

# Advanced Quantum Information Theory Essay\*

## Simulating Chemistry on Quantum Computers: From atoms to algorithms – a holistic review

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*“... because nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical”*

– Richard P. Feynman, *Simulating Physics with Computers* [1]

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# 1 Introduction

The aim of this essay is to provide a holistic overview of the field of quantum chemistry simulation. Given the diverse nature of the subject it is often hard to find literature which gives a full perspective of the field’s many facets. Therefore this paper attempts to give a technical overview of the many areas needed to understand the full challenge presented by quantum chemical situations.

To achieve this Section 2 begins by asking the question of why we want to simulate quantum chemistry, and is it feasible to do so? Section 3 gives a brief overview of the two simulation techniques available: analogue and digital quantum simulation. Having discussed the abstract concept of quantum simulation, Section 4 begins the technical material by discussing the two main chemical systems we typically desire to simulate and gives their characteristic Hamiltonians. With chemical Hamiltonians in hand Section 5 explains the different qubit mappings we can apply to simulate the systems on our quantum computer. Section 6 concludes the technical material by considering the more practical implications of the aforementioned simulation methods with respect to scaling and resource estimation. Lastly, Section 7 finishes by making some final concluding remarks and gives an outlook for the future quantum chemistry simulation research efforts.

## 2 Why quantum simulation?

Though the fields of quantum computation and quantum information theory are now considered cardinal to quantum chemistry simulation, it was the question of simulating quantum systems that originally motivated their study. In Feynman’s now-famous 1982 speech on “Simulating physics with computers” [1] he contended that performing true simulations of certain quantum mechanical systems not only requires resources that grow exponentially with system size, but also that a classical probabilistic computing machine simply can’t reproduce required quantum probability distributions. These claims can be elementarily understood by firstly considering that solving the Schrödinger equation for  $n$  qubits requires solving  $2^n$  simultaneous equations, and secondly that when we consider the “probabilities” associated with certain quantum systems, some appear as negative, and thus are not classically reproducible. Such systems as these include the Hubbard model for interacting fermions and the Ising model for spin lattices – both highly relevant to the study of magnetism, superconductivity and other important materials problems.

As a result of these considerations he asks “If you had discrete quantum systems, what other discrete quantum systems are exact imitators of it, and is there a class against which everything can be matched?” – one of the earliest propositions for universal quantum computers as simulators for quantum systems. One intuitive response to this question is given by Nielsen and Chuang, who note that whilst we can construct unitary operations which *cannot* be simulated efficiently with a universal quantum computer, “we believe that such systems aren’t actually realized in Nature, otherwise we’d be able to exploit them to do information processing beyond the quantum circuit model” [2]. However the answer to Feynman’s question was definitively given in 1998 by Lloyd, providing an efficient technique for the (digital) quantum simulation of time-evolving physical systems using Lie-Trotter expansions [3] (discussed further in section 5.3).

We can therefore be assured that not only is the question of simulating quantum systems relevant, but also that it is feasible to achieve.

## 3 Quantum simulation techniques

The key problem at the centre of almost all simulation efforts is the solving of the time-dependent Schrödinger equation (for a time-independent Hamiltonian  $\hat{H}$ )

$$i\hbar \frac{d}{dt} |\varphi\rangle = \hat{H} |\varphi\rangle \quad \Rightarrow \quad |\varphi(t)\rangle = e^{-i\hbar \hat{H} t} |\varphi(0)\rangle = \hat{U}(t) |\varphi(0)\rangle \quad (1)$$

where  $|\varphi(t)\rangle$  is the evolution of the system we wish to simulate. To achieve this we must first have a physical or “model” Hamiltonian to apply, which is often provided by the theoretical quantum chemist or physicist. This Hamiltonian must then be translated into a form which can be processed by our quantum simulation machine. When considering the fundamental techniques available to said machine there are two distinct methods one can choose: analogue and digital quantum simulation.

### 3.1 Analogue quantum simulation

Analogue quantum simulation requires a direct mapping  $f$  from the Hamiltonian of the system  $H_{\text{sys}}$  to the Hamiltonian of the simulator  $H_{\text{sim}}$ , such that  $H_{\text{sim}} = f H_{\text{sys}} f^{-1}$ . This allows us to model the system’s initial state  $|\varphi(0)\rangle$  using the equivalent simulator state  $|\psi(0)\rangle = f |\varphi(0)\rangle$ , evolve the state under  $H_{\text{sim}}$ , giving  $|\psi(t)\rangle$  and convert back to the final system state  $|\varphi(t)\rangle = f^{-1} |\psi(t)\rangle$ .

Sometimes this method is referred to as ‘dedicated’ quantum simulation, since it is thought that the design of such a simulator would be rather application specific, rather than necessarily universal. However there are some notable advantages of such a simulation. Firstly, such systems can tolerate certain levels of error, especially when qualitative solutions such as phase transitions are sought and secondly, such a simulation allows physical quantities of interest to be measured directly [4] (rather than by tomographic means). However there are still questions to be answered in terms of state preparation and measurement, given that it is difficult to provide general solutions and mappings to analogue quantum simulation problems.

### 3.2 Digital quantum simulation

Alternatively, digital quantum simulation aims at a more universal approach to the simulation problem. Here we initially attempt to map the basis states of the system of interest to a qubit picture. For example, a system described by  $\{|\Psi_i\rangle\}$  for  $i = 1, \dots, 4$  may be mapped to the two-qubit basis states  $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$ , and the Hamiltonian rephrased accordingly. However often it is not simple to ‘rephrase’ such a Hamiltonian and retain operator commutation relations. This is due to the parafermionic nature of qubits, and as such care must be taken to ensure our simulation truly behaves as the system at hand (discussed further in Section 5.2).

This method is also referred to as ‘universal’ quantum simulation given that it is designed to be performed on a universal quantum computer. In theory, given a general mapping and a universal quantum computer it is possible to digital quantum simulation to reproduce the evolution of any physical Hamiltonian. Furthermore one significant advantage of this model is the ability to use well-established field of quantum computing to assist with simulation. For example, if one is not interested in the specific form of an energy eigenstate but rather the energy eigenvalue, the Quantum Fourier Transform can be utilised by the Phase Estimation Algorithm to provide said eigenvalues. This and other simulation algorithms can be performed using the same unitary considered for ‘traditional’ simulation by evolution, providing a good flexibility for digital quantum simulation unitaries.

Given its generality and precedence in current research attempts we shall therefore explicitly focus on digital quantum simulation methods for the rest of this paper.

## 4 Chemical systems

There are a vast range of systems which can be modelled via quantum simulation, ranging from cosmological phenomena such as the expansion of the universe to Dirac particles in high-energy particle physics and even quantum chaos [4]. One particularly common application is that of quantum chemistry.

Due to the difficulty of the problem and the need in research and industry for accurate simulations, there is currently a large research focus on modelling the chemical properties of complex molecules. When simulating a molecule, one must be acutely aware of the laws of quantum mechanics, given that each electron is a fundamentally quantum object. As these molecules increase in complexity, the myriad of electronic interactions and states make any simulation using classical computation wholly inefficient to perform. This make the simulation of molecular chemistry with quantum computers an appealing alternative.

When considering quantum chemistry, there are two physical processes that feature often in the description and understanding of molecular properties: those of molecular vibrations and molecular orbitals.

### 4.1 Molecular vibrations

When considering molecular vibrations, as with any quantum mechanical system we wish to simulate, it is often best to start with a characteristic Hamiltonian

$$\hat{H} = -\frac{\hat{p}^2}{2m} + \hat{V}(x), \quad \text{where} \quad \hat{p} = -i\hbar\frac{\partial}{\partial x} \quad (2)$$

and  $x$  is some arbitrary coordinate. Applying  $\hat{U}(t) = e^{-i\hat{H}t}$  (taking  $\hbar = 1$ ) we can therefore simulate different molecular vibrations by differing the choice in the potential energy function  $\hat{V}(x)$ . These functions are essentially a description of the varying forces or tensions we can apply to the atomic bonds within a molecule. For example, there are two instinctive ways we can apply a stress to interatomic bonds: bond stretching and valence angle bending.

Bond stretching is our typical two masses on a spring example, with vibrations resulting from the stretching and constricting of the bond along its own axis. To parameterise this bond stretching we consider there interatomic distance  $r$ . To give an expression for the potential, we can simply perform a Taylor expansion on  $V(r)$

$$V(r) = V_0 + \left.\frac{\partial V}{\partial r}\right|_{r_0}(r - r_0) + \frac{1}{2}\left.\frac{\partial^2 V}{\partial r^2}\right|_{r_0}(r - r_0)^2 + \frac{1}{6}\left.\frac{\partial^3 V}{\partial r^3}\right|_{r_0}(r - r_0)^3 + \dots \quad (3)$$

where  $r_0$  is the equilibrium bond length and  $V_0 = V(r_0)$  is the energy of the molecule at equilibrium. From this, we can immediately set  $V_0 = 0$  and since  $r_0$  occupies a potential minima,  $\frac{\partial V}{\partial r}\Big|_{r_0} = 0$ . To a good approximation we can therefore represent our system's potential as

$$V(r) = \frac{1}{2} \frac{\partial^2 V}{\partial r^2} \Big|_{r_0} (r - r_0)^2 + \frac{1}{6} \frac{\partial^3 V}{\partial r^3} \Big|_{r_0} (r - r_0)^3 \quad (4)$$

$$= \frac{1}{2} k^{(2)} (r - r_0)^2 + \frac{1}{6} k^{(3)} (r - r_0)^3 \quad (5)$$

where  $k^{(2)}$  is the classical 'spring constant' for a harmonic oscillator and  $k^{(3)}$  can be thought of as the spring constant for the anharmonic component.

