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

Chapter 1

ZX Calculus

The ZX calculus is a diagrammatic language for reasoning about quantum processes that has seen a large increase in applications over the past 10 years. It provides a novel perspective on quantum computation and quantum mechanics.

1.1 Generators

Let us start by introducing two generators: the *Z Spider* (green) and the *X Spider* (red). By sequentially or horizontally composing these generators, we can construct undirected multigraphs known as ZX diagrams [5]. That is, graphs that allow multiple edges between vertices. Since *only connectivity matters* in the ZX calculus, a valid ZX diagram can be deformed as seen fit, provided that the order of inputs and outputs is preserved.

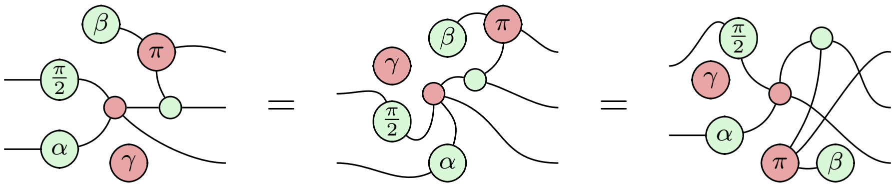
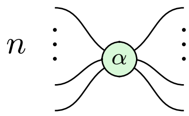


Figure 1.1: Three equivalent ZX diagrams (*only connectivity matters*).

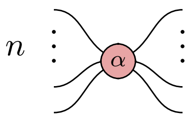
Z Spiders are defined with respect to the Z eigenbasis such that a Z Spider with n inputs and m outputs has the following interpretation as a linear map. Note that in this text, we will interpret the flow of time from left to right.



$$= |0\rangle^{\otimes m} \langle 0|^{\otimes n} + e^{i\alpha} |1\rangle^{\otimes m} \langle 1|^{\otimes n}$$

Figure 1.2: Interpretation of Z Spider as a linear map.

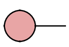
Similarly, X Spiders, which are defined with respect to the X eigenbasis, are interpreted as the following linear map.



$$= |+\rangle^{\otimes m} \langle +|^{\otimes n} + e^{i\alpha} |-\rangle^{\otimes m} \langle -|^{\otimes n}$$

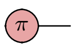
Figure 1.3: Interpretation of X Spider as a linear map.

We can recover the $|0\rangle$ eigenstate using an X Spider that has a phase of zero, or the $|1\rangle$ eigenstate using an X Spider that has a phase of π.



$= |+\rangle + |-\rangle = \sqrt{2}\,|0\rangle$

Figure 1.4: $|0\rangle$ eigenstate



$= |+\rangle - |-\rangle = \sqrt{2}\,|1\rangle$

Figure 1.5: $|1\rangle$ eigenstate

Likewise, we have the $|+\rangle$ and $|-\rangle$ basis states from the corresponding Z Spider

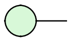
 $= |0\rangle + |1\rangle = \sqrt{2}\,|+\rangle$

Figure 1.6: $|+\rangle$ eigenstate

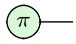
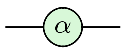
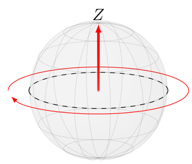
 $= |0\rangle - |1\rangle = \sqrt{2}\,|-\rangle$

Figure 1.7: $|-\rangle$ eigenstate

Whilst we obtain the correct states, we obtain the wrong scalar factor. For the remainder of this thesis, we will ignore global non-zero scalar factors. Hence, equal signs should be interpreted as 'equal up to a global phase'.

Single qubit rotations in the Z basis are represented by a Z Spider with a single input and a single output. Arbitrary rotations in the X basis are represented by the corresponding X spider. We can view these as rotations of the Bloch sphere.

