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Ground-state energy estimation of molecular systems on physical quantum devices

Michael A. Jones, Harish J. Vallury, Charles D. Hill, Lloyd C. L. Hollenberg

Talk Summary

- Variational Quantum Algorithms
  - Encoding a quantum chemistry problem
- Methods
  - Quantum Computed Moments
  - Error mitigation
- Results
  - H_2O
- Conclusion

Variational Quantum Algorithms

- The variational principle:
  - $\langle \Psi(\theta) | \mathcal{H} | \Psi(\theta) \rangle \geq E_{\text{ground}}$

[1] Peruzzo et. al. Nat. Comms. 5, 1, 4213, (2014)

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IBM Quantum Network Hub at the University of Melbourne

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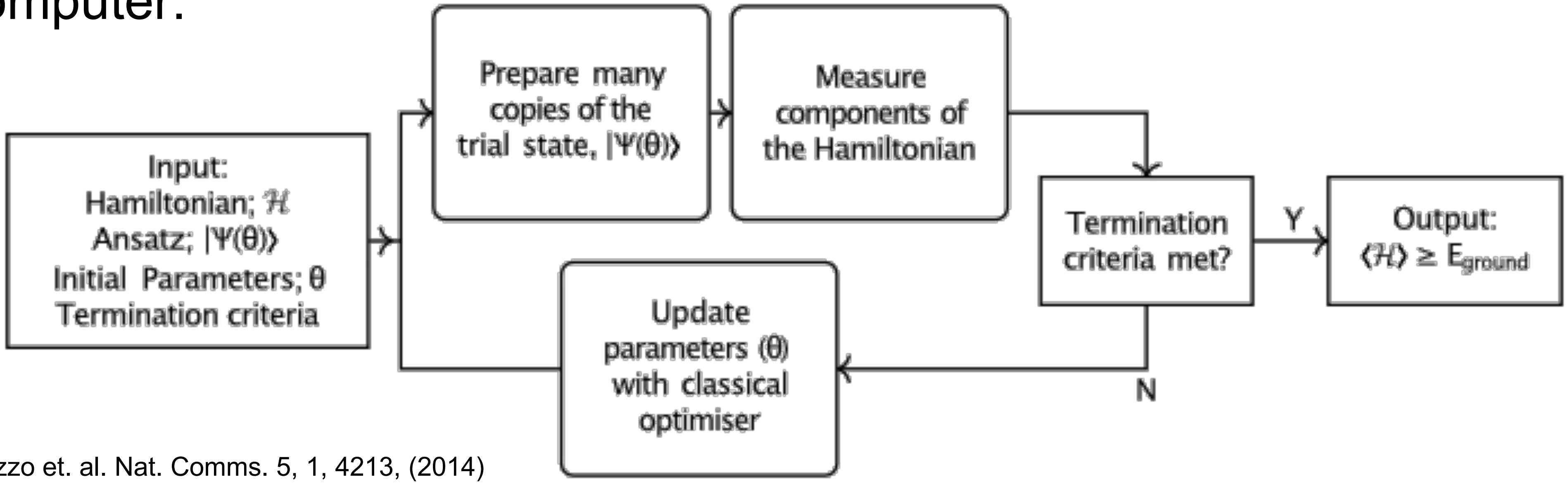
- Method
  - Generate a state: $|\Psi(\vec{\theta})\rangle$
  - Measure its energy: $\langle\Psi(\vec{\theta})|\mathcal{H}|\Psi(\vec{\theta})\rangle$
  - Optimise parameters: $\vec{\theta}$



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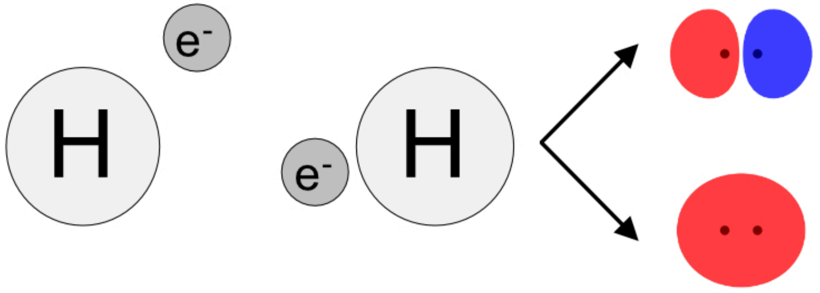
Electronic structure Hamiltonian

- In second quantisation:

$$\mathcal{H} = \sum_{jk} t_{jk} a_j^\dagger a_k + \sum_{jklm} t_{jklm} a_j^\dagger a_k^\dagger a_l a_m$$



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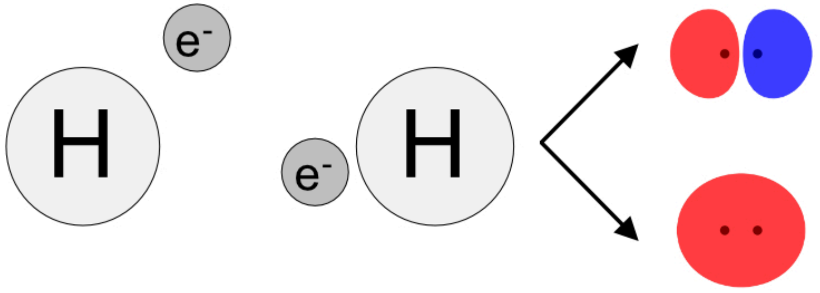
    - add (remove) an electron to basis-state/spin-orbital j



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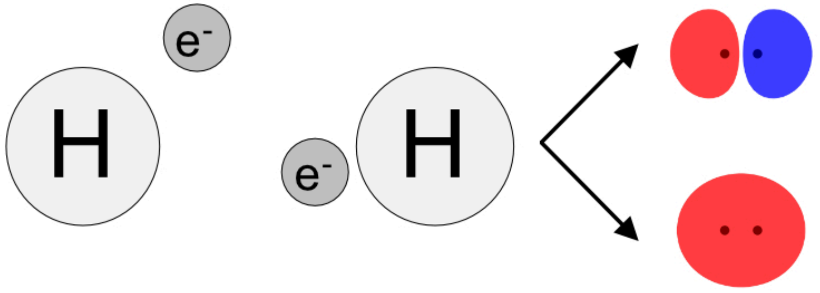
  - t_{jk} (t_{jklm}) one- (two-)electrons integrals
    - define the problem (compute classically)



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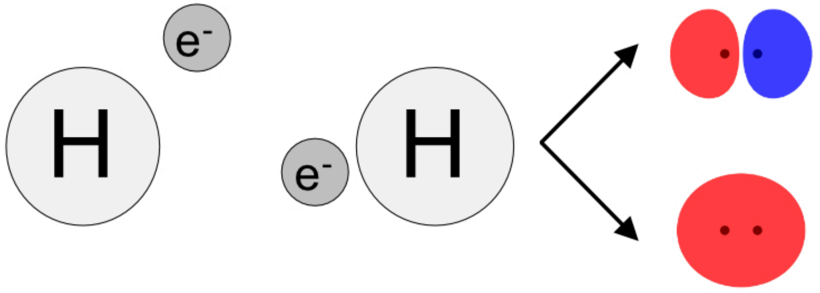

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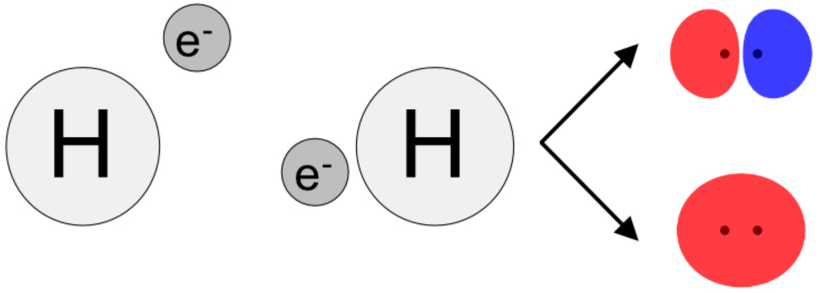

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Coefficients defining the molecule (known):

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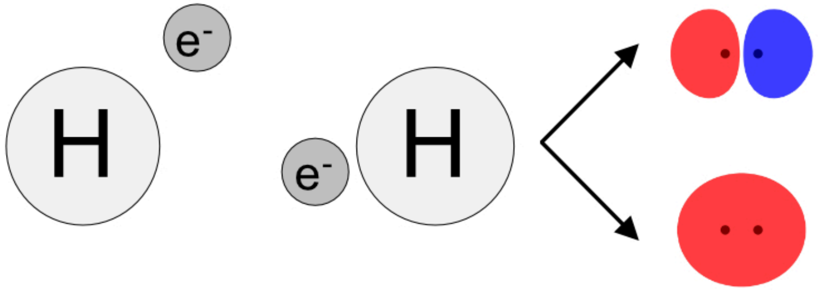