On the other hand valence angle bending describes the movement of bonds perpendicular to the bond axis, defined by the internal angle  $\theta$  between three atoms. For this type of motion, we can similarly express the the potential energy function as

$$V(\theta) = V_0 + \frac{\partial V}{\partial \theta} \Big|_{\theta_0} (\theta - \theta_0) + \frac{1}{2} \frac{\partial^2 V}{\partial \theta^2} \Big|_{\theta_0} (\theta - \theta_0)^2 + \frac{1}{6} \frac{\partial^3 V}{\partial \theta^3} \Big|_{\theta_0} (\theta - \theta_0)^3 + \dots \quad (6)$$

$$\simeq \frac{1}{2} \kappa^{(2)} (\theta - \theta_0)^2 + \frac{1}{6} \kappa^{(3)} (\theta - \theta_0)^3 \quad (7)$$

where  $\kappa$  are the corresponding force constants for angle bending and similarly  $\theta_0$  denotes the equilibrium angle size.

However, as the molecules become more complex, containing  $N$  atoms, the numerous different bond stretching, angle bending and even torsions (i.e. bond twisting) cause various compound vibrational modes. To generalise this, we move to a set of  $3N$  normal coordinates,  $\{\mathbf{Q}\}$  (where  $\mathbf{Q} = (Q_1, Q_2, \dots, Q_{3N})$ ). These coordinates are defined such that they no longer express the motion of individual atoms, but rather positions in terms of the total motion of a vibration (as well as being mass-scaled and in terms of equilibrium displacement). For example, valence angle bending can be thought of as a type of normal coordinate, since the angle  $\theta$  doesn't describe the motion of an individual atom, but rather parameterises the motion of one mode of vibration. Furthermore these are designed to diagonalise the harmonic component, allowing for some simplification of the problem. In general, we can therefore write

$$V(\mathbf{Q}) = \frac{1}{2} \sum_{i=1}^{3N-6} \omega_i^2 Q_i^2 + \frac{1}{6} \sum_{ijk} \phi^{ijk} Q_i Q_j Q_k \quad (8)$$

where  $\omega_i = \frac{\partial^2 V}{\partial Q_i^2}$ ,  $\phi^{ijk} = \frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k}$  and correspond to the 'frequencies' of the different harmonic and anharmonic vibrational modes respectively. The negation of the six vibrational modes occurs as these refer to the six 'zero frequency' modes corresponding to three rigid translations and three rigid rotations.

Once we have the form of our potential energy function, we can apply it to our Hamiltonian (2), which we then attempt to diagonalise to find the energy eigenvalues and the associated eigenfunctions. It is these that chemists are interested in obtaining, as they represent derivative chemical properties such as spectral absorption.

## 4.2 Molecular orbitals

Possibly the most common and straightforward approach to the modelling molecular orbitals is through the variational method. This employs the fact that given no electronic state  $\psi$  or superposition of states  $\Psi = \sum_i \psi_i$  can correspond to an energy state below the ground state energy  $E_0$  (the energy of the lowest eigenstate). Mathematically, this can be expressed as

$$\frac{\int \Psi^* H \Psi d\mathbf{r}}{\int \Psi^2 d\mathbf{r}} \geq E_0 \quad (9)$$

where  $\mathbf{r}$  is any arbitrary coordinate parameterising our system (described by  $H$ ) and states. This now allows us to test different ansatz states or wave functions for their approximation of the ground state-energies (which can be found empirically), performing parameterised searches for the correct form.

For example, consider that we thought the total electron wave function  $\psi$  was defined by some function of the  $N$  individual orbital functions  $\psi_i$ , such that  $\Psi = \sum_{i=1}^N a_i \psi_i$ . The optimal form of  $\psi$  to describe the system could be thus be found through a search over parameters  $a_i$  by minimising the LHS of Equation (9). In fact this is one of the ansatz wave functions actually used, known as the Linear Combination of Atomic Orbitals (LCAO) approach.

The application of the LCAO approach to (9) allows us to derive the following equation

$$E = \frac{\sum_{ij} a_i^* a_j H_{ij}}{\sum_{ij} a_i^* a_j S_{ij}} \quad \text{where} \quad H_{ij} = \int \psi_i^* H \psi_j d\mathbf{r} \quad \text{and} \quad S_{ij} = \int \psi_i^* \psi_j d\mathbf{r} \quad (10)$$

where  $H_{ij}$  and  $S_{ij}$  are known as the ‘resonance’ and ‘overlap integrals’ respectively. To find the optimal ground state analytically, we therefore solve

$$\frac{\partial E}{\partial a_k} = 0 \quad \Rightarrow \quad \sum_{i=1}^N N a_i (H_{ki} - E S_{ki}) = 0 \quad (11)$$

$$\Rightarrow \begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \cdots & H_{1N} - E S_{1N} \\ H_{21} - E S_{21} & H_{22} - E S_{22} & \cdots & H_{2N} - E S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - E S_{N1} & H_{N2} - E S_{N2} & \cdots & H_{NN} - E S_{NN} \end{vmatrix} = 0 \quad (12)$$

where Equation (12) is known as the ‘secular equation’, which is solved to give  $N$  energies  $E_j$ . Each of these solutions give a different set of coefficients  $a_{ij}$  from Equation (11), such that

$$\Psi_j = \sum_{i=1}^N a_{ij} \psi_i \quad (13)$$

where  $\Psi_j$  are therefore the eigenstates of our single-electron wave function in terms of the original orbital wave functions  $\psi_i$ . The  $\Psi_j$  corresponding to the lowest  $E_j$  therefore represents the ground state of our system, and although we have not proved it here, variational principle also holds for the other excited states found [5].

To solve the secular equation, we must first know the associated resonant and overlap integrals  $H_{ij}$  and  $S_{ij}$ . If a model Hamiltonian or even the individual orbital wave functions are not known, one can apply the Hückle Theory. This assumes that: i) the basis set is formed entirely from parallel carbon 2p orbitals, with one per atom, such that  $S_{ij} = \delta_{ij}$ ; ii)  $H_{ii}$  are given simply by the energy of the aforementioned 2p orbitals, and  $H_{ij}$  corresponding to neighbour interactions ( $|i - j| = 1$ ) are derived from experimental information; iii) interactions between non-neighbouring orbitals are not considered, i.e. for  $|i - j| > 1 \Rightarrow H_{ij} = 0$  and iv) the energy of the many-electron wave function is simply the sum over the individual electron wave function energy. This is often known as an ‘effective Hamiltonian’ method.

A somewhat more sophisticated approach to many-electron wave functions is the Hartree product approach, whereby we define a Hamiltonian separable into single-electron hamiltonians  $h_i$

$$H = \sum_{i=1}^N h_i \quad \text{where} \quad h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}} + V_i\{j\} \quad \text{and} \quad V_i\{j\} = \sum_{i \neq j} \int \frac{\rho_j}{r_{ij}} d\mathbf{r} \quad (14)$$

where  $M$  are the total number of nuclei,  $Z_k$  are the number of proton of the  $k$ th nuclei,  $r_{ik}$  and  $r_{ij}$  the electron-nuclei and electron-electron distance respectively and  $\rho_j$  the charge (probability) density produced by electron  $j$ . From this we can see that the terms in  $h_i$  respectively represent the  $i$ th electron’s kinetic energy, the attractive interaction with the molecule’s nuclei and the repulsive interaction with other electrons of the molecule.

Having defined a separable Hamiltonian, we can now represent our many-electron wave function  $\Psi_{\text{HP}}$  (where HP stands for Hartree Product) as a product of all single-electron wave functions, such that

$$\Psi_{\text{HP}} = \prod_{j=1}^N \psi_j = \psi_1 \otimes \psi_2 \otimes \dots \otimes \psi_N \quad (15)$$

$$\Rightarrow H \Psi_{\text{HP}} = \sum_{i=1}^N h_i \prod_{j=1}^N \psi_j = \sum_{i=1}^N \varepsilon_i \prod_{j=1}^N \psi_j = E \Psi_{\text{HP}} \quad (16)$$

where  $\varepsilon_i$  and  $E$  represent the energy of single-electron eigenstates (of  $h_i$ ) and the aggregate many-electron eigenstate (of  $H$ ) respectively.

This separable form of the Hamiltonian and it’s associated product wave function provide a good basis to model our electronic system and as such the Hartree-Product wave function is often considered a good ansatz wave function for variational searches.

## 5 Mapping chemical models to qubits

Once we have a model to simulate, we must now translate that model into a format compatible with the inner workings of our quantum computer. The aim of this process is to ‘map’ the physics of our theoretical model to an equivalent model, acting on and using the fundamental elements and operations of our quantum computer. Therefore given that our quantum computer acts on qubits, using unitary operations, we shall now consider how we can convert our chemical model into a qubit model.

## 5.1 From the first to second quantised picture

Previously, our models have considered the first-quantisation picture, with our Hamiltonian acting on parameterised wave functions. However for both molecular vibrations and orbital models it is desirable to move to a description in terms of state occupation numbers, rather than functions parameterised by some physical quantity. This is known as the second-quantised picture.

