Diagrammatic Design of Ansätze for Quantum Chemistry

Ayman El Amrani

St. John's College

A thesis submitted for the Honour School of Chemistry

Part II 2024

Pour ma mère et mon père.
Merci de m'avoir amené jusqu'ici.

Acknowledgements

Summary

A central challenge in computational quantum chemistry is the accurate simulation of fermionic systems. At the heart of these calculations lies the need to solve the Schrödinger equation to determine the many-electron wavefunction. An exact solution to this problem scales exponentially with the number of electrons. Classical computers struggle to store the increasingly large wavefunctions making this problem computationally intractable in many cases. In contrast, gate-based quantum computing presents a promising solution, offering the potential to represent electronic wavefunctions with polynomially scaling resources [1]. In other words, quantum computers are a natural tool of choice for simulating processes that are inherently quantum [2].

In the last two decades many advancements in quantum computing have been made in both hardware and software bringing us closer to being able to simulate molecular systems. Despite these advancements, we remain in the so-called Noisy Intermediate Scale Quantum (NISQ) era, characterised by challenges such as poor qubit fidelity, low qubit connectivity and limited coherence times. The NISQ era represents a transitional phase in quantum computing, where quantum devices are not yet error-corrected but are still capable of performing computations beyond the reach of classical computers. Overcoming the limitations of the NISQ era is crucial for realising the full potential of quantum computing in various fields, including quantum chemistry and materials science.

The Variational Quantum Eigensolver (VQE) algorithm is a method used to estimate the ground state energy of a molecular Hamiltonian by preparing a trial wavefunction,

calculating its energy, and optimising the wavefunction parameters classically until the energy converges to the best approximation for the ground state energy [3]. It is recognised as a leading algorithm for quantum simulation on NISQ devices due to its reduced resource requirements in terms of qubit count and coherence time [4].

This thesis extends methods developed by Richie Yeung [2] for the preparation and analysis of parametrised quantum circuits, and applies them to ansätze representing fermionic wavefunctions. We are concerned with two main questions on this theme. Firstly, can we use the ZX calculus [cite] to gain insights into the structure of the unitary product ansatz in the context of variational algorithms for quantum chemistry? Secondly, in the context of NISQ devices, can we use these insights to build better ansätze with reduced circuit depth and more efficient resources?

Contents

Contents

Chapter 1

Background

In this chapter, we will discuss the methods and concepts required to simulate fermionic systems on a quantum computer, as well as the notation that we will use throughout the text. Starting with electronic structure theory, we will introduce the the fundamentals of quantum computation, fermion-qubit encodings and finally Unitary Coupled Cluster theory.

Let us first develop a general fermionic simulation scheme. Fermionic states can generally be represented on a quantum computer in the occupation number representation (section 1.1). That is, the state of each qubit is taken to represent the occupancy of each spin orbital. Then, by representing the fermionic creation and annhilation operators in terms of qubit operators in a way that preserves the fermionic anticommutation relations (section 1.3), we are able to express the Hamiltonian in terms of qubit operations. To simulate this Hamiltonian, we obtain the corresponding unitary time evolution operator, usually via a number of Trotter steps.

1.1   Electronic Structure Theory

Electronic Structure Problem

References: [5]

The main interest of electronic structure theory is finding approximate solutions to the eigenvalue equation of the full molecular Hamiltonian. Specifically, we seek solutions to the non-relativistic time-independent Schrödinger equation.

$$H = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{M} \frac{1}{2M_i}\nabla_i^2 - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_j}{|r_i - R_j|} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|r_i - r_j|} + \sum_{i=1}^{M}\sum_{j>i}^{M} \frac{Z_i Z_j}{|R_i - R_j|}$$

Figure 1.1: Full molecular Hamiltonian in atomic units, where Z_i is the charge of nucleus i and M_i is its mass relative to the mass of an electron.

The full molecular Hamiltonian, H, describes all interactions within a system of N interacting electrons and M nuclei. The first term corresponds to the kinetic energy of all electrons in the system and the second term corresponds to the total kinetic energy of all nuclei. The third term corresponds to the pairwise attractive Coulombic interactions between the N electrons and M nuclei, whilst the fourth and fifth terms correspond to all repulsive Coulombic interactions between electrons and nuclei respectively.