 $= |0\rangle\langle 0| + e^{i\alpha}|1\rangle\langle 1| = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\alpha} \end{pmatrix} \rightarrow$ 

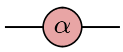
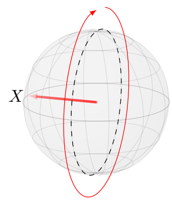
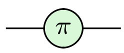
 $= |+\rangle\langle +| + e^{i\alpha}|-\rangle\langle -| = \frac{1}{2}\begin{pmatrix} 1+e^{i\alpha} & 1-e^{i\alpha} \\ 1-e^{i\alpha} & 1+e^{i\alpha} \end{pmatrix} \rightarrow$ 

Figure 1.8: Arbitrary single qubit rotations in the Z and X bases.

We can recover the Pauli Z and Pauli X matrices by setting the angle $\alpha = \pi$.

 $= |0\rangle\langle 0| + e^{i\pi}|1\rangle\langle 1| = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

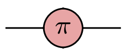
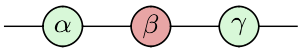
 $= |+\rangle\langle +| + e^{i\pi}|-\rangle\langle -| = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Figure 1.9: Pauli Z and X gates as ZX diagrams.

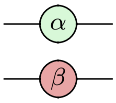
Composition

To calculate the matrix of a ZX diagram consisting of sequentially composed spiders, we take the matrix product. Note that the order of operation of matrix multiplication is the reverse as in the ZX diagram as we have defined it.



$$= \begin{pmatrix} 1 & 0 \\ 0 & e^{i\gamma} \end{pmatrix} \begin{pmatrix} 1+e^{i\beta} & 1-e^{i\beta} \\ 1-e^{i\beta} & 1+e^{i\beta} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & e^{i\alpha} \end{pmatrix}$$

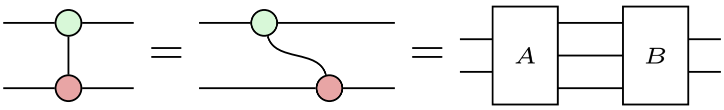
Alternatively, we could have chosen to compose the spiders in parallel, resulting in the tensor product.



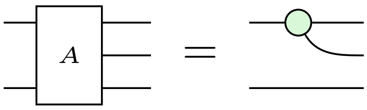
$$= \begin{pmatrix} 1 & 0 \\ 0 & e^{i\alpha} \end{pmatrix} \otimes \begin{pmatrix} 1+e^{i\beta} & 1-e^{i\beta} \\ 1-e^{i\beta} & 1+e^{i\beta} \end{pmatrix}$$

Deriving the CNOT Gate

Let us now derive the CNOT gate, which in the ZX calculus, is represented by a Z spider (control qubit) and an X spider (target qubit). We can arbitrarily deform the diagram and decompose it into matrix and tensor products as follows.

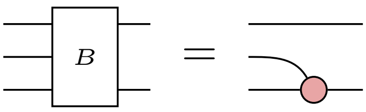


We can calculate matrix A, consisting of a single-input and two-output Z Spider (4×2 matrix) and an empty wire (identity matrix), by taking the tensor product.



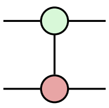
$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Similarly, to calculate the matrix B, we take the following tensor product.



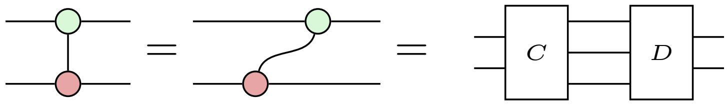
$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

Note that the order of the tensor product depends on the order of the input and output wires. We can then calculate the final matrix by taking the matrix product of matrix A and matrix B as follows.



$$= \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \right] \left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right] = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Since *only connectivity matters*, we could have equivalently calculated the matrix of the CNOT gate by deforming the diagram as follows.



All quantum gates are unitary transformations. Therefore, up to a global phase, an arbitrary single qubit rotation U can be viewed as a rotation of the Bloch sphere about some axis. We can decompose the unitary U using Euler angles to represent the rotation as three successive rotations [5].

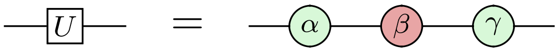


Figure 1.10: Arbitrary single-qubit rotation.