### 5.1.1 Molecular vibrations

For molecular vibrations this shift is motivated by the desire to equate the quantised vibrations of molecules to the theoretical model of a quantum harmonic oscillator (QHO). In QHO theory, we consider the harmonic potential  $\hat{V}(x) = \frac{1}{2}m\omega^2\hat{x}^2$ , such that

$$\hat{H} = \frac{\hat{p}}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2x^2 \quad (17)$$

$$\Rightarrow \Psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega x^2}{2\hbar}} \quad (18)$$

$$\text{where } \hat{H}\Psi_n(x) = E_n\Psi_n(x) = \hbar\omega\left(n + \frac{1}{2}\right)\Psi_n(x) \quad (19)$$

where  $n$  is our state number ( $n = 0$  representing the ground state) and  $H_n(\dots)$  is the  $n^{\text{th}}$  Hermite polynomial. Clearly this is not a particularly eloquent way to talk about our QHO states. Ideally we could define an operator which acts on the eigenstate ‘ladder’, allowing us to consider the relationship between the steps on this ladder of states, rather than the relative dependences of  $\Psi_n$  on  $x$  (especially given the eigenvalues have no  $x$  dependency). To do this we want to be able to develop a language which only considers the hierarchy of eigenvalues  $\Psi_n$ . This process requires the diagonalisation of the superoperator  $\hat{\mathcal{H}}[\hat{a}] = [\hat{H}, \hat{a}] = \hat{H}\hat{a} - \hat{a}\hat{H}$ , such that  $\hat{\mathcal{H}}[\hat{a}] = \lambda\hat{a}$  where  $\lambda$  is some constant. To do so we consider  $\hat{a} = \alpha\hat{x} + \beta\hat{p}$ , and solve to give

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right) \quad \text{and} \quad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right) \quad (20)$$

$$\Rightarrow \hat{\mathcal{H}}[\hat{a}] = [\hat{H}, \hat{a}] = -\hbar\omega\hat{a} \quad \text{and} \quad \hat{\mathcal{H}}[\hat{a}^\dagger] = [\hat{H}, \hat{a}^\dagger] = \hbar\omega\hat{a}^\dagger. \quad (21)$$

This now allows us to derive the eigenvalues of different ladder states (relative to one another) as follows

$$\hat{H}\hat{a}\Psi_n = (\hat{a}\hat{H} - \hbar\omega\hat{a})\Psi_n = (\hat{a}E_n - \hbar\omega\hat{a})\Psi_n = (E_n - \hbar\omega)\hat{a}\Psi_n. \quad (22)$$

and therefore  $\hat{a}\Psi_n$  is an eigenstate of  $\hat{H}$ . From Equation (19) we can see that the associated energy eigenvalue is that associated with eigenstate  $\Psi_{n-1}$ , and hence  $\hat{a}\Psi_n = \Psi_{n-1}$ . Using this reasoning we can also show that  $\hat{a}^\dagger\Psi_n = \Psi_{n+1}$ . We can further show that (by assuming  $\hat{a}$  possesses a non-trivial kernel)  $\hat{a}\Psi_0 = 0$  for  $\Psi_0 \neq 0$ , and hence  $E_0 = \frac{1}{2}\hbar\omega$ .

Furthermore, given the canonical commutation relation  $[\hat{x}, \hat{p}] = i\hbar$ , we can show that  $[\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij}$  (and also  $[\hat{a}_i, \hat{a}_j] = [\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0$ ), where  $i$  and  $j$  denote the ‘modes’ or oscillator ladders on which they operate. This is the same commutation relation that we expect for a bosonic system, and as such we can consider the ladder eigenstates  $\Psi_n$  as representing  $n$ -particle state  $|n\rangle$  of some bosonic quanta. We therefore can consider the operators  $\hat{a}$  and  $\hat{a}^\dagger$  as removing and adding a bosonic excitation quanta respectively, which is equivalent to annihilating and creating bosons in a given state. Hence  $\hat{a}^\dagger$  and  $\hat{a}$  are known as the ‘creation’ and ‘annihilation’ operators and similarly the energy eigenstates  $|n\rangle$  are known as ‘number states’.

These bosonic excitations represent the quantised ‘particle’ of vibrational modes, the phonon, and one can conceptualise the aforementioned operators as creating and annihilating phonons in a given vibrational mode. Physically these bosonic excitations represent an increase in the amplitude of oscillation, at the vibrational frequency of the mode.

To make use of this new second-quantised number state formalism we must now express the first-quantised Hamiltonian and position and momentum operators in terms of our new operators. By rearranging Equation (20) and then substituting into (17), we find

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger) \quad \text{and} \quad \hat{p} = -i\sqrt{\frac{m\omega\hbar}{2}}(\hat{a} - \hat{a}^\dagger) \quad (23)$$

$$\Rightarrow \hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\mathbb{I}\right) = \hbar\omega\left(\hat{n} + \frac{1}{2}\mathbb{I}\right) \quad (24)$$

where  $\hat{n} = \hat{a}^\dagger\hat{a}$  and is known as the ‘number operator’ (since  $\hat{n}|n\rangle = n|n\rangle$ ). We now therefore have a complete model for our QHO system in the second-quantised picture.

Unfortunately, not all molecular vibrations are simply defined by a QHO, and since the QHO is solvable exactly it can be simulated with ease. The vibrational systems which are not easy to simulate classically are those with higher-order anharmonic terms, like that given in Equation (8), which has a cubic potential. This new system no longer can be directly described by the QHO creation and annihilation operators and the associated number eigenstates. To represent anharmonic oscillations in the second-quantised picture one must perform a Bogoliubov transformation to a new set of creation and annihilation operators  $\hat{b}^\dagger, \hat{b}$  and their associated number states  $|n\rangle_b$  [6, 7].

### 5.1.2 Molecular orbitals

Whereas for molecular vibrations we were motivated to a second-quantised picture via a desire to parallel our system to a QHO, for an fermionic electron system, the motivation comes from symmetry arguments. In the first-quantised picture, we are concerned with the wave function of individual electrons, such as the Hartree product wave function in Equation (15).

However as we begin to mature our description of the system to include electronic interactions and anti-symmetric nature of fermion particle exchange, we begin to ask unphysical questions of our system. When we consider indistinguishable particles, we can no longer ask which particle is in which state, and in labelling ‘particle 1 in state 1 and particle 2 in state 2’ and ‘particle 1 in state 2 and particle 2 in state 1’ as separate wave functions, we actually introduce a counterproductive notational redundancy to our model. Instead we consider the occupation of states, irrespective to the individual particles that occupy them.

Given we are interested in fermions, we require two conditions: that each fermionic state can be occupied by at most a single fermion at a time (Pauli’s Exclusion Principle); and that the fermion wave function is antisymmetric under particle exchange. Using these two requirements we can now describe an ‘algebra’ (i.e a set of commutation relations) for our system. As before we shall consider creation and annihilation operators, however we now consider them with respect to a two-state system, such that  $\hat{a}^\dagger|0\rangle = |1\rangle$  as before, but now  $\hat{a}^\dagger|1\rangle = 0$ . Additionally, when considering bosonic creation and annihilation operators, we required  $[\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0$ , and therefore  $\hat{a}_i^\dagger\hat{a}_j^\dagger = \hat{a}_j^\dagger\hat{a}_i^\dagger$ , showing a symmetric exchange symmetry. On the other hand for fermions we require an exchange antisymmetry,  $\hat{a}_i^\dagger\hat{a}_j^\dagger = -\hat{a}_j^\dagger\hat{a}_i^\dagger$  and therefore  $\{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = \hat{a}_i^\dagger\hat{a}_j^\dagger + \hat{a}_j^\dagger\hat{a}_i^\dagger = 0$  (similarly we can also show  $\{\hat{a}_i, \hat{a}_j\} = 0$  and  $\{\hat{a}_i, \hat{a}_j^\dagger\} = \delta_{ij}$ ).

Now we have a second-quantised operator notation for our fermionic system, let us consider the new form of our electronic Hamiltonian given in Equation (14). We can think of the reformulation as describing the dynamics of the system by considering all single and double electron energy eigenstates  $\hat{a}_i^\dagger\hat{a}_i, \hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_i\hat{a}_j$  and interaction terms  $\hat{a}_i^\dagger\hat{a}_j, \hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l$  respectively (where  $i \neq j$  and  $k \neq l$ ), such that

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \sum_{pqrs} h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s \quad (25)$$

$$\text{where } h_{pq} \equiv \int d\mathbf{x} \chi_p^*(\mathbf{x}) \left( -\frac{1}{2} \nabla^2 - \sum_k \frac{Z_k}{r_{ik}} \right) \chi_q(\mathbf{x}) \quad (26)$$

$$\text{and } h_{pqrs} \equiv \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) \chi_r(\mathbf{x}_2) \chi_s(\mathbf{x}_1)}{r_{12}} \quad (27)$$

where  $\chi_i(\mathbf{x}_j) = \varphi_i(\mathbf{x}_j)\sigma_i$  are single-electron wave functions with a spatial  $\varphi_i(\mathbf{x}_j)$  and spin  $\sigma_i$  component (the spin component can be ‘integrated out’, hence we only consider the dependence on spatial component  $\mathbf{x}_j$ ). Whilst in reality there exist three- and four-electron, etc interaction terms, we can achieve a good approximation with the above Hamiltonian and as such it has been used as the model for many recent quantum chemistry realisations [8–16]. For these reasons we shall only consider this archetypical electronic Hamiltonian for the remainder of this work.

## 5.2 Mapping to a qubit picture

Now we have second-quantised forms for both our example bosonic and fermionic systems, we want to map these discretised operators onto operations on the qubits of our quantum computer. Given our qubits individually live in a 2-dimensional space, it would seem intuitive that we want to map the terms of our chemical Hamiltonian onto transformations/rotations within this space. As such we attempt to map our creation and annihilation operators to a representation in terms of the Pauli matrices

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (28)$$

$$\text{where } \sigma^+ = \frac{1}{2}(\sigma^x + i\sigma^y) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \sigma^- = \frac{1}{2}(\sigma^x - i\sigma^y) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (29)$$

These Pauli matrices combined with the identity form the generators of all rotations for a 2D qubit system.

