

Diagrammatic Design of Ansätze for Quantum Chemistry



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Pour ma mère et mon père.
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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

1	Background	1
1.1	Fermionic Simulation Scheme	1
1.2	Electronic Structure Theory	3
 Appendices		
	Bibliography	8

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 ... we will introduce the ... and finally a variational quantum algorithm known as the Variational Quantum Eigensolver.

1.1 Fermionic Simulation Scheme

Let us first develop a general fermionic simulation scheme.

- hamiltonian in first quantisation
- born oppenheimer approximation
- hamiltonian in second quantisation
- anti commutation relations of creation/annihilation 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

1. Background

used throughout this text, is known as the Jordan-Wigner transformation [REF 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. Background

1.2 Electronic Structure Theory

Electronic Structure Problem

The main interest of electronic structure theory is the electronic structure problem, which concerns itself with finding approximate solutions to the non-relativistic time-independent Schrödinger equation, $H|\psi\rangle = E|\psi\rangle$.

It is an eigenvalue equation of the full molecular Hamiltonian H which describes all the possible interactions within a molecular system of N electrons and M nuclei. Below is the 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.

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

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 a purely 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

1. Background

Hamiltonian for N electrons.

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

We will only concern ourselves with the electronic Hamiltonian throughout the remainder of this text, 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

something

Second Quantisation

In second quantisation, both observables and states (by acting on the vacuum state) are represented by operators, namely the creation and annihilation 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 annihilation 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,

1. Background

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 unoccupied.

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

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].

$$|\psi_1\rangle = |0 \dots 1\rangle = \begin{pmatrix} 1 \\ \vdots \\ 0 \end{pmatrix} \quad \dots \quad |\psi_N\rangle = |1 \dots 1\rangle = \begin{pmatrix} 0 \\ \vdots \\ 1 \end{pmatrix}$$

Creation and Annihilation Operators

Operators in second quantisation are constructed from the creation and annihilation 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.

$$a_1^\dagger a_0 |0 \dots 01\rangle = |0 \dots 10\rangle$$

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 annihilation operators introduces a phase to the state that depends on

1. Background

the parity of the spin orbitals preceding the target spin orbital.

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

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

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

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 annihilation operators [5].

Second Quantised Hamiltonian

The Hamiltonian in second quantisation is constructed from creation and annihilation 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.

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

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

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

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.

Appendices

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