Using the Born-Oppenheimer approximation, we are able to simplify this problem to an electronic one. Motivated by the large difference in mass of electrons and nuclei, we can approximate the nuclei as stationary on the timescale of electronic motion such that the electronic wavefunction depends only parametrically on the nuclear coordinates. This allows us to express the full molecular wavefunction as an adiabatic separation as below.

$$\Phi_{\text{total}} = \psi_{\text{elec}}(\{r\}; \{R\})\, \psi_{\text{nuc}}(\{R\})$$

Within this approximation, the nuclear kinetic energy term can be neglected and the nuclear repulsive term is considered to be constant. Since constants in

eigenvalue equations have no effect on the eigenfunctions and simply add to the resulting eigenvalue, we will omit this too. The resulting equation is the electronic Hamiltonian for N electrons.

$$H = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{|r_i - R_j|} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|}$$

Throughout the remainder of this text, we will concern ourselves only with the electronic Hamiltonian, simply referring to it as the Hamiltonian, H. The solution to the eigenvalue equation involving the electronic Hamiltonian is the electronic wavefunction, which depends only parametrically on the nuclear coordinates. It is solved for fixed nuclear coordinates, such that different arrangements of nuclei yields different functions of the electronic coordinates. The total molecular energy can then be calculated by solving the electronic Schrödinger equation and including the constant repulsive nuclear term.

$$E_{\text{total}} = E_{\text{elec}} + \sum_{i=1}^{M} \sum_{j>i}^{M} \frac{Z_i Z_j}{|R_i - R_j|}$$

Many-Electron Wavefunctions

References: [5]

The many-electron wavefunction, which describes all fermions in given molecular system, must satisfy the Pauli principle. This requires that the many-electron wavefunction be antisymmetric with respect to the exchange of any two fermions. Hence, valid many-electron wavefunctions must both be eigenfunctions of the Hamiltonian and must satisfy the Pauli principle.

A spatial molecular orbital is defined as a one-particle function of the position vector, spanning the whole molecule. The spatial orbitals form an orthonormal set $\{\psi_i(\mathbf{r})\}$, which if complete can be used to expand any arbitrary function of the position vector, that is, an arbitrary single-particle molecular wavefunction. In practice, only a finite set of such orbitals is available to us, spanning only a subspace of the complete space. Hence, wavefunctions expanded using this finite set are described as being 'exact' only within the subspace spanned.

1. Background

We will now introduce the spin orbitals $\{\phi_i(\mathbf{x})\}$, that is, the set of functions of the composite coordinate $\mathbf{x}$, which describes both the spin and spatial distribution of an electron. Given a set of K spatial orbitals, we can construct $2K$ spin orbitals by taking the product with the orthonormal spin functions $\alpha(\omega)$ and $\beta(\omega)$. Whilst the Hamiltonian operator makes no reference to spin, it is a necessary component when constructing many-electron wavefunctions in order to correctly antisymmetrise the wavefunction with respect to fermion exchange. Constructing the antisymmetric many-electron wavefunction from a finite set of spin orbitals amounts to taking the appropriate linear combinations of symmetric products of N spin orbitals known as Hatree products.

$$\psi_{1,2}(\mathbf{x_1}, \mathbf{x_2}) = \phi_i(\mathbf{x_1})\phi_j(\mathbf{x_2}) \qquad \psi_{2,1}(\mathbf{x_2}, \mathbf{x_1}) = \phi_i(\mathbf{x_2})\phi_j(\mathbf{x_1})$$

$$\Psi_{1,2}(\mathbf{x_1}, \mathbf{x_2}) = \frac{1}{\sqrt{2}}\left[\psi_{1,2}(\mathbf{x_1}, \mathbf{x_2}) - \psi_{2,1}(\mathbf{x_2}, \mathbf{x_1})\right]$$

Figure 1.2: Symmetric Hartree products of spin orbitals ϕ_i and ϕ_j and antisymmetric linear combination of them.

A general procedure for this is achieved by constructing a Slater determinant from the finite set of spin orbitals, where each row relates to the electron coordinate and each column corresponds to the particular spin orbital. Since exchange any two rows or columns of a determinant changes its sign, the following Slater determinant satisfies the Pauli principle.