What we want to know:

What we need to measure:

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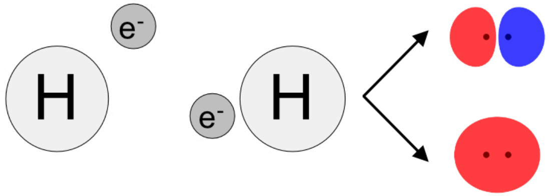

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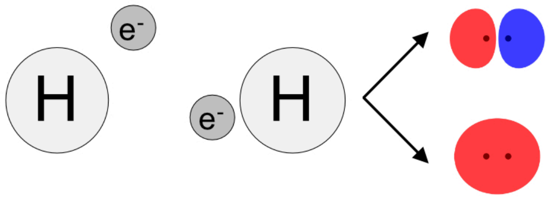
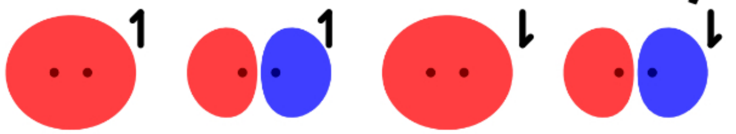


- Hartree-Fock state:

$$|1\quad 0\quad 1\quad 0\rangle$$



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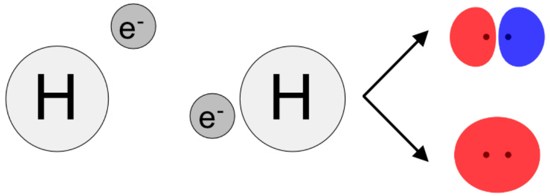

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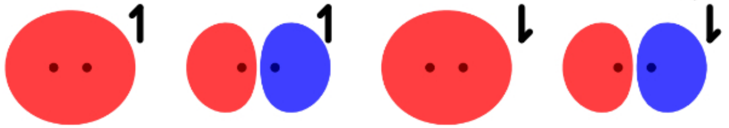

- Doubly-excited state:

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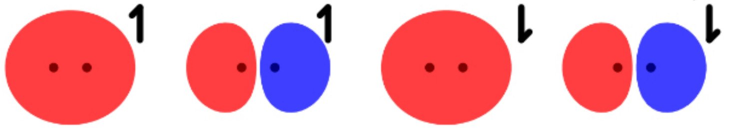

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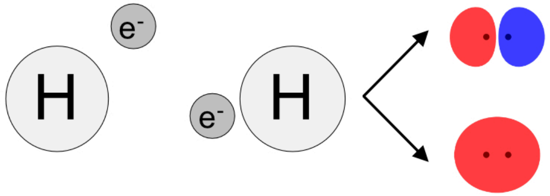

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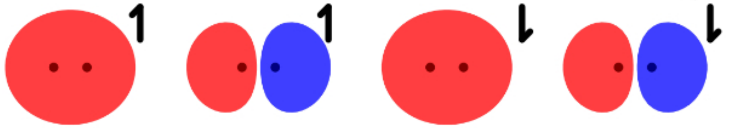

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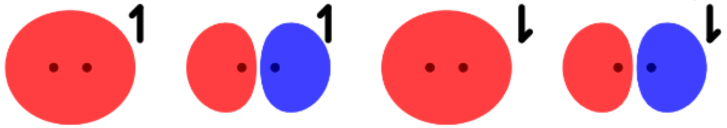

- Multi-determinant state:

$$\cos(\theta)\,|1010\rangle + \sin(\theta)\,|0101\rangle$$

(specific type of entangled states that are "hard" to work with classically)

Past results

	Problem size:		Accuracy (mHa)	
	Electrons	Qubits		
Jones et. al.	2	2	~0.01-0.1	Restricted trial state
	6	6	~1*	Restricted trial state
Eddins et. al.	6 (3)	5	~1-10	Requires weak entanglement
Kawashima et. al.	10 (2)	2	~0.1-1	Highly symmetric system
Nam et. al.	2	4	~1*	
Arute et. al.	12	12	~0.1-1*	Restricted trial state
McCaskey et. al.	2	4	~0.1-1	Exponential scaling with electron number

[1] MAJ, HJV, CDH & LCLH *Sci. Rep.* 12, 1, 8185 (2022)
[2] Eddins et. al. *PRX Quant.* 3, 1, 010309 (2022)
[3] Kawashima et. al. *Nat. Comm. Phys.* 4, 1, 245 (2021)
[4] Nam et. al. *npj Quant. Inf.* 6, 1, 33 (2020)
[5] Arute et. al. *Science,* 369, 6507, 1084 (2020)
[6] McCaskey et. al. *npj Quant. Inf.* 5, 1, 99 (2019)

Methods

- Quantum computed moments[1,2]
  - Use the Hamiltonian moments, $\langle \mathcal{H}^p \rangle$, to correct the ground-state energy estimate[3,4]

$$E_L = c_1 - \frac{c_2^2}{c_3^2 - c_2 c_4}\left(\sqrt{3c_3^2 - 2c_2c_4} - c_3\right)$$

$$c_p = \langle \mathcal{H}^p \rangle - \sum_{j=0}^{p-2} \binom{p-1}{j} c_{j+1} \langle \mathcal{H}^{p-1-j} \rangle$$

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$$E_L(\langle \mathcal{H} \rangle, \langle \mathcal{H}^2 \rangle, \langle \mathcal{H}^3 \rangle, \langle \mathcal{H}^4 \rangle) \begin{cases} E_L = c_1 - \dfrac{c_2^2}{c_3^2 - c_2 c_4}\left(\sqrt{3c_3^2 - 2c_2c_4} - c_3\right) \\ c_p = \langle \mathcal{H}^p \rangle - \displaystyle\sum_{j=0}^{p-2} \binom{p-1}{j} c_{j+1} \langle \mathcal{H}^{p-1-j} \rangle \end{cases}$$

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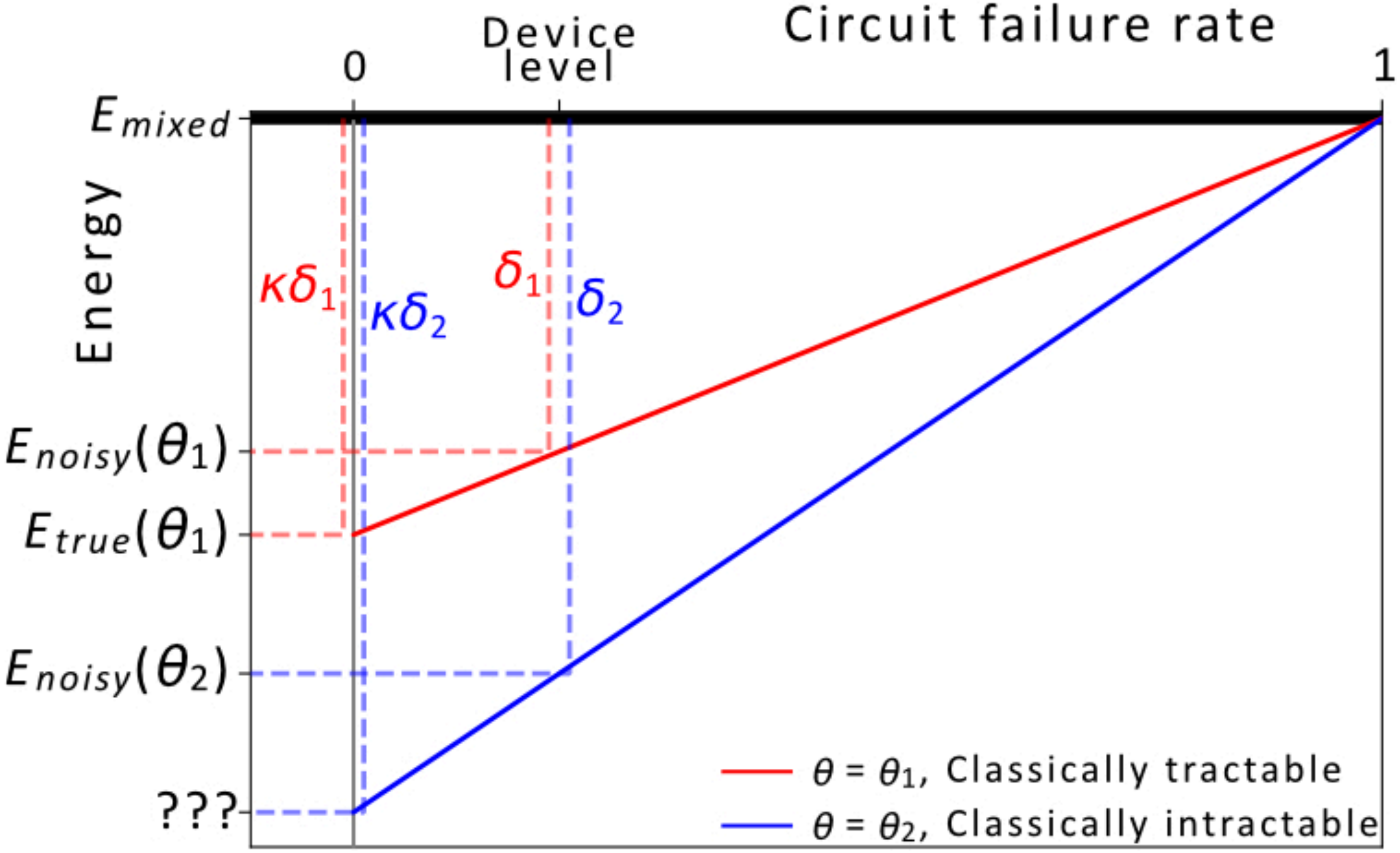

