Modelling the Hydrogen Molecule (H₂) with Quantum Circuits

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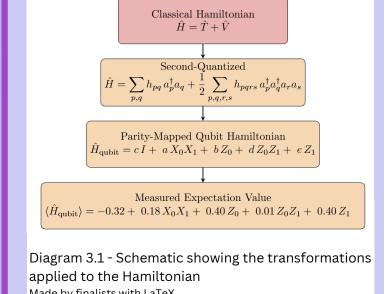
1 - Background

Quantum vs Classical

Quantum Computer	Classical Computer
Uses quantum bits [qubits]	Uses bits
Has quantum properties [eg. superposition & entanglement]	Does not have quantum properties
Innately probabilistic	Deterministic

Table 1.1 - Differences between a Quantum and a Classical computer
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Graphic 1.2 - Visual representation between a bit and a qubit
Made by finalists with Procreate

- Exponential scaling
- Relies of approximations for Quantum Chemistry
- Less accurate & efficient

vs

- Polynomial scaling
- Inherent quantum nature of electrons
- Can handle large molecules

Graphic 1.3 - The quantum advantage
Icons taken from Canva Element Library

Classical Quantum Correspondence

Quantum Gates	⇌	Matrices
Wavefunctions	⇌	Sum of complex vector states
Measurement	⇌	Distribution sampling

Hence, classical computers can simulate quantum circuits

Table 1.4 - Made with Canva

Operator	Gate(s)	Matrix
Pauli-X (X)	[X]	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$
Phase (S, P)	[S]	$\begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix}$
π/8 (T)	[T]	$\begin{bmatrix} 1 & 0 \\ 0 & e^{i\pi/4} \end{bmatrix}$
Controlled Not (CNOT, CX)		$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$

Figure 1.5 [2]

Graphic 1.6 - Schematic showing how Quantum Computational Chemistry is carried out on Quantum Computers [1]

Applications of Quantum Chemistry

- Determining fundamental molecular characteristics
- Drug discovery and biochemistry
- Innovations in material science (nanotech, superconductors, etc)
- Integrations in engineering processes and solutions
- Analyse catalytic and reaction mechanisms

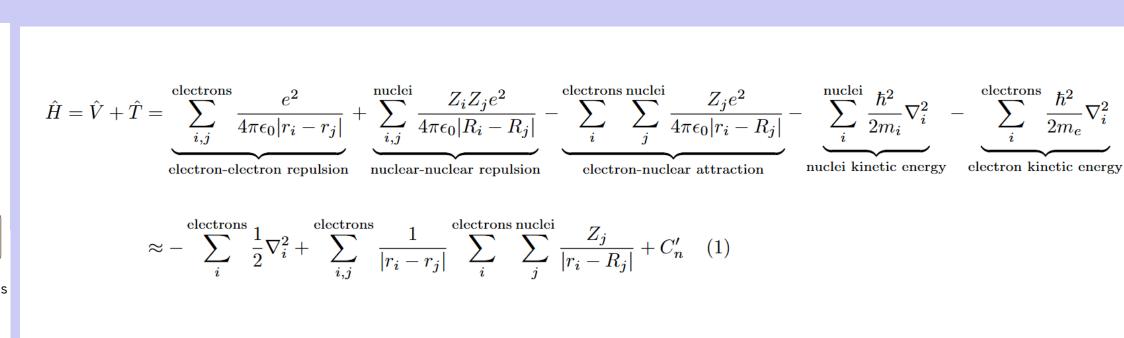Table 1.7 - Made by finalists with Canva

2 - Objective

- Assess the **effectiveness and accuracy** of the Variational Quantum Eigensolver [VQE] in computing molecular ground state energies and molecular geometry
- Quantitatively characterise the **effects of noise**, in particular thermal relaxation noise, on simulation outcomes
- Develop a **well documemted, streamlined framework** for future researchers that leverages the VQE approach

3 - Hamiltonian Representation

The Hamiltonian is the sum of potential and kinetic energy of particles in the system. The **Born-Oppenheimer Approximation** is used to assume the nucleus as stationary and hence the nuclear repulsion energy as a constant C'n. Atomic units [$\hbar = m_e = e = 4\pi\varepsilon_0 = 1$] are used to simplify the expression further.

