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.

Acknowledgements

Thank you Thomas Cervoni for your constant motivation and support.
Thank you David Tew and Stefano Gogioso for your patient supervision.
Thank you Razin Shaikh, Boldizsár Poór, Richie Yeung and Harny Wang for always finding the time to answer my questions.
Thank you to my friends and family for supporting me during this unconvential Master's.

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

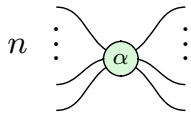
ZX Calculus

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 and the X Spider. By sequentially or horizontally composing these generators, we can construct undirected multigraphs known as ZX diagrams. That is, graphs that allow multiple edges between vertices [5]. A ZX diagram is one level of abstraction above a quantum circuit. It represents the linear map between some input state and some output state.

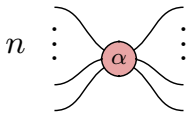
Z Spiders are defined with respect to the Z eigenbasis such that a Z Spider with any number of inputs and outputs has the following interpretation as a linear map. Note that in this text, we will interpret the flow of time from left to right.



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

Figure 1.1: Interpretation of Z Spider as a linear map.

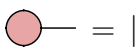
Similarly, X Spiders, which are defined with respect to the X eigenbasis, are interpreted as the following linear map.



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

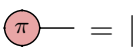
Figure 1.2: Interpretation of X Spider as a linear map.

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



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

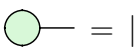
Figure 1.3: $|0\rangle$ eigenstate



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

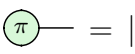
Figure 1.4: $|1\rangle$ eigenstate

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



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

Figure 1.5: $|+\rangle$ eigenstate

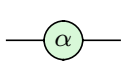


$$= |0\rangle - |1\rangle = \sqrt{2}\,|-\rangle$$

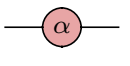
Figure 1.6: $|-\rangle$ eigenstate

Importantly, whilst we recover 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 X basis are represented by a Z Spider with a single input and a single output, whilst single qubit rotations in the X basis are represented by the corresponding X spider.



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



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

Figure 1.7: Arbitrary single qubit rotations in the Z and X bases.

Recall single qubit rotations can be interpreted as rotations of the qubit state vector inside the Bloch sphere.

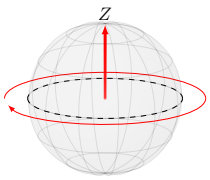


Figure 1.8: lorum ipsum

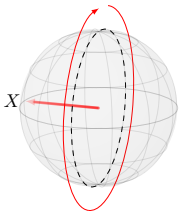
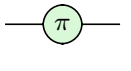
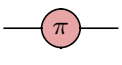


Figure 1.9: lorum ipsum

The Pauli Z and Pauli X matrices are obtained by setting $\alpha = \pi$.



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



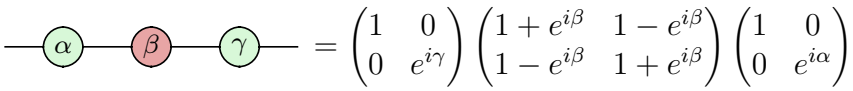
$$= |+\rangle\langle +| + e^{i\pi}|-\rangle\langle -| = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Figure 1.10: Arbitrary single qubit rotations in the Z and X bases.

Only Connectivity Matters

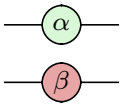
Composition

We can take the matrix product by sequentially composing spiders in a ZX diagram. Note that the order of operation for matrix multiplication is from right to left, the opposite of the ZX diagram as we have defined it.



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

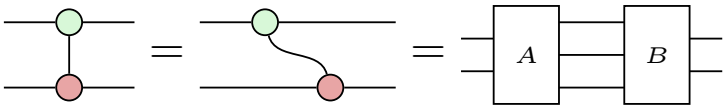
Alternatively, we could have chosen to compose the spider in parallel, resulting in the tensor product.

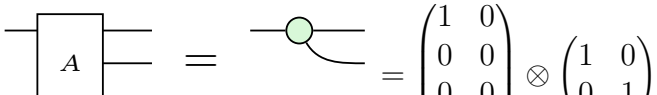


$$= \begin{pmatrix} 1 & 0 \\ 0 & e^{i\alpha} \end{pmatrix} \otimes \begin{pmatrix} 1+e^{i\beta} & 1-e^{i\beta} \\ 1-e^{i\beta} & 1+e^{i\beta} \end{pmatrix}$$

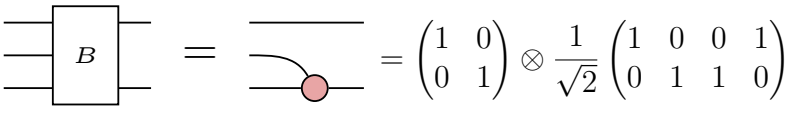
For instance, the CNOT gate, which is defined as the following diagram ...

Can be decomposed into matrix products and tensor products of spiders.

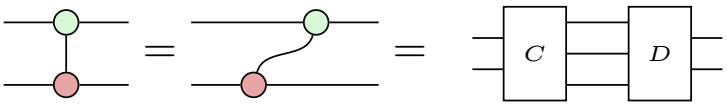


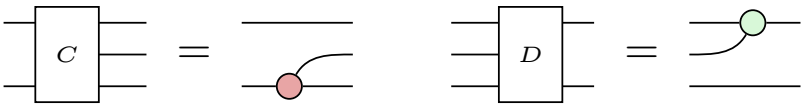


$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$



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




C
=
D
=

1.2 Adjoints and Transpose

Given an arbitrary ZX diagram, we can construct

In order to find the adjoint of a ZX diagram, we simply negate all of the phases in the spiders $\alpha \to -\alpha$, $\beta \to -\beta$, etc.

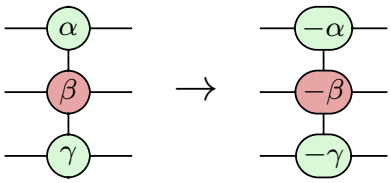


Figure 1.11: Adjoint

1.3 Rewrite Rules

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] van de Wetering, J. Zx-calculus for the working quantum computer scientist (2020). 2012.13966.