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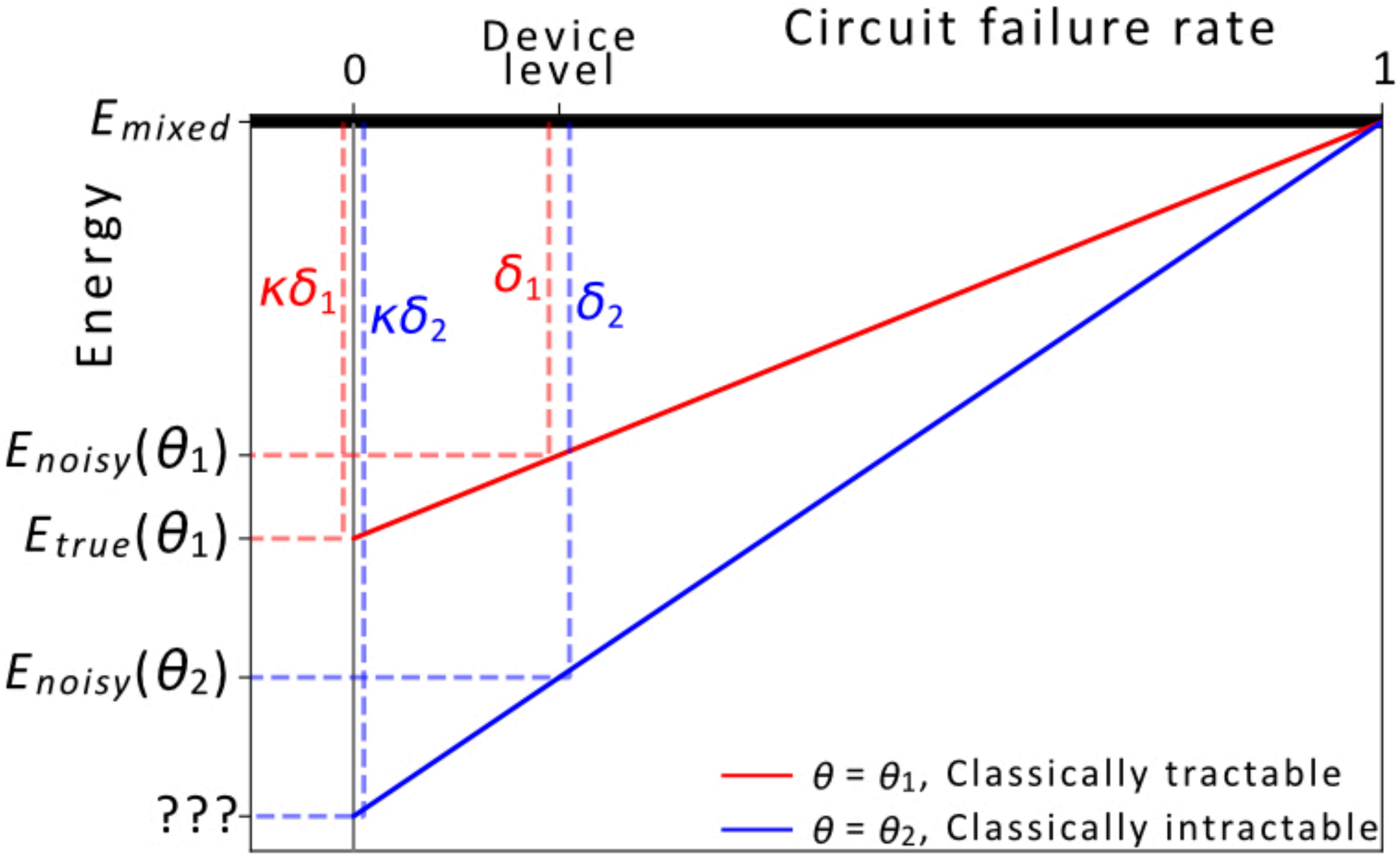

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Methods

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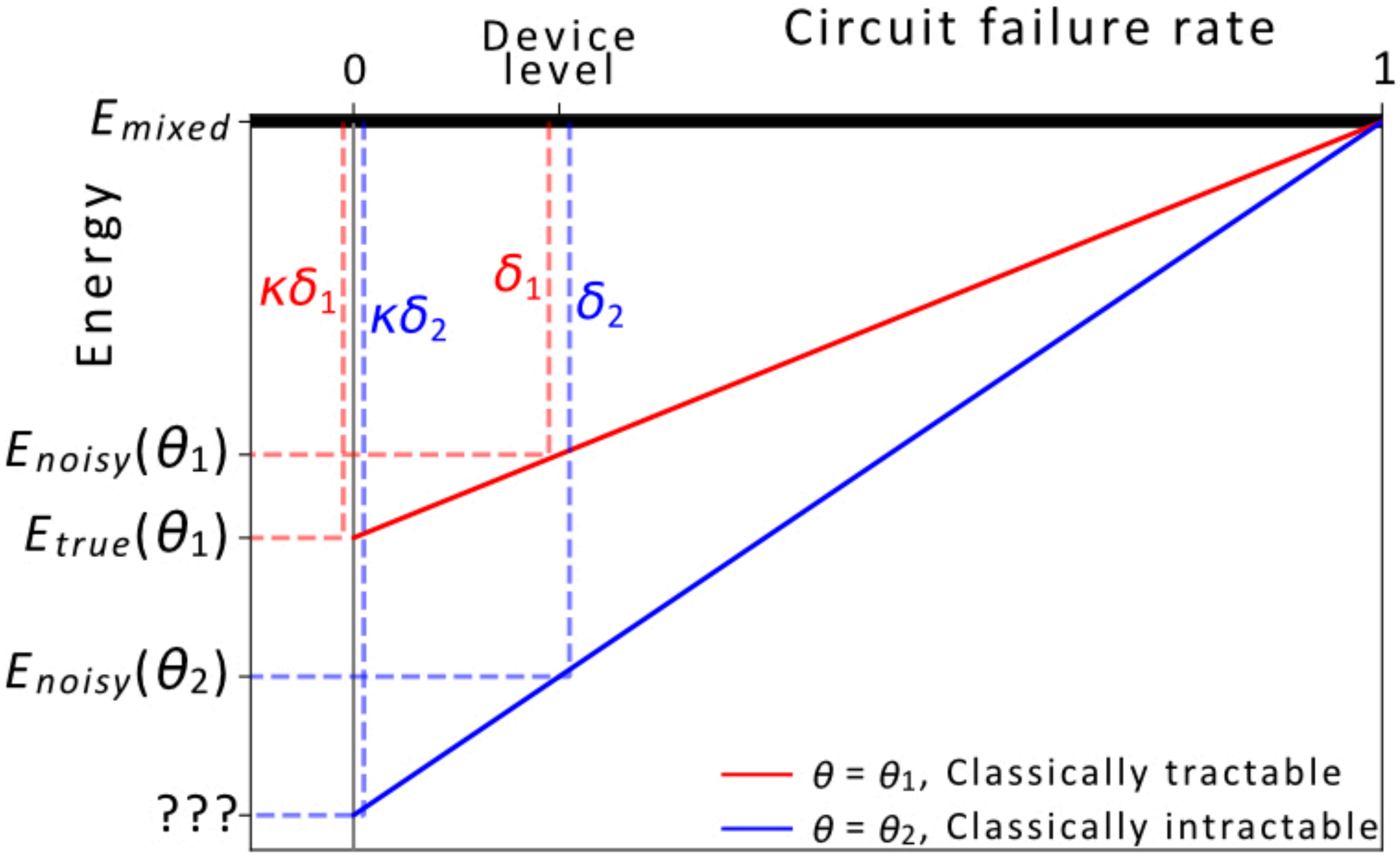