Diagram 3.1 - Schematic showing the transformations applied to the Hamiltonian
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$$\hat{H} = \hat{V} + \hat{T} = \underbrace{\sum_{i<j}^{\text{electrons}} \frac{e^2}{4\pi\varepsilon_0|r_i - r_j|}}_{\text{electron-electron repulsion}} + \underbrace{\sum_{i<j}^{\text{nuclei}} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0|R_i - R_j|}}_{\text{nuclear-nuclear repulsion}} - \underbrace{\sum_{i}^{\text{electrons}} \sum_{j}^{\text{nuclei}} \frac{Z_j e^2}{4\pi\varepsilon_0|r_i - R_j|}}_{\text{electron-nuclear attraction}} - \underbrace{\sum_{i}^{\text{nuclei}} \frac{\hbar^2}{2m_i}\nabla_i^2}_{\text{nuclei kinetic energy}} - \underbrace{\sum_{i}^{\text{electrons}} \frac{\hbar^2}{2m_e}\nabla_i^2}_{\text{electron kinetic energy}}$$

$$\approx -\sum_{i}^{\text{electrons}} \frac{1}{2}\nabla_i^2 + \sum_{i<j}^{\text{electrons}} \frac{1}{|r_i - r_j|} - \sum_{i}^{\text{electrons}} \sum_{j}^{\text{nuclei}} \frac{Z_j}{|r_i - R_j|} + C'_n \quad (1)$$

4 - Methodology [VQE - Varitional Quantum Eigensolver]

1. Second Quantisation

- ☑ Accounts for fermionic properties [**Pauli Exclusion Principle**]
- ☑ Easier to solve for **pairwise** electron interactions.
- ☑ Transforms continuous problem to **discrete, matrix-like** form
- ☑ Formulated with a **finite set of orbitals** [i.e. STO-3G], each being a solution to the Schrödinger equation

One-electron integrals:

$$h_{pq} = \int \phi_p^*(r)\left(-\frac{1}{2}\nabla^2 - \sum_j^{\text{nuclei}} \frac{Z_j}{|r_i - R_j|}\right)\phi_q(r)\, d^3r \quad (2)$$

Two-electron integrals:

$$h_{pqrs} = \int\int \frac{\phi_p^*(r_1)\phi_q^*(r_2)\phi_r(r_2)\phi_s(r_1)}{|r_1 - r_2|}\, d^3r_1\, d^3r_2 \quad (3)$$

Computing all integrals and expressing in terms of fermionic operators:

$$\hat{H} = \sum_{p,q} h_{pq}a_p^\dagger a_q + \frac{1}{2}\sum_{p,q,r,s} h_{pqrs}a_p^\dagger a_q^\dagger a_r a_s \quad (4)$$

Figure 4.1.1 - Made by finalists using Matplotlib

Spin Orbitals

Diagram 4.1.2 - made by finalists in Canva

2. Fermionic Mappings

The **Jordan-Wigner Transformation** [JWT]:
- converts a **fermionic Hamiltonian to a qubit Hamiltonian**
- maps creation and annihilaton operators to **Pauli operators**

$$\hat{a}_p|z_0\ldots,z_{p-1},1,z_{p+1},\ldots,z_{N-1}\rangle = (-1)^{\sum_{q=0}^{p-1} z_q}|z_0\ldots,z_{p-1},0,z_{p+1},\ldots,z_{N-1}\rangle$$
$$\hat{a}_p|z_0\ldots,z_{p-1},0,z_{p+1},\ldots,z_{N-1}\rangle = 0 \quad (5)$$
$$\hat{a}_p^\dagger|z_0\ldots,z_{p-1},0,z_{p+1},\ldots,z_{N-1}\rangle = (-1)^{\sum_{q=0}^{p-1} z_q}|z_0,\ldots,z_{p-1},1,z_{p+1},\ldots,z_{N-1}\rangle$$
$$\hat{a}_p^\dagger|z_0\ldots,z_{p-1},1,z_{p+1},\ldots,z_{N-1}\rangle = 0 \quad (6)$$