### 5.2.1 Fermions

For fermions, the mapping process is well established and is known as a Jordan-Wigner transformation. Originally proposed to translate spin operators in 1D spin lattice models to fermionic creation and annihilation operators, the process can be inverted to map vice versa, such that

$$\hat{a}_j \rightarrow \mathbb{I}^{\otimes j-1} \otimes \hat{\sigma}^+ \otimes (\hat{\sigma}^z)^{\otimes N-j}, \quad \hat{a}_j^\dagger \rightarrow \mathbb{I}^{\otimes j-1} \otimes \hat{\sigma}^- \otimes (\hat{\sigma}^z)^{\otimes N-j} \quad (30)$$

where superscripted tensor product denotes said operator tensor itself the indexed number of times. This mapping retains the aforementioned commutation relationships, namely  $\{\hat{a}_i, \hat{a}_j^\dagger\} = \delta_{ij}$ , and so effectively ‘encodes’ the physical constraints onto the qubit system. This is somewhat unsurprising since the Pauli operators are those used to describe fermionic spin systems, so such a mapping should be expected. More specifically this is due to the parafermionic<sup>1</sup> nature of qubits, which allow for an isomorphic fermion mapping to be performed [17].

As an example, let us consider the mapping for our electronic spin-orbit Hamiltonian given in equation (25). We can see that we can further subdivide the the terms to those producing similar mapped terms

$$\begin{aligned} \hat{H} = & \sum_p h_{pp} \hat{a}_p^\dagger \hat{a}_p + \sum_{pq} (h_{pq} \hat{a}_p^\dagger \hat{a}_q + h_{qp} \hat{a}_q^\dagger \hat{a}_p) + \sum_{pq} h_{pqqp} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_q \hat{a}_p \\ & + \sum_{pqr} (h_{pqqr} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_q \hat{a}_r + h_{rqqp} \hat{a}_r^\dagger \hat{a}_q^\dagger \hat{a}_q \hat{a}_p) + \sum_{pqrs} (h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s + h_{srqp} \hat{a}_s^\dagger \hat{a}_r^\dagger \hat{a}_q \hat{a}_p) \end{aligned} \quad (31)$$

it should be unsurprising that these terms also represent the system’s different energetic state and interaction operators. Respectively they describe: the number operator, excitation operator, Coulomb operator, number with excitation operator, and double excitation operator. Each of these now transforms into the same sequence of mode Pauli operators with individual term coefficients given by the values of  $h_{pq}$  and  $h_{pqrs}$ , a table of which is provided in the Appendix Figure 2.

As an example, let us consider the mapping of the first and simplest term of our electronic Hamiltonian (we shall ignore the operators acting on non- $p$  modes)

$$h_{pp} \hat{a}_p^\dagger \hat{a}_p \xrightarrow{JW} \frac{h_{pp}}{4} (\hat{\sigma}_p^- \hat{\sigma}_p^+) = \frac{h_{pp}}{4} (\hat{\sigma}_p^x - i\hat{\sigma}_p^y)(\hat{\sigma}_p^x + i\hat{\sigma}_p^y) = \frac{h_{pp}}{2} \left( \mathbb{I}_p + \frac{i}{2} [\hat{\sigma}_p^x, \hat{\sigma}_p^y] \right) = \frac{h_{pp}}{2} (\mathbb{I}_p - \hat{\sigma}_p^z) \quad (32)$$

where we have made use of the commutation relation  $[\hat{\sigma}^i, \hat{\sigma}^j] = 2i\varepsilon_{ijk} \hat{\sigma}^k$ . This term can now be used to find the associated unitary evolution on our qubit, which is discussed in Section 5.3.

### 5.2.2 Bosons

For bosons there is no such direct transformation between bosonic creation and annihilation and a 2-dimensional qubit space. To approximate boson dynamics, one can define the boson operators

$$\hat{B} = \frac{1}{\sqrt{N}} \sum_{i=1}^N \hat{a}_i \quad \text{and} \quad \hat{B}^\dagger = \frac{1}{\sqrt{N}} \sum_{i=1}^N \hat{a}_i^\dagger \quad (33)$$

$$\Rightarrow [\hat{B}, \hat{B}^\dagger] = \frac{1}{N} \sum_{i=1}^N (\mathbb{I} - 2\hat{n}_i) = \mathbb{I} - \frac{2\hat{n}}{N} \stackrel{n \ll N}{\approx} \mathbb{I} \quad (34)$$

where  $N$  is the number of qubits available for each boson mapped [17]. Clearly this is not a particularly elegant mapping since it requires a large number of qubits  $N$  per boson, and the level of bosonic excitation  $n$  to be small. Other indirect or approximate mappings from Pauli to creation and annihilation operators do exist and are listed below:

- **Holstein-Primakoff:**

$$\hat{\sigma}^+ = 2\sqrt{2s - \hat{a}^\dagger \hat{a}} \hat{a}, \quad \hat{\sigma}^- = 2\hat{a}^\dagger \sqrt{2s - \hat{a}^\dagger \hat{a}}, \quad \hat{\sigma}^z = 2(s - \hat{a}^\dagger \hat{a}) \quad (35)$$

where  $s$  denotes the spin of the system used to encode the boson state. The bosonic excitations  $|n\rangle_B$  are thus encoded in the spin states  $|s, m_s\rangle$  such that

$$|s, s - n\rangle \rightarrow |n\rangle_B = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle_B \quad (36)$$

<sup>1</sup>Here *parafermionic* refers to the the fact that “a qubit is a vector in a two-dimensional Hilbert space  $\mathcal{H}_i = \text{span}\{|0\rangle_i, |1\rangle_i\}$  (like a fermion) but an  $N$ -qubit Hilbert space has a tensor product structure:  $\mathcal{H} = \otimes_{i=1}^N \mathcal{H}_i$  (like bosons)” [17].

This mapping preserves the hermiticity and commutation relations of the operators, but generates an infinite series of interactions [18]. It is further non-invertible and therefore cannot provide explicit definitions of  $\hat{a}$  and  $\hat{a}^\dagger$ .

- **Dyson-Maleev:**

$$\hat{\sigma}^+ = 2\sqrt{2s - \hat{a}^\dagger \hat{a} \hat{a}}, \quad \hat{\sigma}^- = \hat{a}^\dagger, \quad \hat{\sigma}^z = 2(s - \hat{a}^\dagger \hat{a}) \quad (37)$$

This mapping has the same  $\sigma^+$  and  $\sigma^z$  transformations as the Holstein-Primakoff, except  $\sigma^- = \hat{a}^\dagger$ . This mapping is often used in spin-wave theories of ferromagnetism, given it provides a quicker and more compact description whilst reproducing the perturbative results of a Holstein-Primakoff transformation [18]. However this transformation clearly does not preserve hermiticity, given  $(\sigma^+)^\dagger \neq \sigma^-$ . The larger implications of such an inequality on a system's Hamiltonian and dynamics of a system are unknown.

- **Schwinger:**

$$\hat{\sigma}^+ = \hat{a}_1^\dagger \hat{a}_2, \quad \hat{\sigma}^- = \hat{a}_2^\dagger \hat{a}_1, \quad \hat{\sigma}^z = \frac{1}{2}(\hat{a}_1^\dagger \hat{a}_1 - \hat{a}_2^\dagger \hat{a}_2) \quad (38)$$

This transformation maps the Pauli spin operators onto a system of two uncoupled bosonic QHO modes. Again this mapping does not allow for the explicit expression of individual creation and annihilation operators, but may find use elsewhere or for application-specific models.

Currently the author is investigating the usefulness of the above mappings to the simulation of bosonic systems as part of a larger research effort in this area.

### 5.3 Producing a unitary evolution

As of yet, we have not considered the how we can actually apply the Hamiltonians of our chemical systems to produce a unitary time evolution on states. For a Hamiltonian acting on  $n$  particles that is time independent, the evolution  $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$  (taking  $\hbar = 1$ ) is given by

$$\hat{U}(t) = e^{-iHt} \quad \text{where} \quad \hat{H} = \sum_{i=1}^N \hat{H}_i \quad (39)$$

and  $\hat{U}(t)$  is known as the time evolution operator or propagator for a closed quantum system and  $N$  is poly( $n$ ). Often, we would prefer to not have to compute the whole Hamiltonian's evolution on the overall  $d$ -dimensional system, but rather consider it's action on the subspaces of the system. As such we consider Hamiltonians that we can decompose to a  $k$ -local form (and it is this condition which requires  $N$  be polynomial in  $n$ ). In this form, each term of the Hamiltonian acts non-trivially (i.e. is not the identity) on at most  $k$  qubits. For example, a Hamiltonian that acts on three qubits, but is 1-local can be represented as

$$\hat{H} = \sum_{i=1}^3 \hat{H}_i = \hat{A} \otimes \mathbb{I} \otimes \mathbb{I} + \mathbb{I} \otimes \hat{B} \otimes \mathbb{I} + \mathbb{I} \otimes \mathbb{I} \otimes \hat{C} \quad (40)$$

Clearly this is not an interesting Hamiltonian, since it simply operates on three independent qubits, but for  $k > 1$  local Hamiltonians the dynamics are often non-trivial. If all the terms  $\hat{H}_i$  commute, we can show for an  $N$  qubit Hamiltonian

$$\hat{U}(t) = e^{-i\sum_{i=1}^N \hat{H}_i t} = \prod_{i=1}^N e^{-i\hat{H}_i t} \quad (41)$$

which provides a set of unitaries which act at most on  $k$  qubits and can therefore be efficiently<sup>2</sup> simulated as a series of  $k$ -qubit gates. If the terms  $\hat{H}_i$  do not commute, then we must apply the Lie-Trotter product formula, which states for Hermitian matrices  $A$  and  $B$  such that  $\|A\| \leq K$ ,  $\|B\| \leq K$  and  $K \leq 1$  (where  $K \in \mathbb{R}$ ) then

$$e^{-i(A+B)} = e^{-iA} e^{-iB} + O(K^2) \quad (42)$$

which when extended to our Hamiltonian becomes

$$e^{-iH} = e^{\sum_{i=1}^N \hat{H}_i} = e^{-i\hat{H}_1} e^{-i\hat{H}_2} \dots e^{-i\hat{H}_N} + O(N^3 K^2). \quad (43)$$

<sup>2</sup>We have not specifically addressed the efficiency of performing unitaries on qubits. Regarding this, the Solovay-Kitaev theorem states that this can be done to an arbitrary accuracy efficiently on  $O(1)$  qubits given a universal set of gates.