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_i(\mathbf{x}_1) & \phi_j(\mathbf{x}_1) & \dots & \phi_k(\mathbf{x}_1) \\ \phi_i(\mathbf{x}_2) & \phi_j(\mathbf{x}_2) & \dots & \phi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \phi_i(\mathbf{x}_N) & \phi_j(\mathbf{x}_N) & \dots & \phi_k(\mathbf{x}_N) \end{vmatrix}$$

Figure 1.3: Slater determinant representing an antisymmetrised N-electron wavefunction.

Slater determinants constructed from orthonormal spin orbitals are themselves normalised. N electron Slater determinants constructed from different orthonormal

spin orbitals are orthogonal to one another [5].

By constructing Slater determinants, we have antisymmetrised the many-electron wavefunction to meet the requirements of the Pauli principle. In so doing, we have incorporated exchange correlation, in that, the motion of two electrons with parallel spins is now correlated.

We will now introduce the Hartree-Fock approximation, which yields a set of orthonormal spin orbitals, which when used to construct a single Slater determinant, gives the best variational approximation to the ground state of a system [5]. By treating electron-electron repulsion in an average way, the Hartree-Fock approximation allows us to iteratively solve for spin orbitals until they become the same as the eigenfunctions of the Fock operator. This is known as the Self Consistent Field (SCF) method and is an elegant starting point for finding approximate solutions to the many-electron wavefunction.

For an N electron system, and given a set of $2K$ Hartree-Fock spin orbitals, where $2K > N$, there exist many different single determinants. The Hartree-Fock groundstate being one of these. The remainder are known as excited determinants, recalling that they must all be orthogonal to one-another. By treating the Hartree-Fock ground state as a reference state, we can describe all possible excited states relative to the reference state, as single, double, ..., N-tuple excited states.

Second Quantisation

References: [6], [7]

In second quantisation, both observables and states (by acting on the vacuum state) are represented by operators, namely the creation and annhilation operators [6]. In contrast to the standard formulation of quantum mechanics, operators in second quantisation incorporate the relevant Bose or Fermi statistics each time they act on a state, circumventing the need to keep track of symmetrised or antisymmetrised products of single-particle wavefunctions [7]. Put differently, the antisymmetry of an electronic wavefunction simply follows from the algebra of the creation and

annhilation operators [6], which greatly simplifies the discussion of systems of many identical interacting fermions [7].

The Fock space is a linear abstract vector space spanned by N orthonormal occupation number vectors [6], each representing a single Slater determinant. Hence, given a basis of N spin orbitals we can construct 2^N single Slater determinants, each corresponding to a single occupation number vector in the full Fock space.

Talk about how on dirac notation is binary representation of on vector

The occupation number vector for fermionic systems is succinctly denoted in Dirac notation as below, where the occupation number f_j is 1 if spin orbital j is occupied, and 0 if spin orbital j is unnoccupied.

$$|\psi\rangle = |f_{n-1}\ f_{n-2}\ldots f_1\ f_0\rangle \qquad \text{where } f_j \in 0,1$$

Whilst there is a one-to-one mapping between Slater determinants with canonically ordered spin orbitals and the occupation number vectors in the Fock space, it is important to distinguish between the two since, unlike the Slater determinants, the occupation number vectors have no spatial structure and are simply vectors in an abstract vector space. [6].

Creation and Annhilation Operators

References: [6]

Operators in second quantisation are constructed from the creation and annhilation operators $a_j^\dagger$ and a_j, where the subscripts i and j denote the spin orbital. $a_j^\dagger$ and a_j are one another's Hermitian adjoints, and are not self-adjoint [6].

Taking the excitation of an electron from spin orbital 0 to spin orbital 1 as an example, we can construct the following excitation operator.

$$a_1^\dagger a_0 |0\ldots01\rangle = |0\ldots10\rangle$$

show ladder operators acting on opposite states

1. Background

Due to the fermionic exchange anti-symmetry imposed by the Pauli principle, the action of the creation and annhilation operators introduces a phase to the state that depends on the parity of the spin orbitals preceding the target spin orbital.

$$a_j^\dagger \left| f_{n-1} \ldots f_{j+1}, \; 0, \; f_{j-1} \ldots f_0 \right\rangle = (-1)^{\sum_{s=0}^{j-1} f_s} \left| f_{n-1} \ldots f_{j+1}, \; 1, \; f_{j-1} \ldots f_0 \right\rangle$$

$$a_j \left| f_{n-1} \ldots f_{j+1}, \; 1, \; f_{j-1} \ldots f_0 \right\rangle = (-1)^{\sum_{s=0}^{j-1} f_s} \left| f_{n-1} \ldots f_{j+1}, \; 0, \; f_{j-1} \ldots f_0 \right\rangle$$