Expressing the above in terms of Pauli Matrices:

$$a_j^\dagger = \frac{1}{2}(X_j - iY_j)\prod_{k=0}^{j-1} Z_k \qquad a_j = \frac{1}{2}(X_j + iY_j)\prod_{k=0}^{j-1} Z_k \quad (7)$$

Parity Mapper

Spin Orbitals [Assume only spin-up WLOG for spin-down]

Diagram 4.2.1 - made by finalists in Canva

No matter the configuration, this box is always empty and hence can be tapered off

Some states are impossible and qubits can be tapered off to improve efficiency.
- Spin must be conserved
- Total number of electrons is constant

3. Ansatz Preparation [UCC - Unitary Coupled Cluster]

UCC approximates a molecule's wavefunction by applying a **unitary exponential operator** to a reference state, typically the Hartree Fock [HF] state, which is an initial approximation of the molecule's ground state.

H₂ HF state and excitation parameters

Spin-Orbital Mapping $|\Psi_{HF}\rangle = |1100\rangle$:
$|0\rangle_3 \rightarrow 2\beta$ (virtual spin-orbital for β)
$|0\rangle_2 \rightarrow 2\alpha$ (virtual spin-orbital for α)
$|1\rangle_1 \rightarrow 1\beta$ (occupied spin-orbital for β)
$|1\rangle_0 \rightarrow 1\alpha$ (occupied spin-orbital for α)

UCCSD Excitations:
$\theta_a: \quad 1\alpha \rightarrow 2\alpha$
$\theta_\beta: \quad 1\beta \rightarrow 2\beta$
$\theta_{\alpha\beta}: \quad 1\alpha\,1\beta \rightarrow 2\alpha\,2\beta$