Hadamard Generator

Recall that the Hadamard gate H switches between the $|0\rangle/|1\rangle$ and $|+\rangle/|-\rangle$ bases. That is, it corresponds to a rotation of the Bloch sphere by π radians about the line bisecting the X and Z axes. By choosing $\alpha = \beta = \gamma = \frac{\pi}{2}$, we obtain the Hadamard gate up to a global phase of $e^{-i\frac{\pi}{4}}$. We define the Hadamard generator as follows.

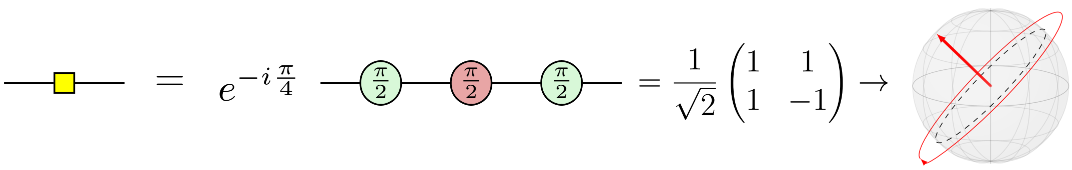


Figure 1.11: Hadamard generator in the ZX calculus.

There are many equivalent ways of decomposing the Hadamard gate using Euler angles. The rightmost representations need no scalar corrections.

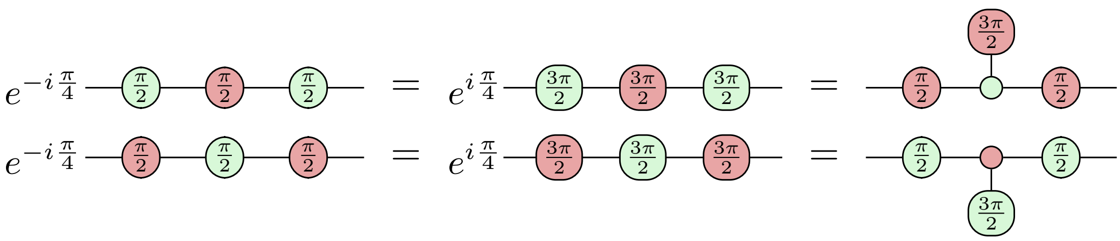
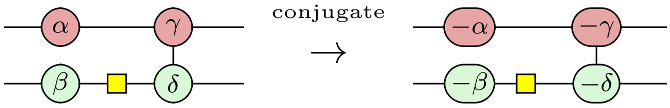


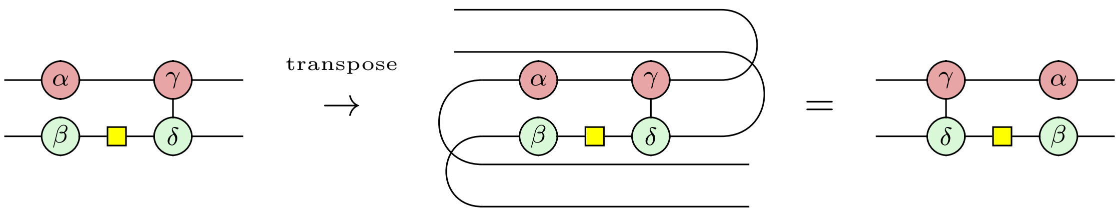
Figure 1.12: Equivalent definitions of the Hadamard generator.

Conjugate, Transpose and Adjoint

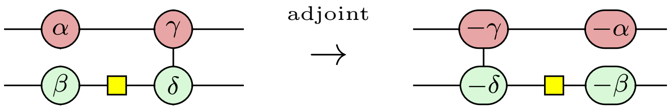
We can find the conjugate of a ZX diagram by simply negating the phases of all spiders in the diagram, $\alpha \to -\alpha, \beta \to -\beta, \ldots$.



Intuitively, we can find the transpose of a ZX diagram by turning all inputs into outputs and all outputs into inputs.



It is then a simple matter to find the Hermitian adjoint of a ZX diagram by first finding its conjugate, then its transpose.



Appendices

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