In second quantisation, this exchange anti-symmetry requirement is accounted for by the anti-commutation relations of the creation and annhilation operators.

$$\{\hat{a}_j, \hat{a}_k\} = 0 \qquad \{\hat{a}_j^\dagger, \hat{a}_k^\dagger\} = 0 \qquad \{\hat{a}_j, \hat{a}_k^\dagger\} = \delta_{jk}\hat{1} \qquad (1.1)$$

That is, the phase factor required for the second quantised representation to be consistent with the first quantised representation is automatically kept track of by the anticommutation relations of the creation and annhilation operators [6].

Hamiltonian in Second Quantisation

The Hamiltonian in second quantisation is constructed from creation and annhilation operators as follows.

$$\hat{H} = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} h_{ijkl} a_i^\dagger a_j^\dagger a_k a_l + h_{\text{Nu}}$$

Where the one-body matrix element h_{ij} corresponds to the kinetic energy of an electron and its interaction energy with the nuclei.

$$h_{ij} = \int_{-\infty}^{\infty} \psi_{i(x_1)}^* \left(-\frac{1}{2}\nabla^2 + \hat{V}_{(x_1)} \right) \psi_{j(x_1)} \; d^3x_1$$

The two-body matrix element h_{ijkl} corresponds to the repulsive interaction between electrons i and j.

$$h_{ijkl} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_{i(x_1)}^* \psi_{j(x_2)}^* \left(\frac{1}{|x_1 - x_2|} \right) \psi_{k(x_2)} \psi_{l(x_1)} \; d^3x_1 d^3x_2$$

h_{Nu} is a constant corresponding to the repulsive interaction between nuclei. These matrix elements are computed classically, allowing us to compute only the inherently quantum aspects of the problem on a quantum computer.
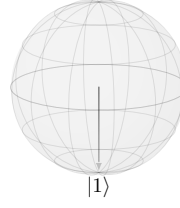
1.2   Quantum Computation

Introduction to Qubits

In quantum computing, the $|0\rangle$ and $|1\rangle$ states form the computational basis. They are vectors in a two-dimensional complex Hilbert space $\mathbb{C}^2$. We can depict these computational basis states on a Bloch sphere.
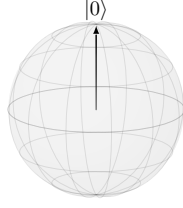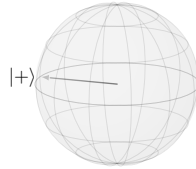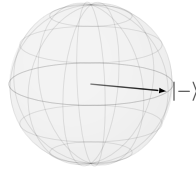
Figure 1.4: $|0\rangle$ state

Figure 1.5: $|1\rangle$ state

We can choose any pair of orthonormal states to form our computational basis.

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

Figure 1.6: $|+\rangle$ state

Figure 1.7: $|-\rangle$ state

More generally, any qubit $|\psi\rangle$ can be represented as complex linear combination of the chosen basis, provided that the qubit state vector is normalised.

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle \qquad |\alpha|^2 + |\beta|^2 = 1 \qquad \alpha, \beta \in \mathbb{C}$$

1.3   Fermion-Qubit Encodings

Jordan-Wigner Transformation

References: [8]

The form of the occupation number representation vector and the qubit statevector suggests the following identification between electronic states and qubit states.

$$|f_{n-1} \dots f_0\rangle \quad \rightarrow \quad |q_{n-1} \dots q_0\rangle$$

That is, we allow each qubit to store the occupation number of a given spin-orbital. Hence, in order to actually simulate a Hamiltonian we must map the fermionic creation and annhilation operators onto qubit operators, and these operators must behave in the same way as their fermionic analogues.

$$\hat{Q}^+ |0\rangle = |1\rangle \qquad \hat{Q}^+ |1\rangle = 0 \qquad \hat{Q} |1\rangle = |0\rangle \qquad \hat{Q} |0\rangle = 0$$

The qubit operators must also preserve the fermionic anti-commutation relations in order to satisfy the Pauli antisymmetry requirement.