$$|\Psi_{UCC}\rangle = e^{T-T^\dagger}|\Phi_{HF}\rangle \quad (9)$$

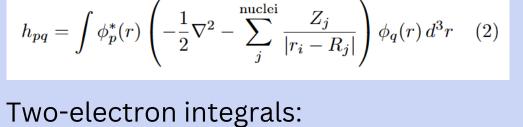The cluster operator T encodes electron excitations with weights θ that modify the **electron density** in different orbitals.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} \theta_i^a a_a^\dagger a_i + \frac{1}{4}\sum_{i,j,a,b} \theta_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \quad (8)$$
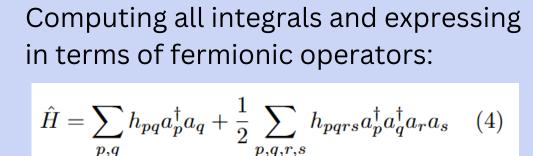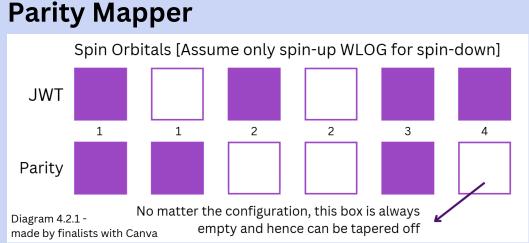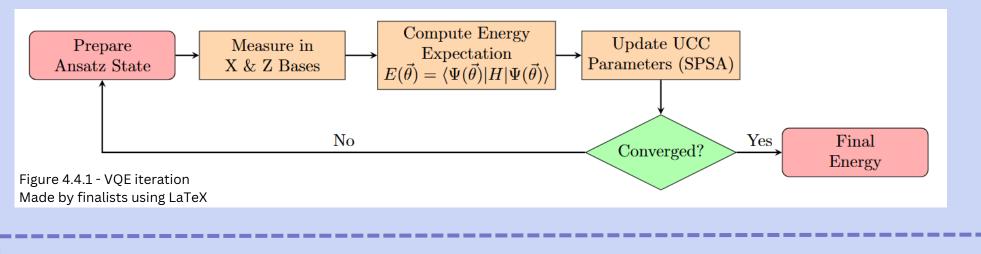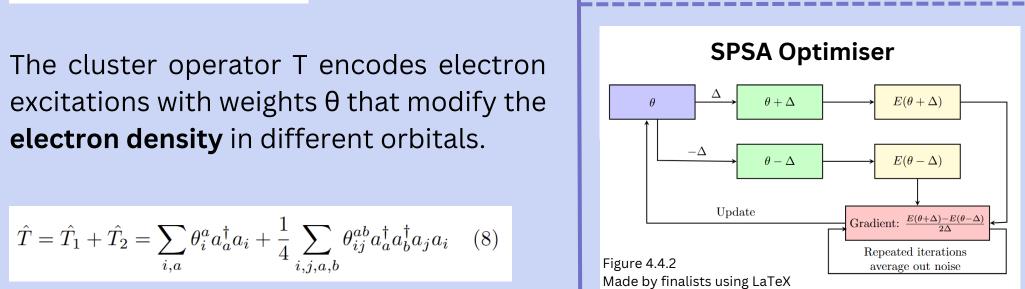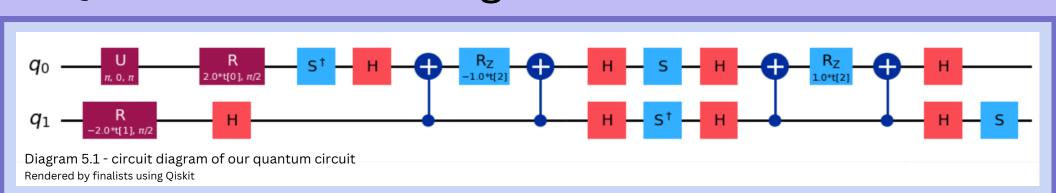
4. Measurement and Optimisation

Figure 4.4.1 - VQE iteration
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Figure 4.4.2
Made by finalists using LaTeX

The Simultaneous Perturbation Stochastic Approximation (SPSA) algorithm is typically used due to its **effectiveness in noisy environments**. Noisy effects tend to cancel out across multiple iterations due to its stochastic nature.
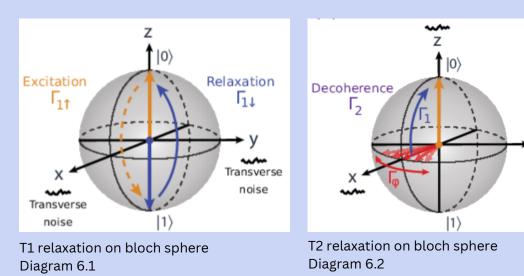
5 - Quantum Circuit Diagram

Diagram 5.1 - circuit diagram of our quantum circuit
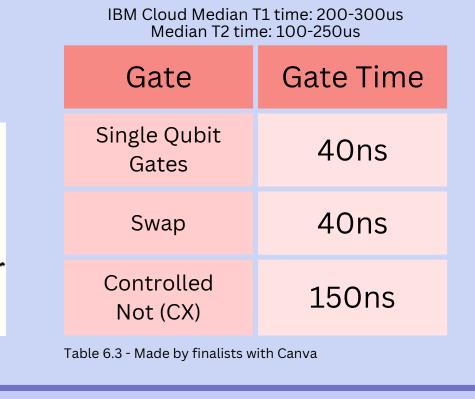Rendered by finalists using Qiskit

6 - Thermal Relaxation Noise

Qubits face noise from many sources. Besides measurement and readout noise, 2 critical parameters in characterising such noise are T1 and T2 times.