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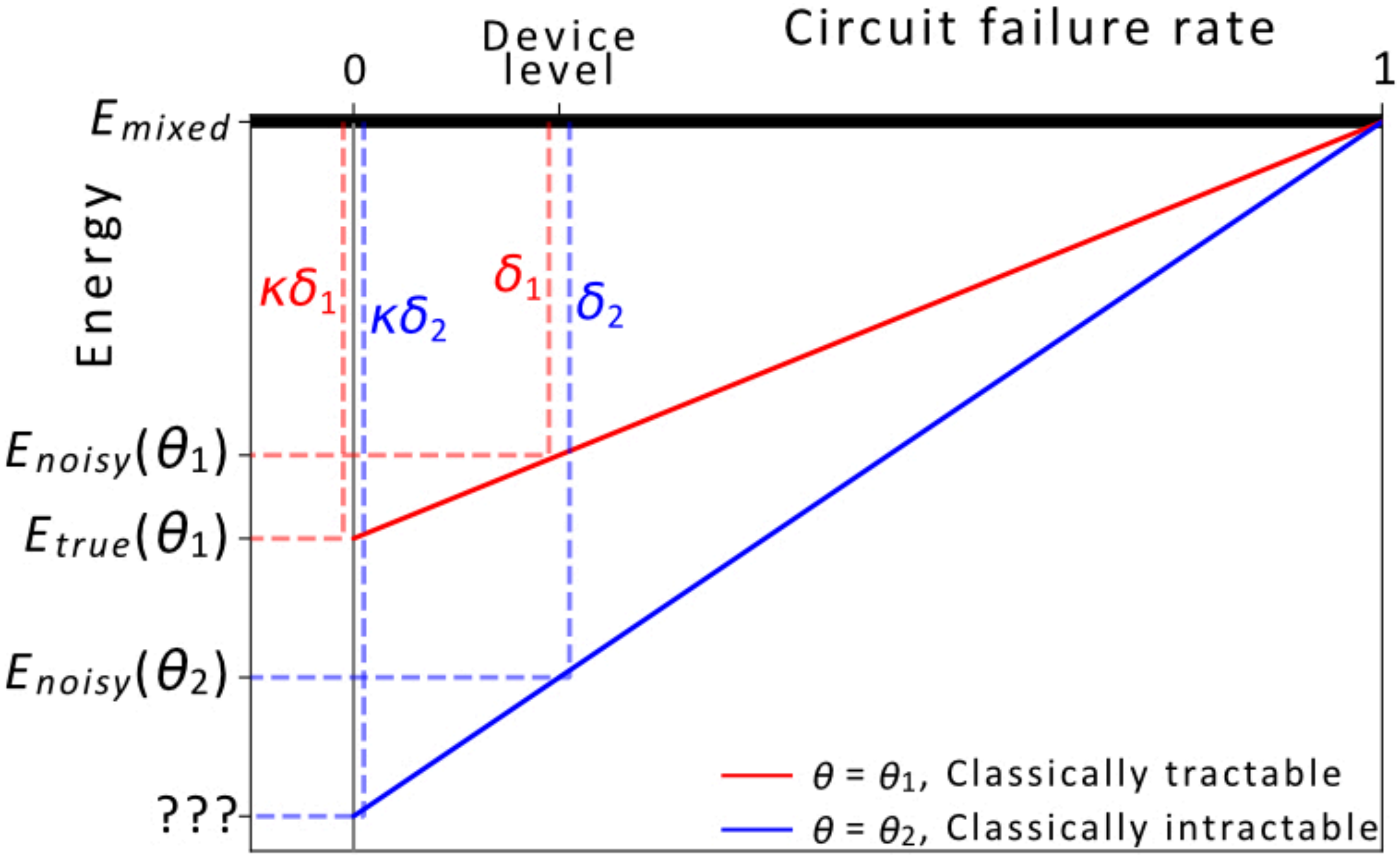
Methods

- Reference-state calibration[1,2]
  - Assume a noise model
  - Use classically tractable reference states to fit parameters
  - Invert model to correct noisy estimates



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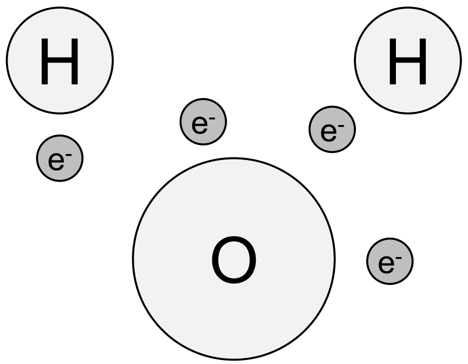
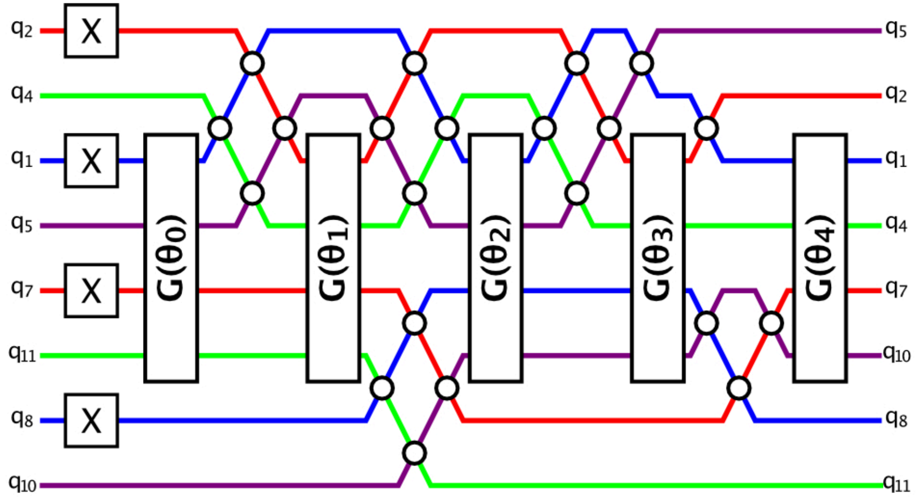
Results

- Application to the water molecule:
  - Simulated with and without noise
  - up to 8 qubits (4 electrons)
  - 5 variational parameters
  - up to ~100 CNOTs

  - Quantum Computed Moments
  - Reference state calibration
  - Symmetry verification[1]
  - Reduced density matrix rescaling[2]



Trial circuit:



[1] Bonet-Monroig et al. *Phys. Rev. A*, 98, 062339 (2018)
[2] Tilly et al. *Phys. Rev. Research, 3,* 033230 (2021)