$$\{\hat{Q}_j, \hat{Q}_k\} = 0 \qquad \{\hat{Q}_j^\dagger, \hat{Q}_k^\dagger\} = 0 \qquad \{\hat{Q}_j, \hat{Q}_k^\dagger\} = \delta_{jk}$$

One such qubit encoding is known as the Jordan-Wigner transformation. It expresses the fermionic creation and annhilation operators as a linear combination of the Pauli matrices.

$$\hat{Q}^+ = |1\rangle \langle 0| = \frac{1}{2}(X - iY) \qquad \hat{Q} = |0\rangle \langle 1| = \frac{1}{2}(X + iY)$$

When dealing with **multiple-qubits**, we must also account for the occupation parity of the qubits preceding the target qubit j.

$$a_j^\dagger |f_{n-1} \dots f_{j+1}, \ 0, \ f_{j-1} \dots f_0\rangle = (-1)^{\sum_{s=0}^{j-1} f_s} |f_{n-1} \dots f_{j+1}, \ 1, \ f_{j-1} \dots f_0\rangle$$

We do this by introducing a string of Pauli Z operators that computes the parity of the qubits preceding the target qubit.

$$\hat{a}_j^+ = \frac{1}{2}(X - iY) \prod_{k=1}^{j-1} Z_k \qquad \hat{a}_j = \frac{1}{2}(X + iY) \prod_{k=1}^{j-1} Z_k$$

Where $\prod$ is the tensor product.

A more compact notation is,

$$\hat{a}_j^+ = \frac{1}{2}(X - iY) \otimes Z_{j-1}^{\rightarrow} \qquad \hat{a}_j = \frac{1}{2}(X + iY) \otimes Z_{j-1}^{\rightarrow}$$

Where $Z_i^{\rightarrow}$ is the parity operator with eigenvalues ± 1, and ensures the correct phase is added to the qubit state vector.

$$Z_i^{\rightarrow} = Z_i \otimes Z_{i-1} \otimes \cdots \otimes Z_0$$

For instance, the creation operator $a_3^{\dagger}$ maps to the following Pauli string,

$$\hat{a}_3^{\dagger} = \frac{1}{2}(X_3 - iY_3) \otimes Z_2 \otimes Z_1 \otimes Z_0$$
$$\hat{a}_3^{\dagger} = \frac{1}{2}(X_3 \otimes Z_2 \otimes Z_1 \otimes Z_0) - \frac{1}{2}i(Y_3 \otimes Z_2 \otimes Z_1 \otimes Z_0)$$

Usually we drop the subscript specifying the orbital acted on.

1.4   Unitary Coupled Cluster

References: [9], [3], [10]

Within the traditional coupled-cluster framework, the ground electronic state is prepared by applying the CC operator to a reference state (usually Hartree-Fock).

$$|\psi\rangle = e^{\hat{T}}|\phi_0\rangle$$

Where $\hat{T}$ is the cluster excitation operator.

Quantum gates, however, must be unitary operators, so instead, we work within the UCC framework.

$$|\psi\rangle = e^{\hat{T}}|\phi_0\rangle$$

Where $\hat{T}$ is now an **anti-Hermitian** operator, and $e^{\hat{T}}$ is unitary.

In general, we can prepare exact electronic states by applying a sequence of k parametrised unitary operators to our reference state.

$$|\psi\rangle = \prod_i^k U_i(\theta_i)|\phi_0\rangle$$

Where $U_i(\theta_i)$ is a parametrised unitary operator

The parameters θ_i are then optimised to find the ground state energy.

General fermionic single and double excitation operators are defined as,

$$a_q^\dagger a_p \text{ and } a_r^\dagger a_s^\dagger a_q a_p$$

Exciting one electron from p to q, and two electrons from p, q to r, s respectively.

1. Background

Taking a linear combination of these, we obtain **anti-Hermitian** fermionic single and double excitation operators.

$$\hat{\kappa}_p^q = a_q^\dagger a_p - a_p^\dagger a_q$$

$$\hat{\kappa}_{pq}^{rs} = a_r^\dagger a_s^\dagger a_q a_p - a_p^\dagger a_q^\dagger a_s a_r$$

Such that upon exponentiating, we obtain **unitary** operators.