T1: **lifetime** of a qubit's excited state [∝ time to relax from $|1\rangle$ to $|0\rangle$]
T2: **coherence** of superposition [∝ time to lose its relative phases]

T1 relaxation on bloch sphere
Diagram 6.1

T2 relaxation on bloch sphere
Diagram 6.2

Superconducting Qubits Noise Levels

IBM Cloud Median T1 time: 200-300us
Median T2 time:100-250us

Gate	Gate Time
Single Qubit Gates	40ns
Swap	40ns
Controlled Not (CX)	150ns

Table 6.3 - Made by finalists in Canva

7 - Implementation and Graph Plotting

By varying the H–H distance, we used VQE in a noiseless simulation to map the **energy landscape** [Fig. 8.1]. To find the **true ground state energy** and **optimal geometry**, we concurrently optimized interatomic distance and electron excitation parameters using a custom algorithm [Fig. 8.2, noisy conditions].

We then explored noise effects—specifically **thermal relaxation**—with T₁ set to 2T₂. Averaging 20 runs per point yielded a smooth curve described by the product of an **exponential decay and inverse power function** [Fig. 8.3].

For all graphs, we compare our results with Self Consistent Field [SCF] and Full Configuration Interaction [FCI], where FCI offers the most accurate energy. Closer agreement with FCI indicates a better result.
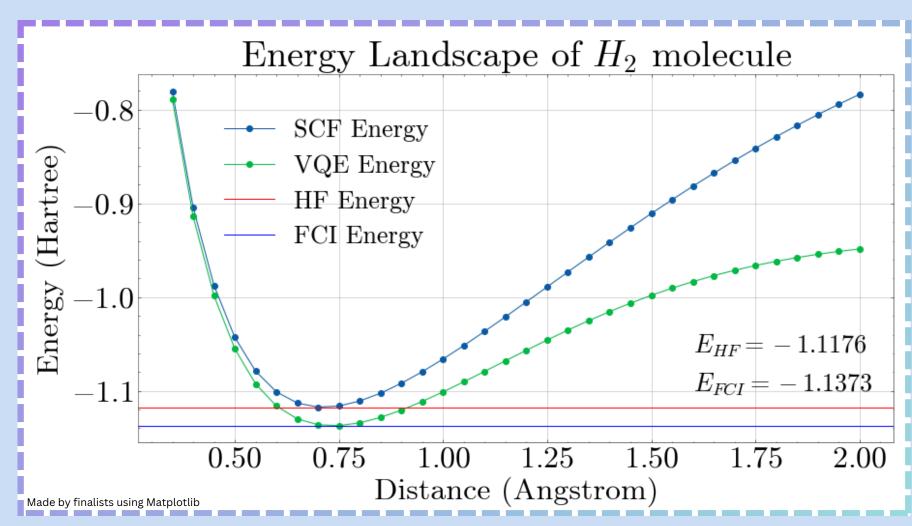
8 - Results