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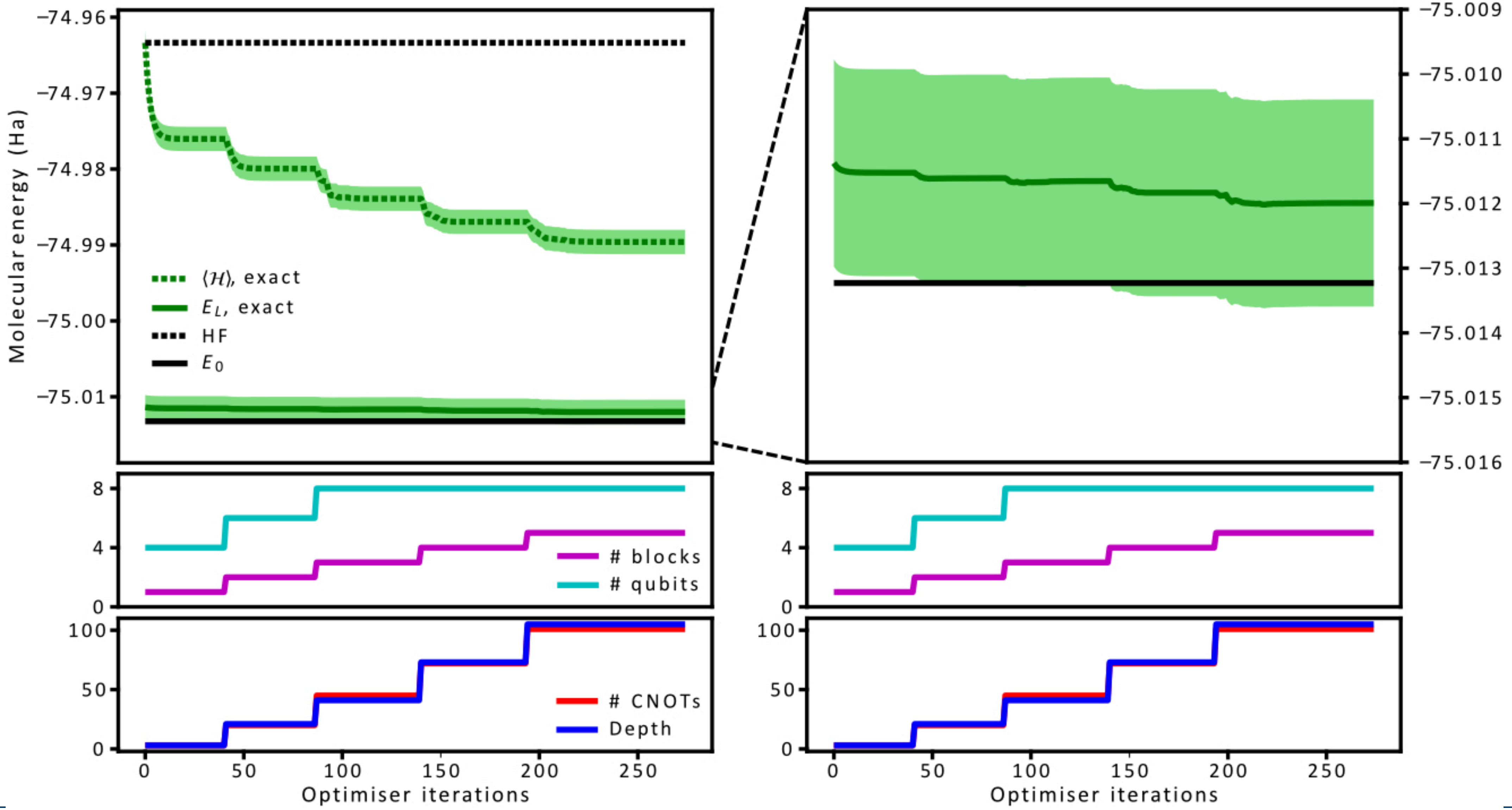
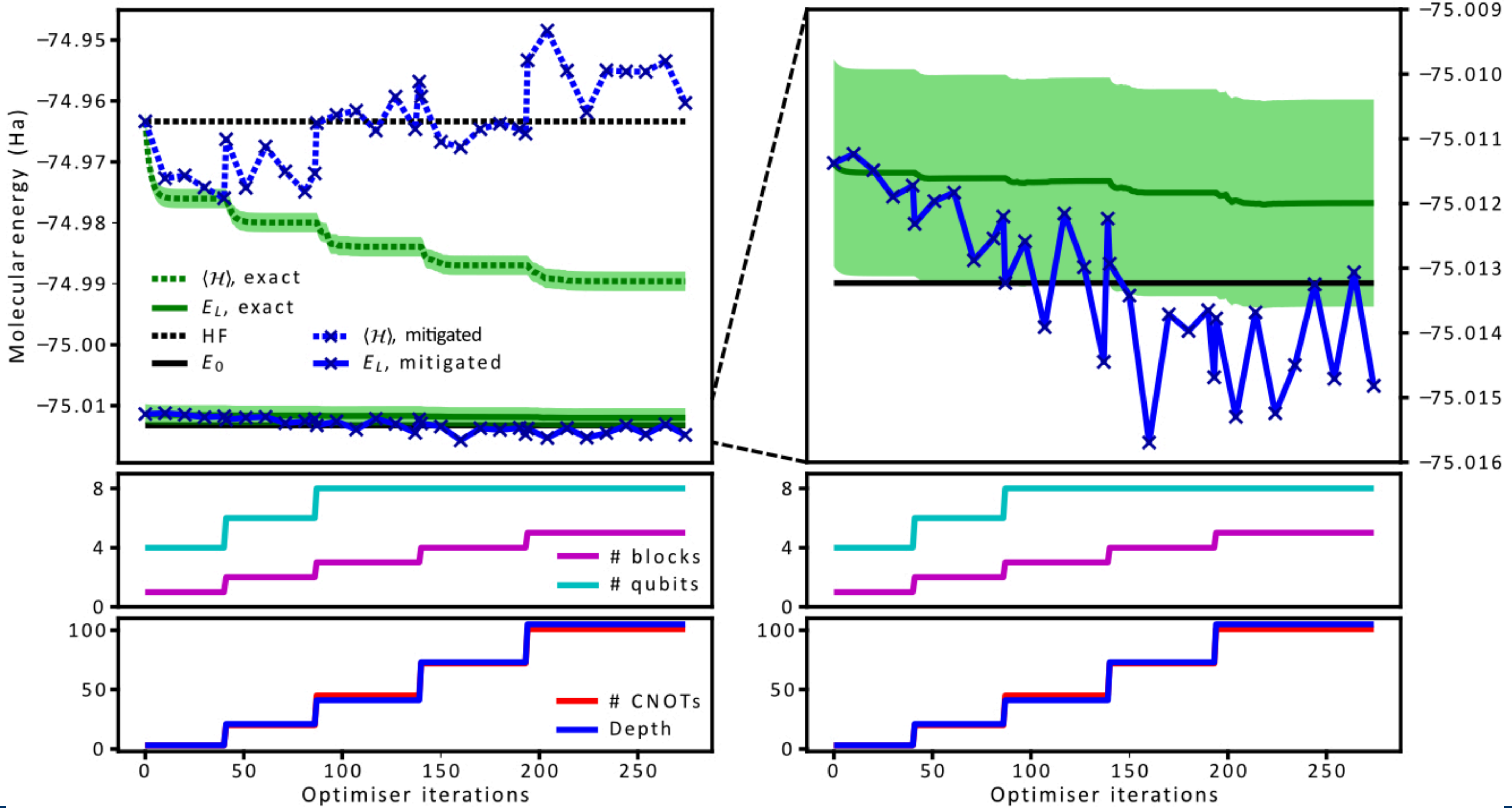


−74.96
−74.97
−74.98
−74.99
−75.00
−75.01
Molecular energy (Ha)
⟨H⟩, exact
E_L, exact
HF
E_0
−75.009
−75.010
−75.011
−75.012
−75.013
−75.014
−75.015
−75.016
8
4
0
blocks
qubits
100
50
0
CNOTs
Depth
0
50
100
150
200
250
Optimiser iterations

Results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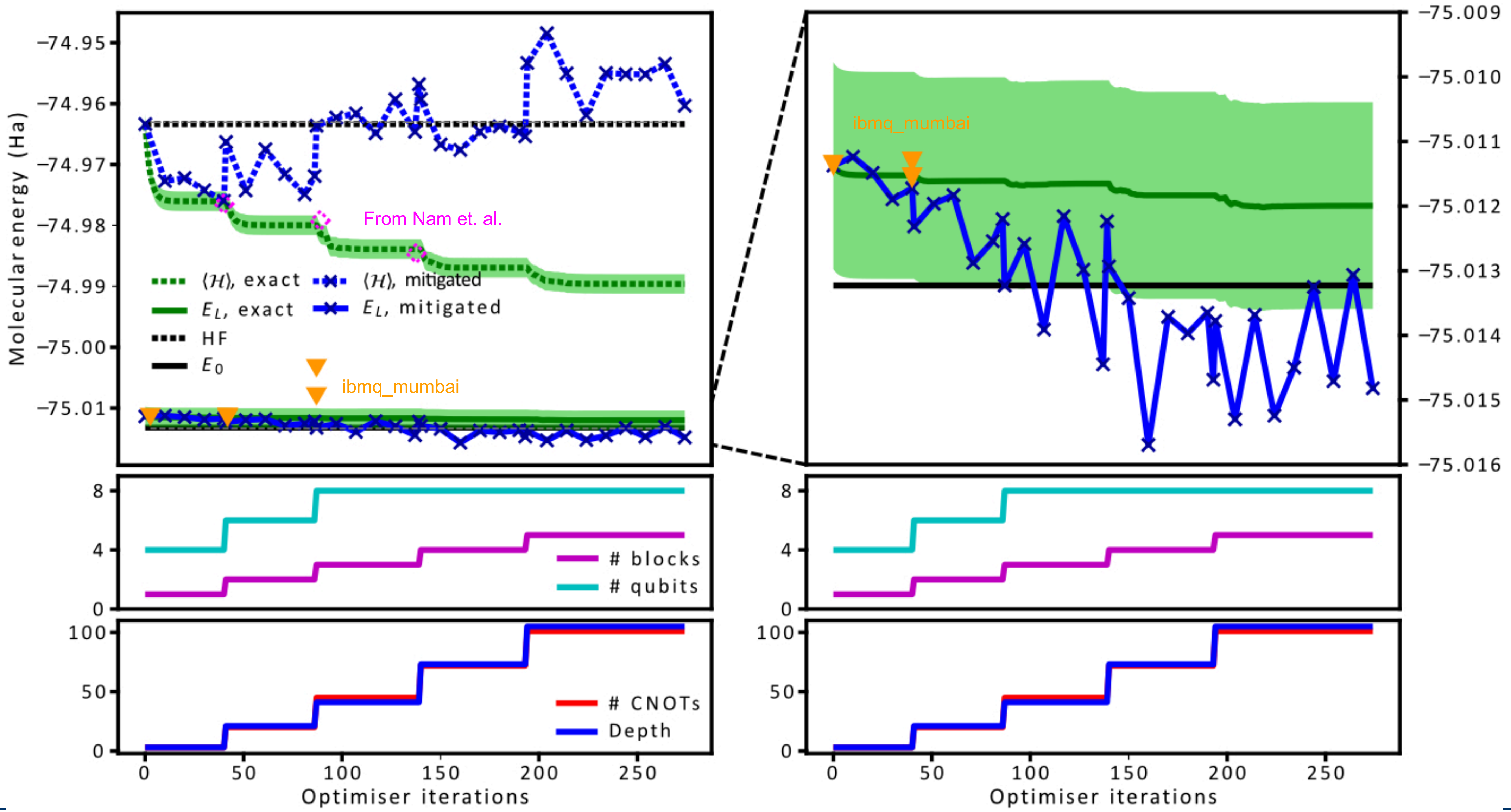

