Diagrammatic Design of Ansätze for Quantum Chemistry

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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

Chapter 1

Background

In this chapter, we will discuss the methods required to simulate fermionic systems on a quantum computer. Starting with the Hamiltonian of the system, we will introduce the second quantisation, unitary coupled cluster theory and finally a variational quantum algorithm known as the Variational Quantum Eigensolver.

1.1 Fermionic Simulation Scheme

- hamiltonian in first quantisation

- born oppenheimer approximation

- hamiltonian in second quantisation

- anti commutation relations of creation/annhilation operators

- introduction to unitary coupled cluster theory

In order to simulate a fermionic system on a quantum computer, we must map the fermionic state to a qubit state. This is usually done using the occupation number representation [REF SECTION]. We then act on the qubit state with unitary operations that represent the fermionic operations. In order not to violate the Pauli principle, we must choose a fermion-qubit mapping that preserves the fermionic anti-commutation relations. The most common mapping, and the one used throughout this text, is known as the Jordan-Wigner transformation [REF

1. Background

SECTION]. Then, by acting on the qubit state with the unitary qubit operator, we obtain the resultant qubit state, which in the occupation number representation, simply represents the fermionic wavefunction.

A successful simulation scheme is one that reproduces the action of the fermionic operator [CITE BRAVYI-KITAEV PAPER].

1.2   Electronic Structure Theory

In second quantisation, both observables and states (by acting on the vacuum state) are represented by operators, namely the creation and annhilation operators [5]. 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 [6]. Put differently, the antisymmetry of an electronic wavefunction simply follows from the algebra of the creation and annhilation operators [5], which greatly simplifies the discussion of systems of many identical interacting fermions [6].

Occupation Number Representation

The Fock space is a linear abstract vector space spanned by N orthonormal occupation number vectors [5], 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. [5].

$$|\psi_1\rangle = |0\ldots 1\rangle = \begin{pmatrix} 1 \\ \vdots \\ 0 \end{pmatrix} \qquad \ldots \qquad |\psi_N\rangle = |1\ldots 1\rangle = \begin{pmatrix} 0 \\ \vdots \\ 1 \end{pmatrix}$$

Creation and Annhilation Operators

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 [5].

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

$$a_1^\dagger a_0 \left|0 \ldots 01\right\rangle = \left|0 \ldots 10\right\rangle$$

SHOW LADDER OPERATORS ACTING ON OPPOSITE STATES 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.

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

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 [5].

Second Quantised Hamiltonian

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.

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

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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.

1.3   Fermion-Qubit Encodings

see [7]

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.

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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

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.

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

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

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

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

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

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,

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

$$U_{pq}^{rs}(\theta) = \exp\left(i\frac{\theta}{8}(X_p X_q Y_s X_r + \cdots - Y_p Y_q Y_s X_r - Y_p Y_q X_s Y_r) \prod_{k=p+1}^{q-1} Z_k \prod_{l=r+1}^{s-1} Z_l \right)$$

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

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

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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.

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

Appendices

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