Figure 8.1 - Applying the VQE approach to varying interatomic distances of H₂, the two horizontal lines representing the minimum ground state energy calculated via the 2 different methods [HF and FCI]
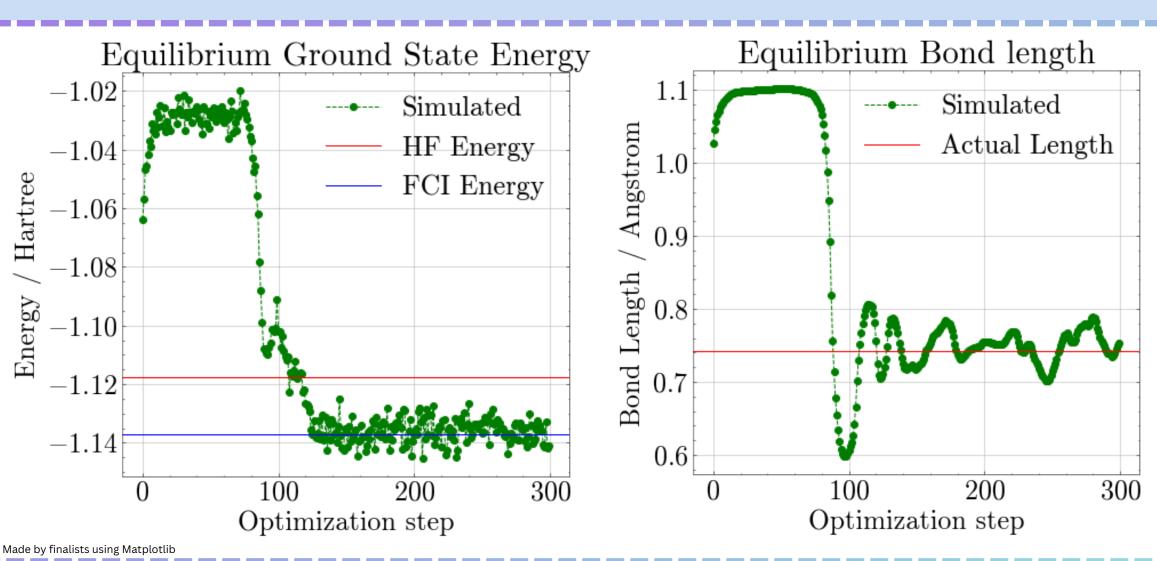

Figure 8.2 - The intermediate results of one execution from our algorithm that optimises interatomic distance [bond length] and electron excitation parameters concurrently.
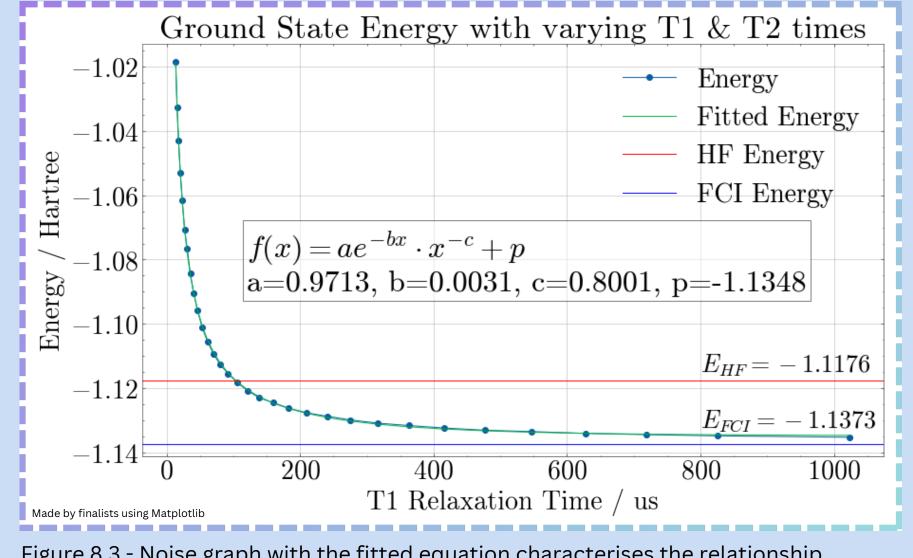

Figure 8.3 - Noise graph with the fitted equation characterises the relationship between thermal relaxation noise and simulation outcome. Energy approaches the FCI Energy as the simulation decreases in noise.

9 - Conclusion

1. **VQE is accurate and effective, even under noisy environments.** Extremely close agreement (**0.0134%** error) of the true ground state energy to FCI energy given by the energy landscape simulation. **Concurrent optimisation** of molecular geometry and excitation parameters is feasible and yielded great results with **0.11%** error on energy and **1.9%** error on bond length.
2. **Quantitatively characterised the correlation between thermal relaxation and simulation outcome**, modelled as the product of an exponential decay and inverse power function.
3. In conclusion, the project is **successful** in meeting its objectives. A comprehensive Jupyter Notebook with **code and detailed documentation** of the VQE process in quantum chemistry is **available on GitHub for future researchers**.