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Summary

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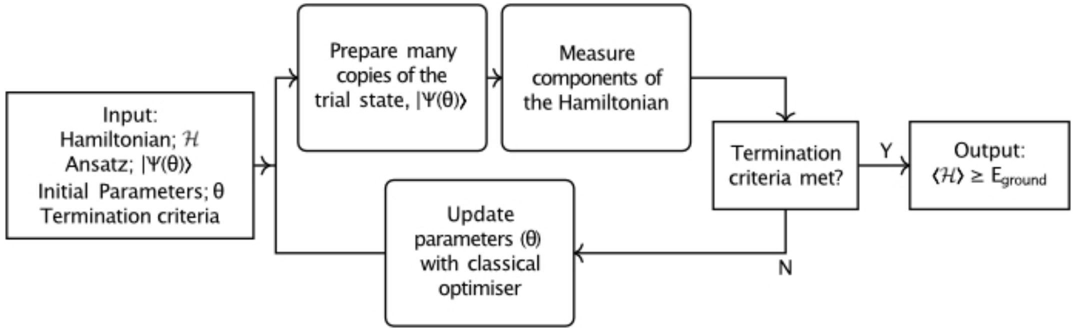
Input:
Hamiltonian; $\mathcal{H}$
Ansatz; $|\Psi(\theta)\rangle$
Initial Parameters; θ
Termination criteria
Prepare many copies of the trial state, $|\Psi(\theta)\rangle$
Measure components of the Hamiltonian
Termination criteria met?
Y
Output:
$\langle\mathcal{H}\rangle \geq E_{ground}$
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Update parameters (θ) with classical optimiser

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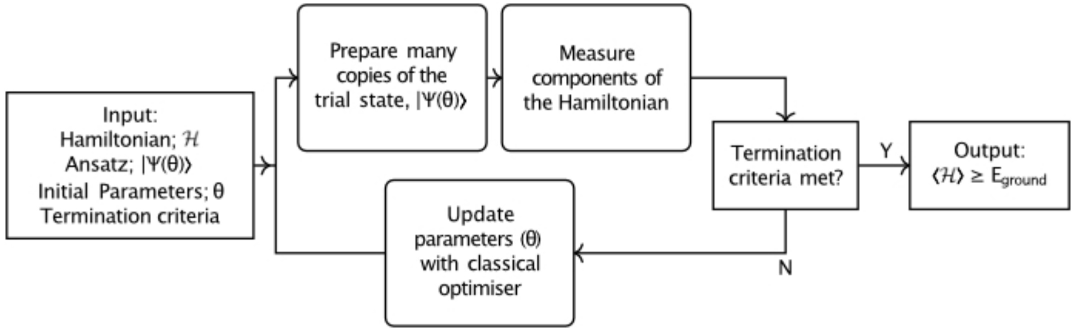
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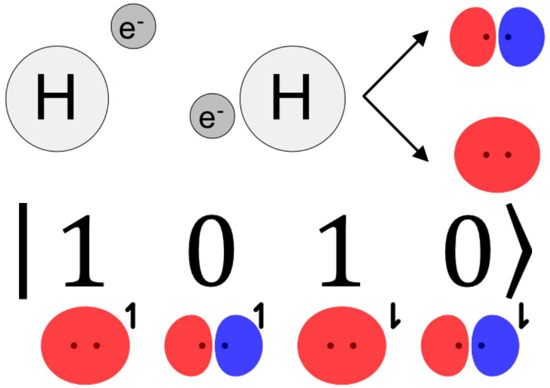
e-
H
e-
H
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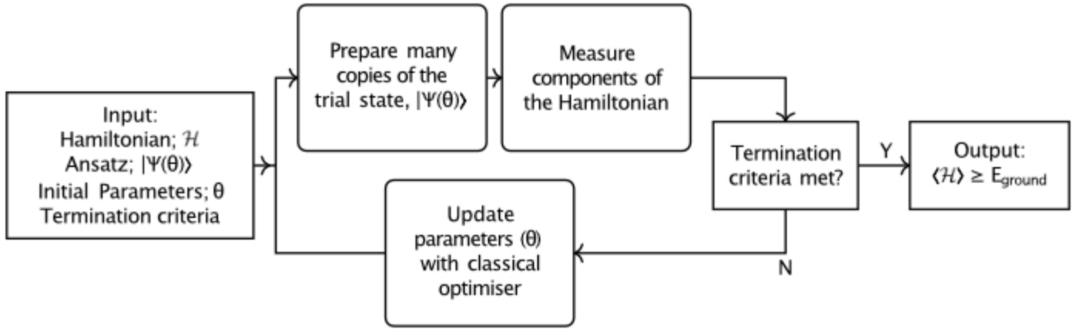

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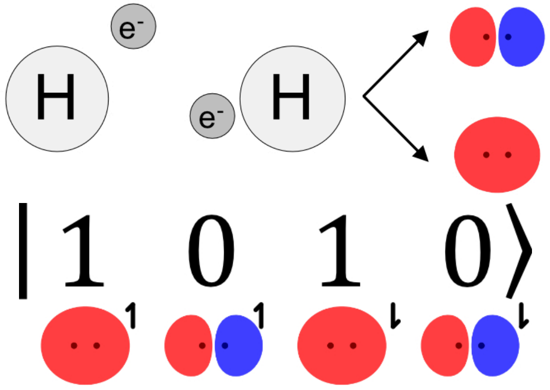

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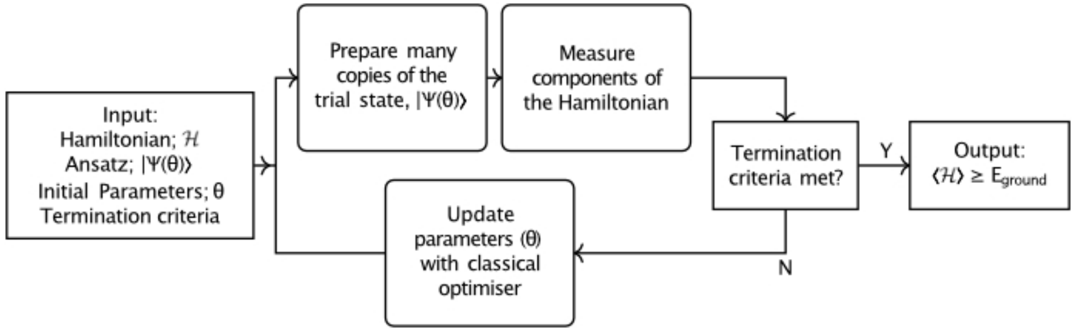

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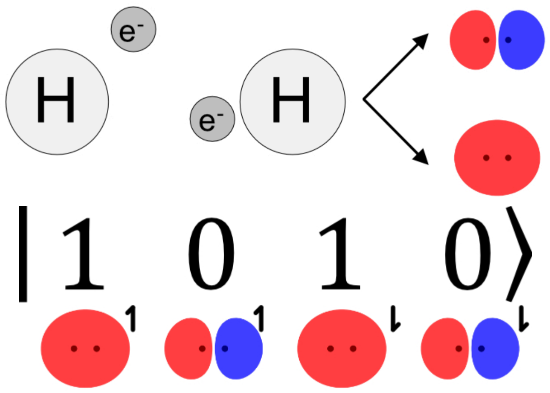