$$U_p^q = e^{\hat{\kappa}_p^q} \qquad U_{pq}^{rs} = e^{\hat{\kappa}_{pq}^{rs}}$$
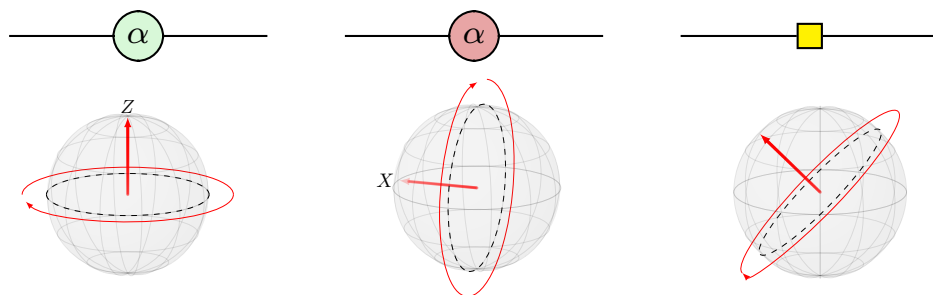
Chapter 2

ZX Calculus

[Insert introductory paragraph]

2.1 Generators

Z and X Spiders

Single Qubit Rotations

An arbitrary rotation in the X basis can be depicted by a single X spider with phase α.

Figure 2.1: Bloch sphere representation.

2.2 Rewrite Rules

2.3   Phase Gadgets

1. zx representation

2. algebraic structure

3. relation to chemistry

4. phase gadget decomposition / ladder / bricklayering

2.4   Pauli Gadgets

$$C \in \text{Clifford} \qquad P \in \text{Pauli}$$

$$\text{prove: } Ce^{P}C^{\dagger} = e^{CPC^{\dagger}}$$

$$CP^{n}C^{\dagger} = (CPC^{\dagger})^{n}$$

$$Ce^{P}C^{\dagger} = C \sum_{n=0}^{\infty} \left(\frac{P^{n}}{n!} \right) C^{\dagger} = \sum_{n=0}^{\infty} \frac{CP^{n}C^{\dagger}}{n!} = \sum_{n=0}^{\infty} \frac{(CPC^{\dagger})^{n}}{n!}$$

2.5   ZxFermion Software Package

ZxFermion is a Python package built on top of PyZX designed for the manipulation and visualisation of circuits of Pauli gadgets. With built-in Clifford tableau logic using Stim, ZxFermion allows users to quickly implement proofs and test ideas.

VQE algorithms used in quantum chemistry often utilise the UCC framework in which excitation operators have a natural representation as Pauli gadgets. ZxFermion provides a comprehensive toolset designed to be used in a Jupyter notebook environment. Export functionality can be used to generated research paper quality diagrams.

Creating Gadgets

Creating Circuits of Gadgets

Pauli & Clifford Algebra

from zxfermion.gates **import** X, XPlus, XMinus, Z, ZPlus

```
XPlus + XMinus
>> Identity
```

Architecture-Aware Circuit Extraction

Chapter 3

Variational Quantum Eigensolver

[Insert introductory paragraph]

3.1 Variational Principle

3.2 Exponential Excitation Operators

Recalling the Jordan-Wigner encoding for the creation and annhilation operators,

$$\hat{a}_j^+ = \frac{1}{2}(X - iY) \otimes Z_{j-1}^{\rightarrow} \qquad \hat{a}_j = \frac{1}{2}(X + iY) \otimes Z_{j-1}^{\rightarrow}$$

The anti-Hermitian fermionic single and double excitation operators κ_p^q and κ_{pq}^{rs}

$$F_p^q = \frac{i}{2}(Y_p X_q - X_p Y_q) \prod_{k=p+1}^{q-1} Z_k$$

$$F_{pq}^{rs} = \frac{i}{8}(X_p X_q Y_s X_r + Y_p X_q Y_s Y_r + X_p Y_q Y_s Y_r + X_p X_q X_s Y_r -$$

$$Y_p X_q X_s X_r - X_p Y_q X_s X_r - Y_p Y_q Y_s X_r - Y_p Y_q X_s Y_r) \prod_{k=p+1}^{q-1} Z_k \prod_{l=r+1}^{s-1} Z_l$$

Multiplying by θ and exponentiating yields the parametrised unitary qubit operators,

$$U_p^q(\theta) = \exp\left(i\frac{\theta}{2}(Y_p X_q - X_p Y_q) \prod_{k=p+1}^{q-1} Z_k\right)$$