To approximate the time evolution we use the above statement to produce a first-order approximation of our unitary, known as Trotter splitting or ‘‘trotterization’’ [3], such that

$$e^{-iHt} = \left( e^{-i\hat{H}_1\Delta t} e^{-i\hat{H}_2\Delta t} \dots e^{-i\hat{H}_N\Delta t} \right)^{\frac{t}{\Delta t}} + O(t\Delta t) \quad (44)$$

where  $\frac{t}{\Delta t}$  is known as the ‘Trotter number’ and is the number of individual time-steps duration  $\Delta t$  used to approximate the full time  $t$ . We can in fact make further, higher order approximations, known as Suzuki-Trotter formulas, such as the second-order approximation

$$e^{-iHt} = \left[ \left( e^{-i\hat{H}_1\frac{\Delta t}{2}} \dots e^{-i\hat{H}_{N-1}\frac{\Delta t}{2}} \right) e^{-i\hat{H}_N\Delta t} \left( e^{-i\hat{H}_{N-1}\frac{\Delta t}{2}} \dots e^{-i\hat{H}_1\frac{\Delta t}{2}} \right) \right]^{\frac{t}{\Delta t}} + O(t(\Delta t)^2). \quad (45)$$

Using these approximations, we can therefore begin to approximate the true dynamics due to a Hamiltonian’s unitary evolution.

## 5.4 Reproducing unitaries in the quantum circuit model

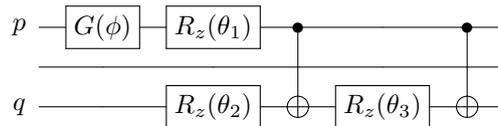
Once we have our trotterized unitary expanded as multiplicative series of unitaries acting on at most  $k$  qubits, we must now represent this as a series of gates acting on qubits in a quantum circuit picture. Using the fact that any arbitrary can be decomposed into a series of single and two-qubit gates (specifically the set of all single qubit  $U(2)$  and the two-qubit CNOT gates) [19,20], we can begin to produce the circuits associated with each Hamiltonian term.

This process now requires us to evaluate our unitary’s exponentiated Hamiltonian operator to find our gate representation. As an example, recall our example Hamiltonian term in equation (32), represented in Pauli matrices as  $\frac{h_{pp}}{2} (\mathbb{I}_p - \hat{\sigma}_p^z)$ , when exponentiated as a term in our trotter expansion this becomes

$$\begin{aligned} \hat{U}(t) &= e^{-\frac{i}{2}h_{pp}(\mathbb{I}_p - \hat{\sigma}_p^z)t} = \sum_{n=0}^{\infty} \frac{\left[ -\frac{i}{2}h_{pp}(\mathbb{I}_p - \hat{\sigma}_p^z)t \right]^n}{n!} \quad \text{where} \quad (\mathbb{I}_p - \hat{\sigma}_p^z)^n = 2^{n-1}(\mathbb{I}_p - \hat{\sigma}_p^z) \quad \forall n \in \mathbb{Z}^+ \quad (46) \\ \Rightarrow \hat{U}(t) &= \frac{1}{2} \sum_{n=0}^{\infty} \frac{(-ih_{pp}t)^n}{n!} (\mathbb{I}_p - \hat{\sigma}_p^z)^n - \frac{1}{2} (\mathbb{I}_p - \hat{\sigma}_p^z) + \mathbb{I}_p = \frac{1}{2} e^{-ih_{pp}t} (\mathbb{I}_p - \hat{\sigma}_p^z) + \frac{1}{2} (\mathbb{I}_p + \hat{\sigma}_p^z) \\ &= \frac{1}{2} e^{-\frac{1}{2}ih_{pp}t} \left[ \left( e^{\frac{1}{2}ih_{pp}t} + e^{-\frac{1}{2}ih_{pp}t} \right) \mathbb{I}_p + \left( e^{\frac{1}{2}ih_{pp}t} - e^{-\frac{1}{2}ih_{pp}t} \right) \hat{\sigma}_p^z \right] \\ &= e^{-\frac{1}{2}ih_{pp}t} \left( \cos \frac{h_{pp}t}{2} \mathbb{I}_p + i \sin \frac{h_{pp}t}{2} \hat{\sigma}_p^z \right) \\ &= e^{-\frac{1}{2}ih_{pp}t} \left[ \left( \cos \frac{h_{pp}t}{2} + i \sin \frac{h_{pp}t}{2} \right) \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \left( \cos \frac{h_{pp}t}{2} - i \sin \frac{h_{pp}t}{2} \right) \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \right] \\ &= e^{-\frac{1}{2}ih_{pp}t} \left[ e^{\frac{1}{2}ih_{pp}t} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + e^{-\frac{1}{2}ih_{pp}t} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \right] \\ &= \begin{pmatrix} 1 & 0 \\ 0 & e^{-ih_{pp}t} \end{pmatrix} \quad (47) \end{aligned}$$

which is sometimes known as the one qubit  $T(\theta)$  gate, where here  $\theta = h_{pp}t$  and performs  $|0\rangle \xrightarrow{T} |0\rangle$  and  $|1\rangle \xrightarrow{T} e^{-i\theta}|1\rangle$ . We can therefore express the contribution of the  $h_{pp}\hat{a}_p^\dagger\hat{a}_p$  hamiltonian terms in our trotterized representation as single qubit rotations.

To simulate all Hamiltonian terms acting on two modes we can therefore include the two-qubit CNOT gate with the complete set of single qubit gates. For example, the qubit gate representation for the Coulomb operator term  $h_{pqqp}\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_q\hat{a}_p$  can be generally represented as



where  $G(\phi)$  represents the global phase gate  $e^{-i\phi\mathbb{I}}$ ,  $R_z(\theta_i)$  the standard  $z$ -rotation and each  $\theta_i$  can have a unique value dependent on  $h_{pp}t$ . Similar circuit decompositions can be performed for every characteristic term of (31) and these are given accordingly in Appendix Figure 3. Furthermore whilst we have taken the electronic spin-orbit Hamiltonian as an example, this methodology will extend to other Hamiltonians given a successful mapping.

Having now produced the relevant evolutions to perform on our ‘processor’ qubits we now therefore have all the tools necessary to actually implement said evolutions on a quantum computer.

## 6 Scaling and resource estimation

Now we have established a generalised process to simulate our system's unitary evolution, we shall consider the actual implementation of these methods to simulate systems of interest. Here it is worth defining what systems are actually of interest. Currently, classical computers can simulate systems of 50-70 spin orbitals (and Hamiltonian described by (25)) with exact or approximate techniques [11], so for a significant advantage around 100 orbitals need be simulated by quantum simulation techniques. Given its widespread use in the literature, from here on (unless otherwise stated) we shall consider the electronic spin-orbit Hamiltonian as our figure of merit for comparisons.

Firstly, when considering an  $N$  electron Hamiltonian it is the non-commutative electron-electron interaction terms which will require trotterization to simulate. Even with the ability to set  $h_{pqrs} = 0$  for many terms, there still remains  $O(N^4)$  terms left to expand, which increases to  $O(N^5)$  after a Jordan-Wigner transformation. To then perform a (second order) Trotter expansion requires a further  $O(N^6)$  terms, giving an upper bound of  $O(N^{11})$ , with initial empirical estimates only a few orders less at  $O(N^9)$  [10].

However if we are clever with the ordering of said terms and are aware of cancellations that are possible between terms we can begin to optimise our algorithm to reduce this factor further.

### 6.1 Algorithm optimisation methods

There are many application specific optimisation methods available for a given problem, however outlined below are those generally relevant to quantum chemistry simulation [11]:

- **Cancelling Jordan-Wigner Strings:**

When we consider the Jordan-Wigner mapping for our creation and annihilation operators we find that we can generalise the form of the unitaries produced by  $H_{pq}$  ( $p < q$ ) and  $H_{pqrs}$  ( $p < q < r < s$ ) terms (here  $H_{pq}$  and  $H_{pqrs}$  refer to the terms  $h_{pq}\hat{a}_p^\dagger\hat{a}_q$  and  $h_{pqrs}\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s$  respectively) as

$$\hat{U}(h_{pq}) = e^{i(\hat{\sigma}_p^X \hat{\sigma}_q^X + \hat{\sigma}_p^Y \hat{\sigma}_q^Y)(\hat{\sigma}_{p+1}^Z \hat{\sigma}_{p+2}^Z \dots \hat{\sigma}_{q-1}^Z)\theta} \quad (48)$$

$$\text{and } \hat{U}(h_{pqrs}) = e^{i(\hat{\sigma}_p^i \hat{\sigma}_q^j \hat{\sigma}_r^k \hat{\sigma}_s^l)(\hat{\sigma}_{p+1}^Z \dots \hat{\sigma}_{q-1}^Z)(\hat{\sigma}_{r+1}^Z \dots \hat{\sigma}_{s-1}^Z)\theta} \quad (49)$$

where  $i, j, k, l = \{X, Y\}$  and  $\theta$  is a constant that depends on  $h_{pq}$  ( $h_{pqrs}$ ). For each term's specific choice of  $p, q, r$  and  $s$  we therefore have a set of 'subterms' associated with a different set of  $i, j, k$  and  $l$ . Under the standard construction each of these subterms would represent a unique circuit in our algorithm. However by noticing that  $H\hat{\sigma}^Z H = \hat{\sigma}^X$  and  $Y^\dagger \hat{\sigma}^Y Y = \hat{\sigma}^Z$  where

$$H = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \quad \text{and} \quad Y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} \quad (50)$$

it can be shown that the common components represented by  $\hat{\sigma}_n^Z$  in the unitary can be reduced to a single set per term rather than each subterm. This process is shown in Appendix Figure 4.