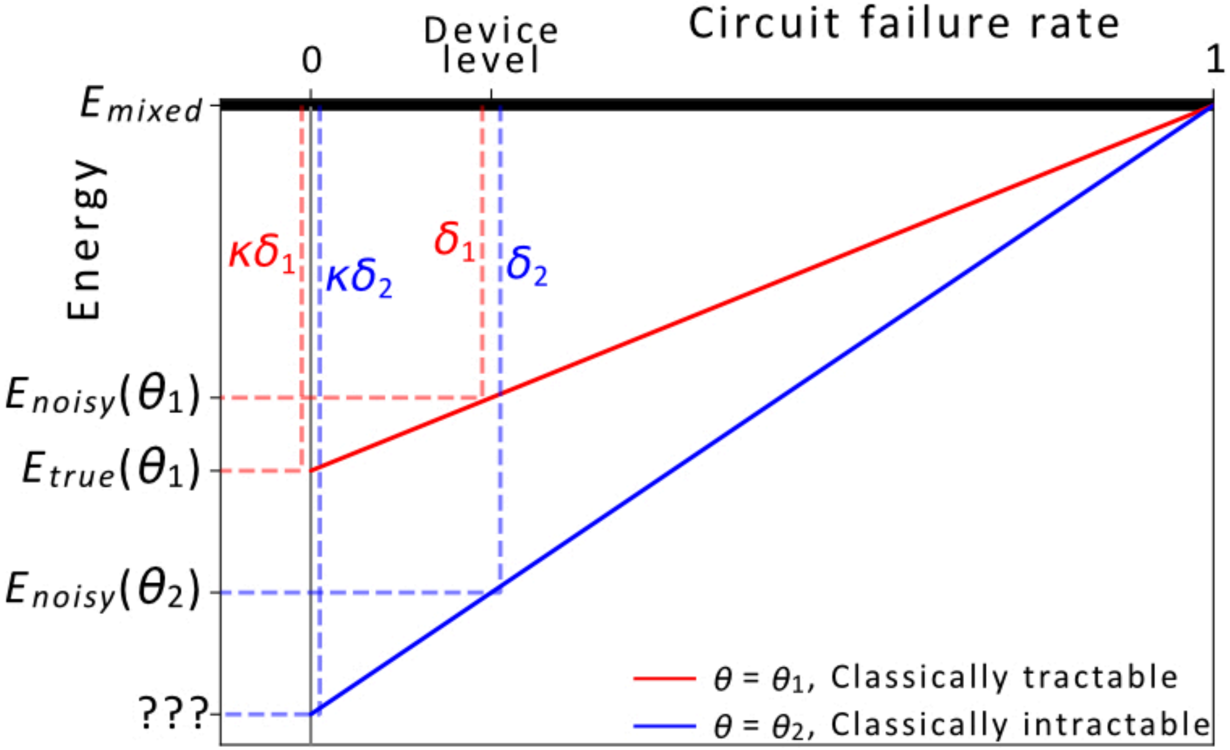

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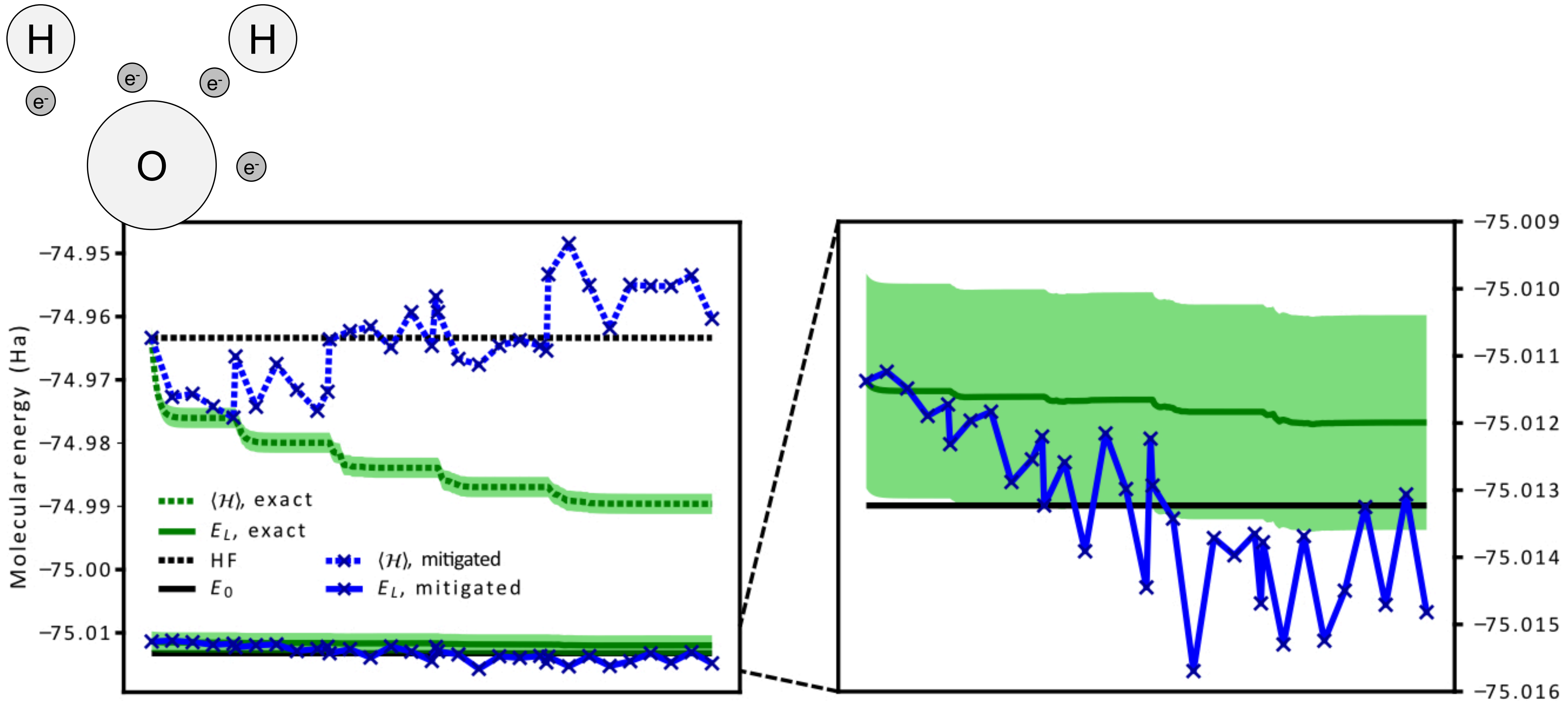
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    - QREM
    - Dynamical decoupling
    - Probabilistic error mitigation
  - Improved sampling efficiency:
    - Bypass measurement of RDMs
    - Hamiltonian decomposition
      - extension to moments?
  - Larger / more interesting systems:
    - Strongly correlated molecules

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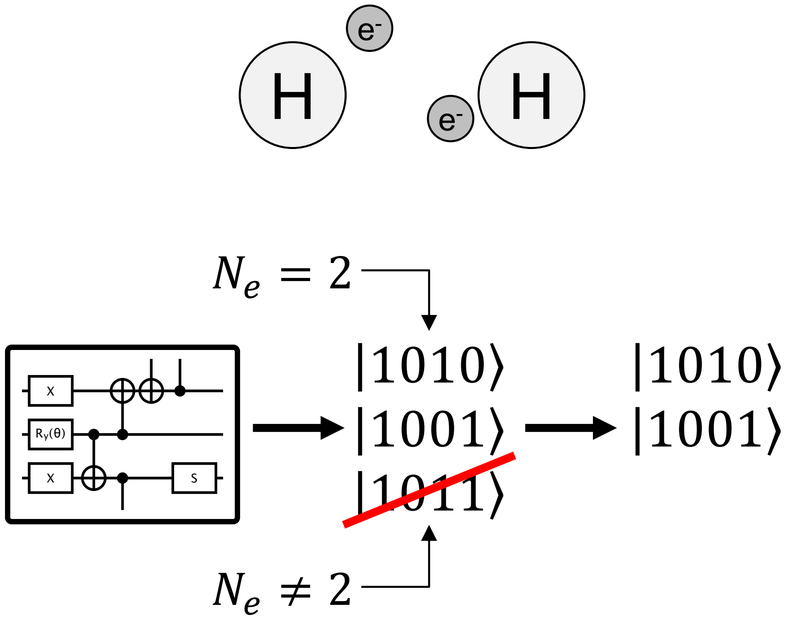
Methods

- Symmetry verification[1]