10 - Future Work

Investigation into its actual applicability on Quantum Computers
- Requires comparison with the data obtained from running the circuit on an actual Quantum Computer
- If applicable, investigate other parameteres that affect the final graph shape/coefficients
- If not applicable, investigate possible reasons for this discrepancy and if it reflects improvement that could be made to current simulation methods
- Research on Quantum Error Correction Codes (QECC) and their effectiveness in quantum chemistry

Investigation the effectiveness of VQE in simulating more complex molecules
- Likely only achievable on Quantum Computers
- Assess its accuracy, computational resources, and simulation results

References

[1] Figure 1.5 - Taken from Wikipedia before making secondary cropping [https://en.wikipedia.org/wiki/Quantum_logic_gate#/media/File:Quantum_Logic_Gates.png]
[2] Graphic 1.6 - Taken from research paper [https://doi.org/10.1016/j.xcrp.2024.102105] accessed via ScienceDirect [https://www.sciencedirect.com/science/article/pii/S2666386424003837]
Jared D. Weidman, Manas Sajjan, Camille Mikolas, Zachary J. Stewart, Johannes Pollanen, Sabre Kais, Angela K. Wilson, *Quantum computing and chemistry*, Published in: Cell Reports Physical Science, Volume 5, Issue 9, 2024, 102105, ISSN 2666-3864, https://doi.org/10.1016/j.xcrp.2024.102105.
[3] Diagram 6.1 - Taken from research paper [https://doi.org/10.1063/1.5089550] accessed via ArXiv [https://arxiv.org/abs/1904.06560] Figure 4b
P. Krantz (MIT, LNS and Goteborg, ITP), M. Kjaergaard (MIT, LNS), F. Yan (MIT, LNS), T.P. Orlando (MIT, LNS), S. Gustavsson (MIT, LNS) et al. *A quantum engineer's guide to superconducting qubits,* Published in: Appl.Phys.Rev. 6 (2019) 2, DOI: 10.1063/1.5089550
[4] Diagram 6.2 - Taken from research paper [https://doi.org/10.1063/1.5089550] accessed via ArXiv [https://arxiv.org/abs/1904.06560] Figure 4d
P. Krantz (MIT, LNS and Goteborg, ITP), M. Kjaergaard (MIT, LNS), F. Yan (MIT, LNS), T.P. Orlando (MIT, LNS), S. Gustavsson (MIT, LNS) et al. A quantum engineer's guide to superconducting qubits, Published in: Appl.Phys.Rev. 6 (2019) 2, DOI: 10.1063/1.5089550
[5] D. A. Fedorov, B. Peng, N. Govind, and Y. Alexeev. *Vqe method: A short survey and recent developments,* 2021.
[6] Q. Guo and P.-X. Chen. *Optimization of vqe-ucc algorithm based on spin state symmetry.* Frontiers in Physics, 9, 2021.
[7] M. Qing and W. Xie. *Use vqe to calculate the ground energy of hydrogen molecules on ibm quantum,* 2023
[8] J. Tilly, H. Chen, S. Cao, D. Picozzi, K. Setia, Y. Li, E. Grant, L. Wossnig, I. Rungger, G. H. Booth, and J. Tennyson. *The variational quantum eigensolver: A review of methods and best practices.* Physics Reports, 986:1–128, Nov. 2022.
[9] A. Anand, P. Schleich, S. Alperin-Lea, P. W. K. Jensen, S. Sim, M. D'iaz-Tinoco, J. S. Kottmann, M. Degroote, A. F. Izmaylov, and A. Aspuru-Guzik. *A quantum computing view on unitary coupled cluster theory.* Chemical Society Reviews, 51(5):1659–1684, 2022.