 Z9 Y10]
+ (0.008517325982662263) [X0 Z1 Z2 X3 X5 Z6 Z7 Z8 Z9 X10]
+ (0.008517325982662263) [X0 Z1 Z2 Y3 Y5 Z6 Z7 Z8 Z9 X10]
+ (0.008517325982662263) [Y1 X2 X4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.008517325982662263) [Y1 Y2 Y4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.008517325982662263) [X1 X2 X4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.008517325982662263) [X1 Y2 Y4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.01477483394901577) [Y0 Z1 Z2 Z3 Z4 Z5 Y6 Y7 Z8 Y9]
+ (0.01477483394901577) [Y0 Z1 Z2 Z3 Z4 Z5 Y6 X7 Z8 X9]
+ (0.01477483394901577) [X0 Z1 Z2 Z3 Z4 Z5 X6 Y7 Z8 Y9]
+ (0.01477483394901577) [X0 Z1 Z2 Z3 Z4 Z5 X6 X7 Z8 X9]
+ (-0.01906004694665534) [Y0 Z1 Z2 X3 X4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.01906004694665534) [X0 Z1 Z2 Y3 Y4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.010093525104935722) [Y0 Y1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (-0.010093525104935722) [X0 X1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (-0.002482434944470818) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 X10 Y11]
+ (-0.002482434944470818) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 Y10 X11]
+ (0.002482434944470818) [Y0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 Y9 X10 X11]
+ (0.002482434944470818) [X0 Z1 Z2 Z3 Z4 Z5 Z6 Z7 Z8 X9 Y10 Y11]
+ (0.010093525104935722) [Y0 X1 X2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
+ (0.010093525104935722) [X0 Y1 Y2 Z3 Z4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
+ (0.01906004694665534) [Y0 Z1 Z2 Y3 X4 Z5 Z6 Z7 Z8 Z9 Z10 X11]
```
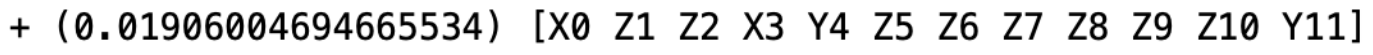

Figure A.13: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$. Part 6



```
+ (0.01906004694665534) [X0 Z1 Z2 X3 Y4 Z5 Z6 Z7 Z8 Z9 Z10 Y11]
```

Figure A.14: qubit Hamiltonian of H_2O for $r_{H-O} = 0.958\mathring{A}$ and $\phi = 104.5°$. Part 7

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