However such cancellations will only produce a constant factor of improvement, and so more intelligent cancellation need be applied. Firstly, by intelligently ordering the  $H_{pqrs}$  terms, one can conveniently cancel the CNOT gates between successive terms (given that  $\text{CNOT}^2 = \mathbb{I}$ ) and secondly further reductions can be achieved with the introduction of additional ancilla qubits, shown in Appendix Figures 5 and 6 respectively.

- **Parallelisation:**

As noted above, when we consider quantum simulation algorithms, the main resource requirement is the number of sequential gates required, with the number of coherent qubits as a relatively cheap resource. With this in mind we can attempt to reduce the gate count through the addition of some extra ancillary qubits.

Often called 'nesting' this procedure identifies which terms can be executed simultaneously without affecting their operation, allowing them to be 'nested' into one-another. For the most simple case we can consider two  $H_{pqrs}$  terms for  $p, q, r, s$  and  $p', q', r', s'$ , such that  $p < q < r < s < p' < q' < r' < s'$ , where we can clearly see that the two unitaries act on completely separate qubits and therefore can be executed simultaneously. Such a simple optimisation however can only lead to a constant improvement, so to further optimise more sophisticated nestings must be designed.

A series of different nesting examples are shown in Figure 1. The rule of thumb for such nestings is that for any given choice of  $p, q, r, s$  and  $p', q', r', s'$ , the number of intersections between modes must be even (or zero), such that there is no change of parity due to their exchange.

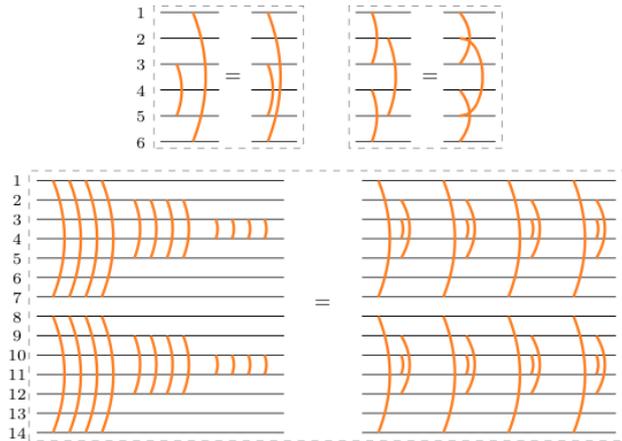


Figure 1: A diagrammatic representation of different nesting optimisations [11].

These nesting techniques (with the addition of a small number of additional ancillae qubits) have been shown to allow up to  $\Theta(N)$  terms to be executed in parallel with appropriate term ordering. An example of the compactness of such an optimisation procedure is given in Appendix Figure 7. Furthermore combining this technique with the Jordan-Wigner string cancelations provided a reduction from  $O(N^9)$  gate depth to  $O(N^7)$ .

- **Term Ordering:**

There are also gains to be made by considering the physical restrictions of the system. In the standard Hartree-Fock model we know that for  $p \neq q$

$$h_{pq} + \frac{1}{2} \sum_r h_{prrq} n_r = 0 \quad (51)$$

where  $n_r = 0, 1$  is the occupancy of the  $r$ -th orbital. This is equivalent to saying that the “effective” hopping becomes diagonal in the basis.

Whilst this condition is only strictly true for the Hartree-Fock solution, it is a condition that can be reasonably approximated in many other similar systems. As such we can evaluate the terms in an “Interleaved Term Order”:

1. Perform all  $H_{pp}$  and  $H_{pqqp}$  terms
2. For each  $p, q$ :
  - a. Perform  $H_{pq}$  and all  $H_{prrq}$  terms
3. Perform all  $H_{pqrs}$  terms

which is designed such that stages 1 and 2a only contain terms that commute with each other. It is the terms in  $H_{pqrs}$  that we can then apply the above optimisation methods.

- **Coalescing:**

One slightly less orthodox method is the idea of choosing the Trotter number on a term-wise basis, only using large expansions for the terms which require them. One such metric is to require  $\Delta_t^{(k)} \|h_k\|$  to be equal for every term  $H_k$ .

This optimisation is motivated by the fact that in the Hartree-Fock basis many of the off-diagonal elements are small and therefore produce unitaries close to the identity. Such terms can therefore be approximated with a much larger Trotter time step  $\Delta_t^{(k)}$ .

However this new scheme will also accrue errors due to the altered term ordering and therefore introduces a trade-off between grouping terms and keeping errors constant. This can be remedied by using a ‘bucketing’ scheme, whereby the terms are sorted into ‘buckets’ according to  $\|h_k\|$ . The buckets containing larger  $\|h_k\|$  are then executed more frequently, and lower  $\|h_k\|$  less frequently, thus reducing the overall error.

- **Lie-Trotter expansion order and Trotter step number:**

One choice we have yet to consider explicitly is the order of the Lie-Trotter expansion used for our unitary and the subsequent choice of Trotter number (assuming Coalescing is not used). These two can be thought of as the two main determinants of accuracy for our model, a higher expansion order providing a more

accurate representation of the true unitary and a higher trotter number reducing the error associated with each term of the expansion.

Intuitively we would assume that using a higher order expansion will always produce a scalable improvement in accuracy. However in [10] they find that for a simulation of a single water molecule within chemical accuracy a first-order expansion error was already found to behave as  $O(\Delta_t)$  (thought to be due to a generic cancellation of errors). Furthermore it was found that even though a fourth-order expansion allowed a ten-fold improvement in the number of Trotter steps, the increase in the number of gates per time step was by a larger factor, rendering it disadvantageous.

Therefore we must take a more empirical approach to the degree of expansion and timestep utilised by our simulation, trialling and testing different simulation parameters for a given simulation.

## 7 Discussion and concluding remarks

During this paper we have looked at the many faces of quantum chemistry simulation, starting with the chemical models themselves, their mappings onto a quantum computer system, and the reality of performing the associated quantum algorithms. By doing so we have described the tools to build the simulation, but we have yet to truly approach the question of the realism of such a proposal.

### 7.1 The reality of realisation

Firstly we have yet to consider the actual platform on which we perform the simulation. Regardless of our platform (excluding theoretical topological quantum computing proposals) we shall need some form of quantum error correction, with even modest schemes requiring tens of physical qubits per logical qubit, and each logical gate operation requiring between 100 and  $10^5$  physical gate operations.

Furthermore even excluding quantum error correction, we are currently an order of magnitude below the  $\sim 100$  coherent qubits needed and 15 orders of magnitude below the  $\sim 10^{18}$  gates needed to simulate useful molecules to within chemical accuracy. In [10] they note that *“even if we assume that Moore’s law applies to quantum computers, i.e. the number of gates that can be executed doubles every 18 months, it will take 75 years to be able to simulate  $Fe_2S_2$  [...]. Even then, assuming a clock speed of 1 GHz (i.e. 1 ns per gate<sup>3</sup>) for gate operations, the calculation for  $Fe_2S_2$  will require 1.5 years to complete”*.

While this does appear to be a bleak outlook for the potential of quantum computers revolutionising the way we compute within our lifetime, it should instead be considered a motive for the importance of further research into the algorithmic side of quantum computation. At first glance it seems that going from an algorithm that requires  $O(N^9)$  to  $O(N^7)$  gates is a negligible improvement given the already large index. However if such optimisation methods are improved on or better algorithms designed this could significantly reduce the challenge at hand since this is currently a larger blockade than the technology itself.

Lastly it is worth noting a point which is often ignored when considering large-scale quantum computation devices: the classical computation bottleneck. Many quantum computation algorithms make use of classical computers to outsource classical optimisation problems or other efficiently computable processes. Given the common view that we are reaching the  $\sim 1$  GHz speed plateau on a serial classical computation processor imposed by locality and chip miniaturisation, we must also consider this when estimating potential quantum computer speed-ups. Not only must our quantum algorithm be efficient, but any classical algorithms associated with the optimisation or running of the quantum algorithm must also be achieved in a reasonable time-frame.

### 7.2 Open problems

There are a couple significant problems that have not been fully addressed when considering quantum simulation algorithms which may also provide future difficulties:

- **State preparation and measurement:**

When considering our models of quantum chemistry we must be careful to pick only those which can be prepared efficiently on our quantum computing device. If the physical description of the molecule is parameterised by a set of variables which does not scale efficiently with size then preparing that quantum state will also not be efficient, let alone performing a variational searching for an unknown ground state.

For example in [9] they overcome this by considering the Unitary Coupled Cluster description for electronic systems, which is described by a polynomial number of parameters. However due to its simplicity this model can be classically simulated efficiently and so is not in the class of models interesting to quantum chemistry simulation (and was accordingly used in [9] as a simple proof-of-principle model). Whether there

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<sup>3</sup>Current ion traps and superconducting qubit gates operate at 100 kHz (100 $\mu$ s) and 10 MHz (100ns) respectively.

exist models that can be parameterised efficiently which are not possible to simulate classically is an open question and the subject of efforts associated with the author's current research.

Furthermore, the inefficiency of full state tomography the question of state measurement must also be addressed. For algorithms such as Phase Estimation, we need not perform tomography on the final state (only the ancillae qubits need be measured). However for modelling the unitary evolution of a state, this may be necessary. If this is the case it may be important to identify the expectation values of interest, rather than performing a full-state tomography. Again this question has yet to be addressed fully, but need be for a true realisation of quantum chemistry simulation.

- **General mappings:**

As previously mentioned in Section 4.1 there are many systems of interest that are not described by a fermionic Hamiltonian. However as considered in Section 5.2.2 a true boson mapping has not yet been achieved, and will need be for general simulation needs. Currently this question can be side-stepped by utilising a Vibrational Coupled Cluster theory, treating the bosons as a fermionic-esque system and using a Jordan-Wigner transformation as before.