3. Variational Quantum Eigensolver

$$U_{pq}^{rs}(\theta) = \exp\left(i\frac{\theta}{8}(X_pX_qY_sX_r + \cdots - Y_pY_qY_sX_r - Y_pY_qX_sY_r) \prod_{k=p+1}^{q-1} Z_k \prod_{l=r+1}^{s-1} Z_l\right)$$

To summarise, we constructed anti-Hermitian single and double excitation operators from a linear combination of fermionic excitation operators,

$$\hat{\kappa}_p^q = a_q^\dagger a_p - a_p^\dagger a_q \qquad \hat{\kappa}_{pq}^{rs} = a_r^\dagger a_s^\dagger a_q a_p - a_p^\dagger a_q^\dagger a_s a_r$$

We then mapped these to qubit operators using the Jordan-Wigner transformation,

$$\hat{\kappa}_p^q \xrightarrow{\text{JW}} F_p^q \qquad\qquad \hat{\kappa}_{pq}^{rs} \xrightarrow{\text{JW}} F_{pq}^{rs}$$

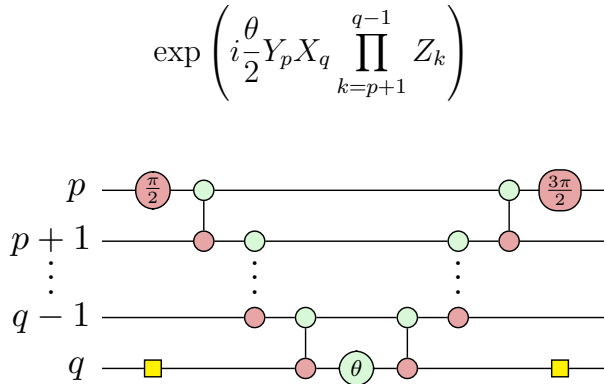And finally, we exponentiated to yield the parametrised unitary qubit operators.

$$U_p^q(\theta) = e^{\theta_p^q F_p^q} \qquad U_{pq}^{rs}(\theta) = e^{\theta_{pq}^{rs} F_{pq}^{rs}}$$

Let's look again at the parametrised single-body unitary operator,

$$U_p^q(\theta) = \exp\left(i\frac{\theta}{2}(Y_pX_q - X_pY_q) \prod_{k=p+1}^{q-1} Z_k\right)$$

$$U_p^q(\theta) = \left(\exp\left[i\frac{\theta}{2}Y_pX_q \prod_{k=p+1}^{q-1} Z_k\right]\right)\left(\exp\left[-i\frac{\theta}{2}X_pY_q \prod_{k=p+1}^{q-1} Z_k\right]\right)$$

The first exponential term can be implemented by the following phase gadget.

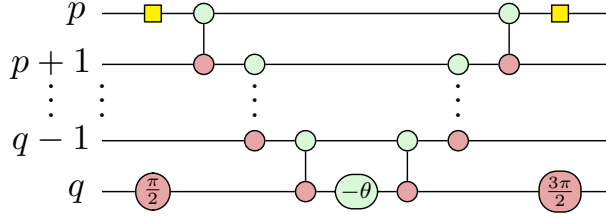$$\exp\left(i\frac{\theta}{2}Y_pX_q \prod_{k=p+1}^{q-1} Z_k\right)$$

Left CNOT ladder construction calculates the parity of the qubit state, and applies a rotation in the Z basis if the parity is odd.

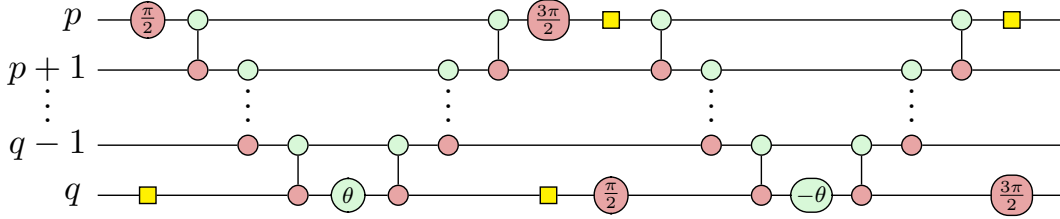*3. Variational Quantum Eigensolver*

Whilst the second exponential term can be implemented by the phase gadget.

$$\exp\left(-i\frac{\theta}{2}X_p Y_q \prod_{k=p+1}^{q-1} Z_k\right)$$

Together, they constitute the single-body unitary excitation operator $U_p^q(\theta)$