Furthermore there may also be other systems of interest with composite boson-fermion systems parastatistics that forego mappings based on either individual method. The question of mappings and their efficiencies must therefore be considered further than the tradition Jordan-Wigner map used so far.

To conclude, quantum simulation of chemical systems is a complex, many faceted problem which requires skills from a variety of different fields of study, it is by no means a trivial problem to solve. For a quantum chemist, it requires understanding which systems can be cleanly mapped to a quantum system, not only in terms of maintaining correct dynamics, but also the ability to define the system efficiently. For a quantum information theorist, it requires understanding the chemical systems at hand enough to design a faithful mapping that can be implemented efficiently and allows for potential optimisation procedures. For a quantum computer scientist, it requires understanding the optimisations that can be made not only from considerations of the quantum algorithm, but also by physical approximations, whilst keeping in mind factors which affect experimental implementation.

Due to the complexity of such a field it is often difficult to feel comfortable with the technical aspects of each elementary component, and the aim of this material was to provide a basis in each of the aforementioned parts. For other, more in-depth reviews of the subject see [4, 21, 22].

With respect to the future of quantum chemistry simulation, the continued realisation of multi-qubit processors will almost certainly bring further progress and interest to the field. Often considered as one of the main 'killer app' of quantum computation, research into quantum simulation will undoubtedly be increased as devices become more sophisticated. Already we are seeing companies such as Microsoft investing in algorithm optimisations, readying to implement when the needed devices are realised. Furthermore it has the potential to be the first quantum computation technique to undeniably beat its classical counterpart, with a clear commercial payoff if it can be done.

For these reasons I believe it to be one of the more interesting and promising areas of research of quantum computation, and one that I will personally be pursuing in the future. Watch this space.

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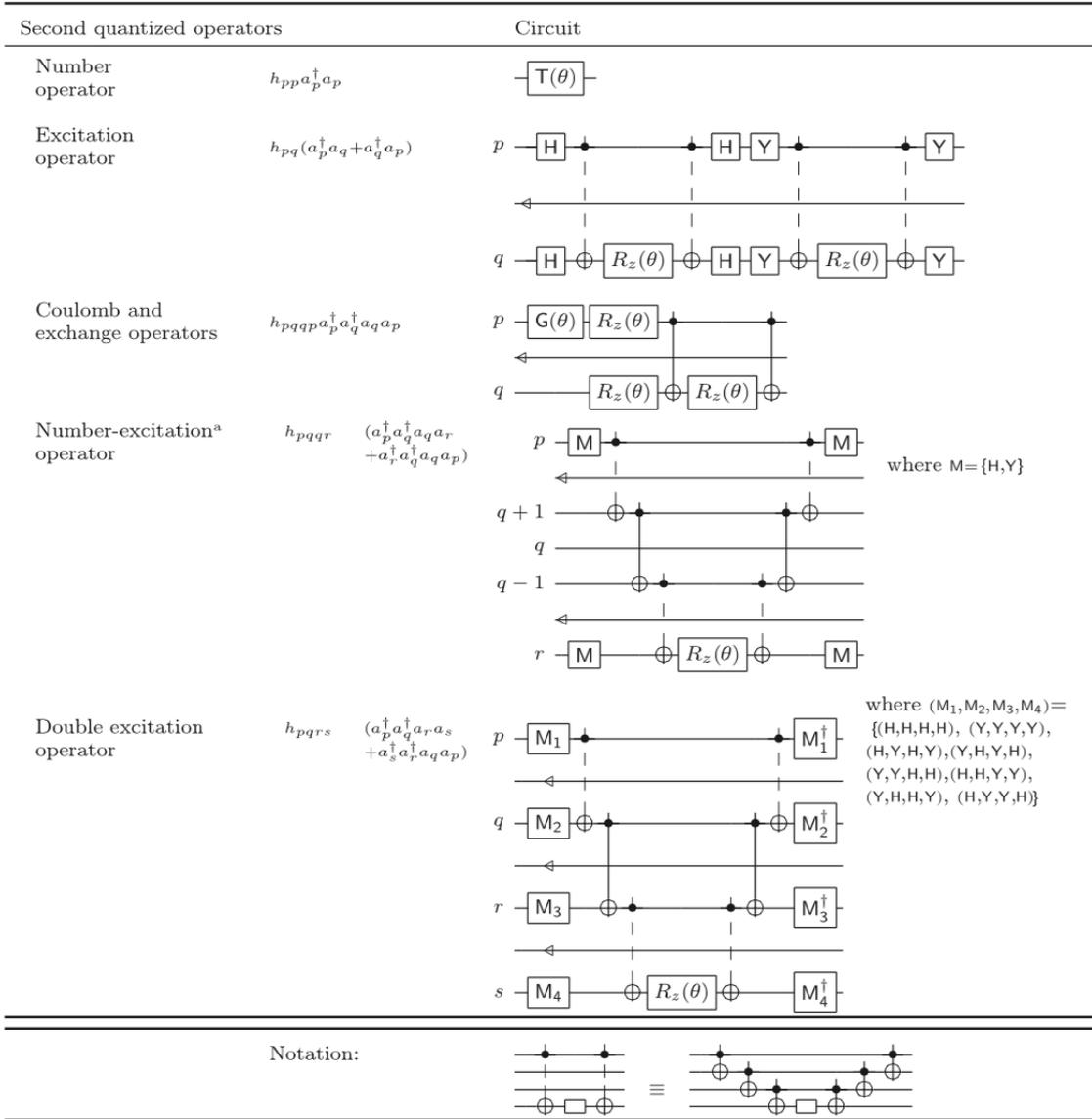
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# 8 Appendix

| Description                                  | Second Quantization <sup>a</sup>  | Pauli representation  |
|--|---|---|
| Number Operator                              | $h_{pp}a_p^\dagger a_p$   | $\frac{h_{pp}}{2}(\mathbf{1}_p - \sigma_p^z)$   |
| Excitation Operator                          | $h_{pq}a_p^\dagger a_q + h_{qp}a_q^\dagger a_p$                                     | $\frac{1}{2} \left( \bigotimes_{k=q+1}^{p-1} \sigma_k^z \right) \left( \begin{array}{c} \Re\{h_{pq}\}(\sigma_q^x \sigma_p^x + \sigma_q^y \sigma_p^y) \\ + 1m\{h_{pq}\}(\sigma_q^x \sigma_p^y - \sigma_q^y \sigma_p^x) \end{array} \right)$  |
| Coulomb Operators                            | $h_{ppqp}a_p^\dagger a_p^\dagger a_q a_q$   | $\frac{h_{ppqp}}{4}(\mathbf{1} - \sigma_p^z - \sigma_q^z + \sigma_p^z \sigma_q^z)$  |
| Number with <sup>b</sup> Excitation Operator | $h_{pqqr}a_p^\dagger a_q^\dagger a_r a_s + h_{rqpq}a_r^\dagger a_s^\dagger a_q a_p$ | $\left( \bigotimes_{k=r+1}^{p-1} \sigma_k^z \right) \left[ \left( \begin{array}{c} \Re\{h_{pqqr}\}(\sigma_p^x \sigma_r^x + \sigma_p^y \sigma_r^y) \\ + 1m\{h_{pqqr}\}(\sigma_p^x \sigma_r^y - \sigma_p^y \sigma_r^x) \end{array} \right) - \sigma_q^z \left( \begin{array}{c} \Re\{h_{rqpq}\}(\sigma_p^x \sigma_r^x + \sigma_p^y \sigma_r^y) \\ + 1m\{h_{rqpq}\}(\sigma_p^x \sigma_r^y - \sigma_p^y \sigma_r^x) \end{array} \right) \right]$  |
| Double Excitation Operator                   | $h_{pqrs}a_p^\dagger a_q^\dagger a_r a_s + h_{srqp}a_s^\dagger a_r^\dagger a_q a_p$ | $\left( \bigotimes_{k=s+1}^{r-1} \sigma_k^z \right) \left( \bigotimes_{k=q+1}^{p-1} \sigma_k^z \right) \left( \begin{array}{c} \frac{\Re\{h_{pqrs}\}}{8} \left( \begin{array}{c} \sigma_p^x \sigma_r^x \sigma_q^y \sigma_s^y - \sigma_p^x \sigma_r^y \sigma_q^x \sigma_s^y + \sigma_p^x \sigma_r^y \sigma_q^y \sigma_s^x \\ + \sigma_p^y \sigma_r^x \sigma_q^x \sigma_s^y + \sigma_p^y \sigma_r^y \sigma_q^x \sigma_s^x - \sigma_p^y \sigma_r^x \sigma_q^y \sigma_s^x \\ + \sigma_p^y \sigma_r^y \sigma_q^y \sigma_s^x + \sigma_p^x \sigma_r^x \sigma_q^x \sigma_s^y - \sigma_p^x \sigma_r^y \sigma_q^y \sigma_s^x \end{array} \right) \\ + \frac{1m\{h_{pqrs}\}}{8} \left( \begin{array}{c} \sigma_p^x \sigma_r^y \sigma_q^x \sigma_s^y - \sigma_p^x \sigma_r^x \sigma_q^y \sigma_s^x + \sigma_p^y \sigma_r^x \sigma_q^x \sigma_s^y \\ + \sigma_p^y \sigma_r^y \sigma_q^y \sigma_s^x + \sigma_p^x \sigma_r^x \sigma_q^y \sigma_s^x - \sigma_p^x \sigma_r^y \sigma_q^x \sigma_s^y \\ + \sigma_p^y \sigma_r^x \sigma_q^y \sigma_s^x + \sigma_p^y \sigma_r^y \sigma_q^x \sigma_s^y \end{array} \right) \end{array} \right)$ |

Notes: <sup>a</sup>It is assumed that  $p > q > r > s$  for all cases listed.  
<sup>b</sup>The spin variable representation of this operator depends if  $q$  is an orbital in the range  $p$  to  $r$  or if it is outside this range.

Figure 2: Terms found in a spin-orbit Hamiltonian and their respective Jordan-Wigner representation [8].



Note: <sup>a</sup>The spin variable representation of this operator depends on whether  $q$  lies in the range  $p$  to  $r$  or outside of it.

Figure 3: Terms found in a spin-orbit Hamiltonian and their respective quantum circuit representation [8].

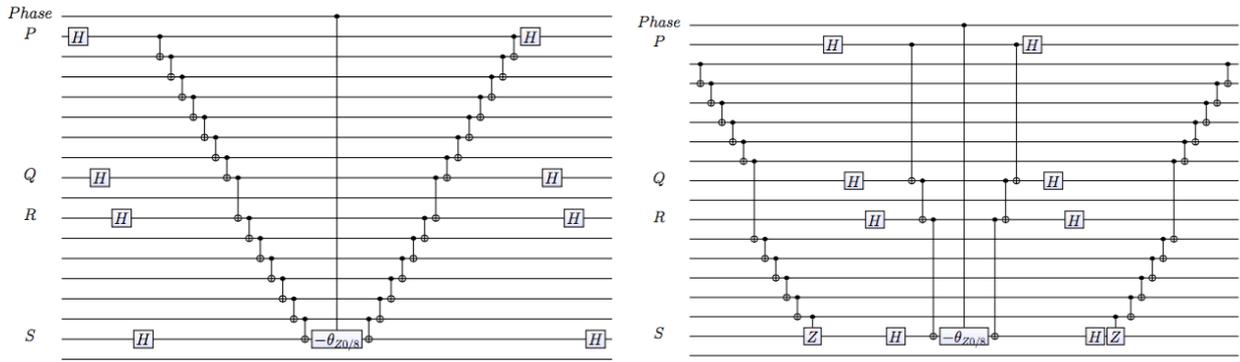


Figure 4: The effect of moving the Jordan-Wigner strings outside of each subterm [11].

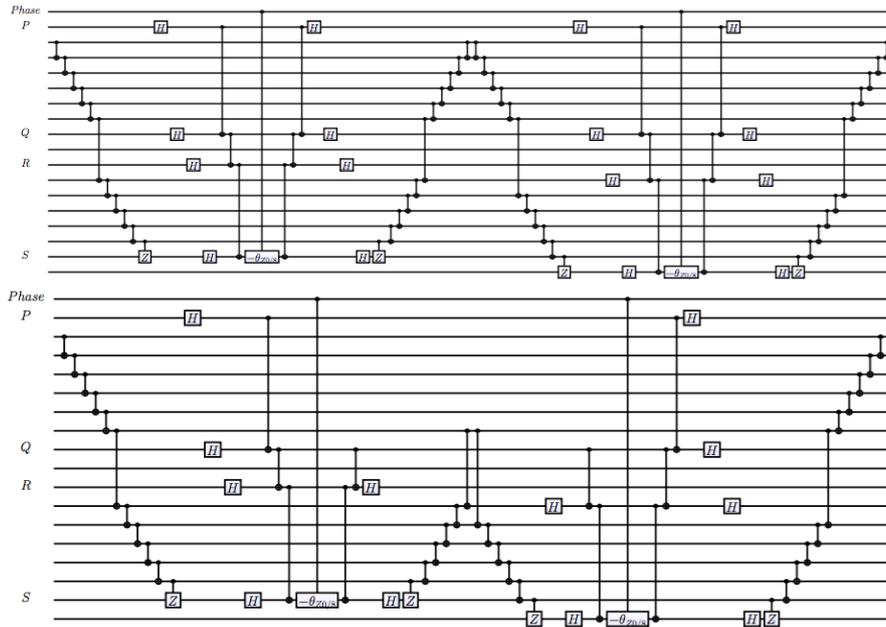


Figure 5: The effect of cancellation of Jordan-Wigner strings between two adjacent terms [11].

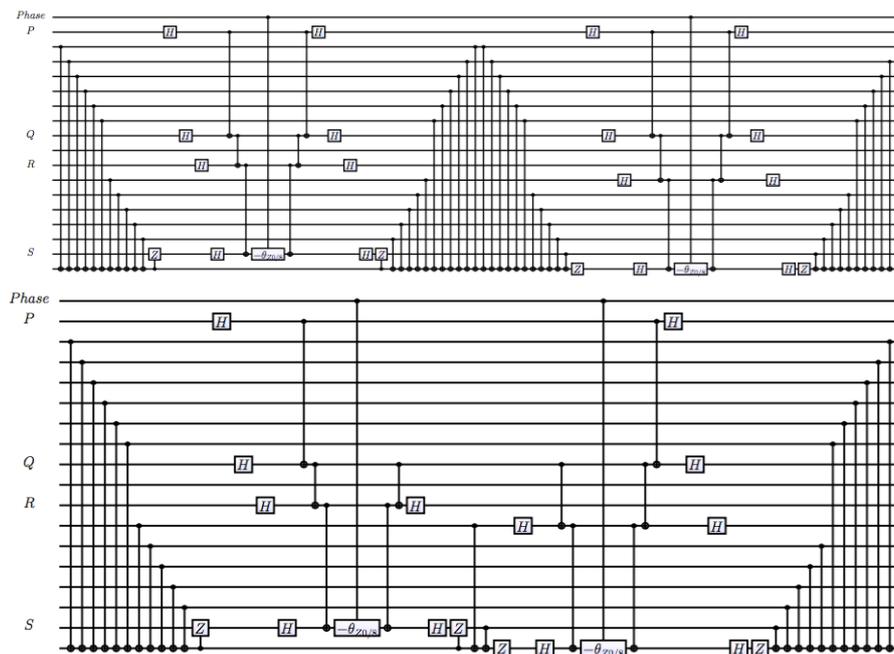


Figure 6: The increased cancellation of Jordan-Wigner strings between two terms using ancillae [11].

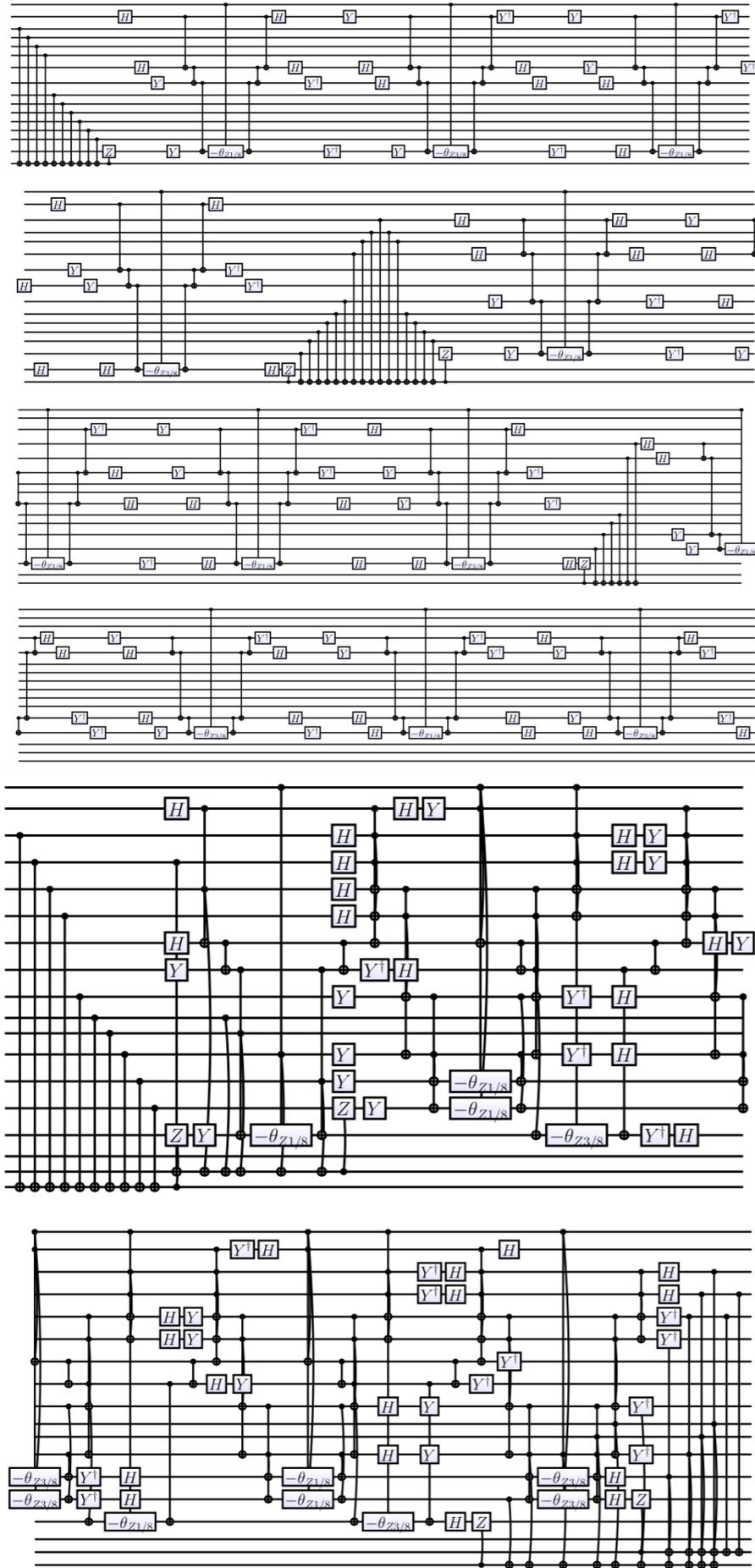


Figure 7: An example of the extent of optimisation achieved for a characteristic set of terms [11].