By defining the ordering of spin-orbitals such that adjacent spin-orbitals share the same spatial orbital, adjacent single-body operators commute.

$$\left[\hat{\kappa}_p^q, \hat{\kappa}_{p+1}^{q+1}\right] = 0$$

The same is therefore true for the resulting qubit operators,

$$\left[F_p^q, F_{p+1}^{q+1}\right] = 0$$

$$p, q \in \text{even} \qquad p+1, q+1 \in \text{odd}$$

This allows us to define the parametrised unitary qubit operators in terms of spin-adapted excitation operators.

$$U_p^q(\theta) = \exp\left[\theta\left(F_p^q + F_{p+1}^{q+1}\right)\right]$$

3. Variational Quantum Eigensolver

In other words, since F_p^q and F_{p+1}^{q+1} commute, we can think of them as a single operator with a single parameter.

3.3 Discretely-Optimised VQE

Excitation Operators in ZXC

3.4   One Body Excitation Operator

3.5   Two Body Excitation Operator
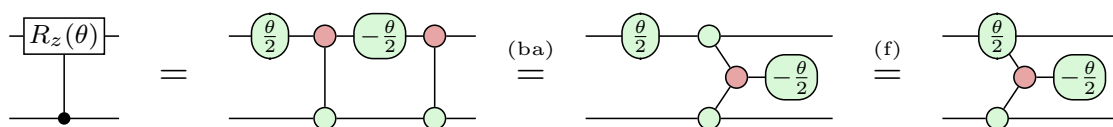
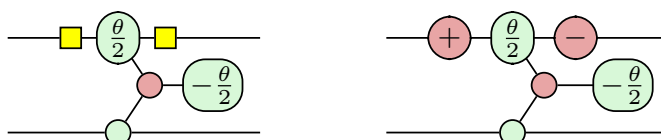## 3.6 Spin-Adapted Single Body Excitations

Chapter 4

Controlled Rotations

4.1 Singly-Controlled Rotations

Singly-controlled Z rotation.

Singly-controlled X and Y rotations obtained by conjugating the control qubit.

4.2 Doubly-Controlled Rotations

hello world

4.3 Triply-Controlled Rotations

hello world hello world

Appendices

Bibliography

[1] Burton, H. G. A., Marti-Dafcik, D., Tew, D. P. & Wales, D. J. Exact electronic states with shallow quantum circuits from global optimisation. *npj Quantum Information* **9** (2023).

[2] Yeung, R. Diagrammatic design and study of ansätze for quantum machine learning (2020). `2011.11073`.

[3] McClean, J. R., Romero, J., Babbush, R. & Aspuru-Guzik, A. The theory of variational hybrid quantum-classical algorithms. *New Journal of Physics* **18**, 023023 (2016).

[4] Kirby, W. M. & Love, P. J. Variational quantum eigensolvers for sparse hamiltonians. *Phys. Rev. Lett. 127, 110503 (2021)* **127**, 110503 (2020). `2012.07171`.

[5] Szabó, A. v. & Ostlund, N. S. *Modern quantum chemistry : introduction to advanced electronic structure theory* (Mineola (N.Y.) : Dover publications, 1996). URL `http://lib.ugent.be/catalog/rug01:000906565`.

[6] Helgaker, T., Jørgensen, P. & Olsen, J. *Molecular Electronic-Structure Theory* (Wiley, 2000).

[7] Fetter, A. L., Walecka, J. D. & Kadanoff, L. P. *Quantum Theory of Many Particle Systems*, vol. 25 (AIP Publishing, 1972).

[8] Seeley, J. T., Richard, M. J. & Love, P. J. The bravyi-kitaev transformation for quantum computation of electronic structure. *The Journal of Chemical Physics* **137** (2012). `1208.5986`.

[9] Anand, A. *et al.* A quantum computing view on unitary coupled cluster theory. *Chemical Society Reviews* **51**, 1659–1684 (2021). `2109.15176`.

[10] Chan, H. H. S., Fitzpatrick, N., Segarra-Martí, J., Bearpark, M. J. & Tew, D. P. Molecular excited state calculations with adaptive wavefunctions on a quantum eigensolver emulation: reducing circuit depth and separating spin states. *Physical Chemistry Chemical Physics* **23**, 26438–26450 (2021).