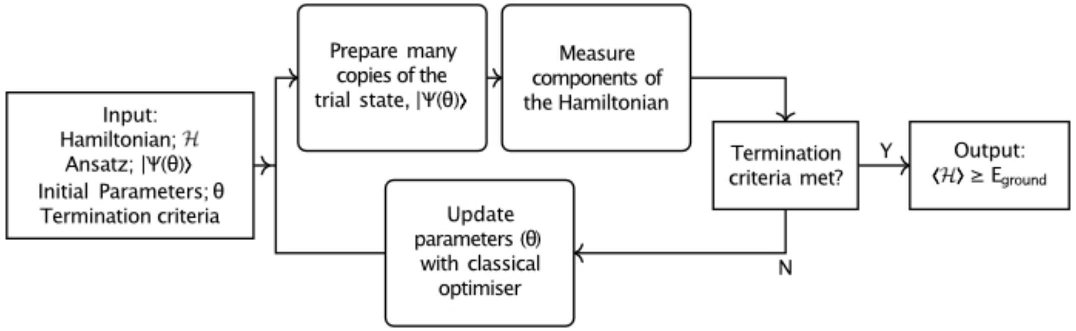
- Reduced density matrix rescaling[2]
  - The p-body reduced density matrix contains information about p-body interactions
  - Efficient scaling with n_e and n_s
  - In general need, at most, the 8-RDM for QCM

$$\mathrm{Tr}(\mathbf{R}_{\mathrm{ideal}}) = \frac{n_e!}{p!\,(n_e - p)!}$$

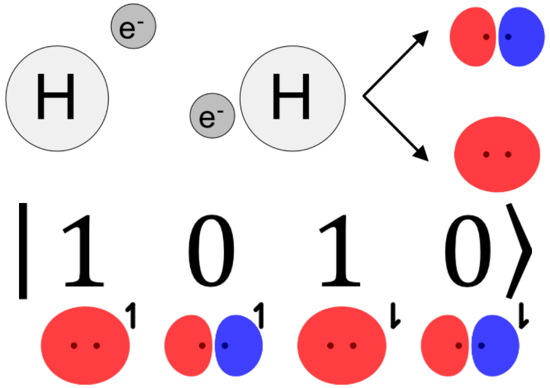
$$\mathbf{R}_{\mathrm{corrected}} = \frac{\mathrm{Tr}(\mathbf{R}_{\mathrm{ideal}})}{\mathrm{Tr}(\mathbf{R}_{\mathrm{noisy}})} \cdot \mathbf{R}_{\mathrm{noisy}}$$

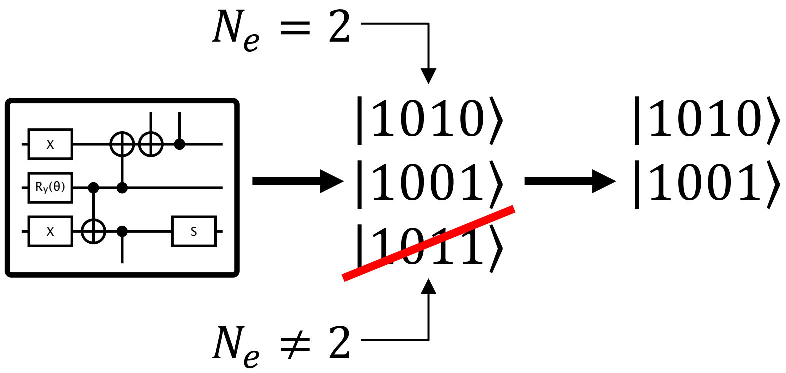
[1] Bonet-Monroig et al. *Phys. Rev. A*, 98, 062339 (2018)
[2] Tilly et al. *Phys. Rev. Research, 3,* 033230 (2021)

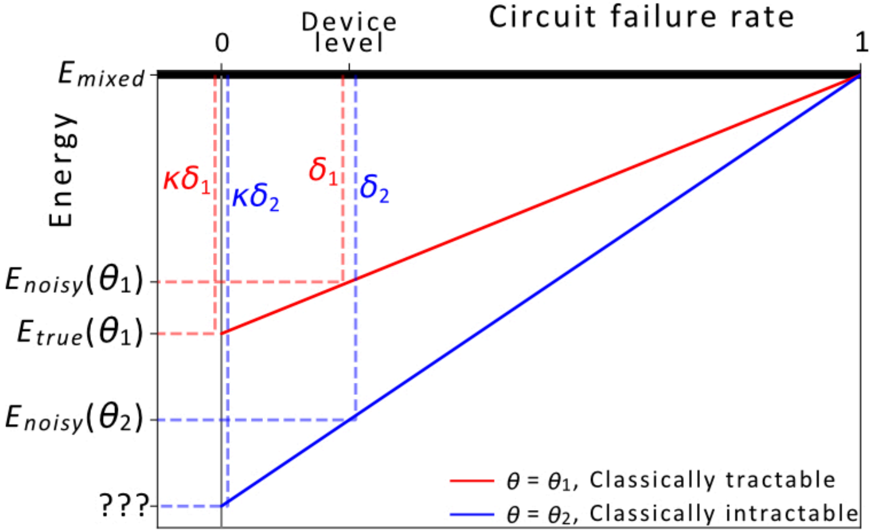
Summary



$$E_L = c_1 + \frac{c_2^2}{c_2 c_4 - c_3^2}\left(\sqrt{3c_3^2 - 2c_2c_4} - c_3\right)$$

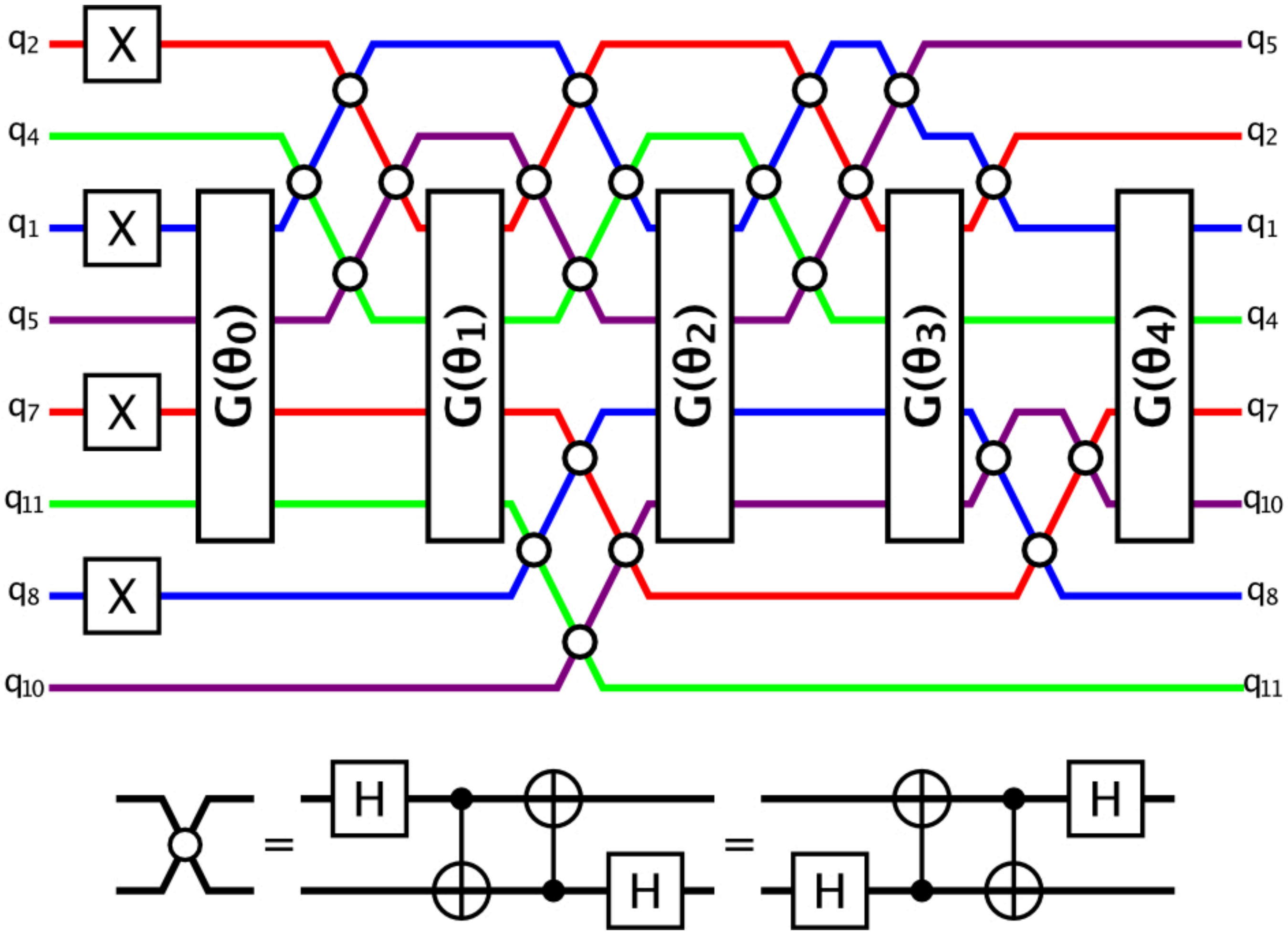






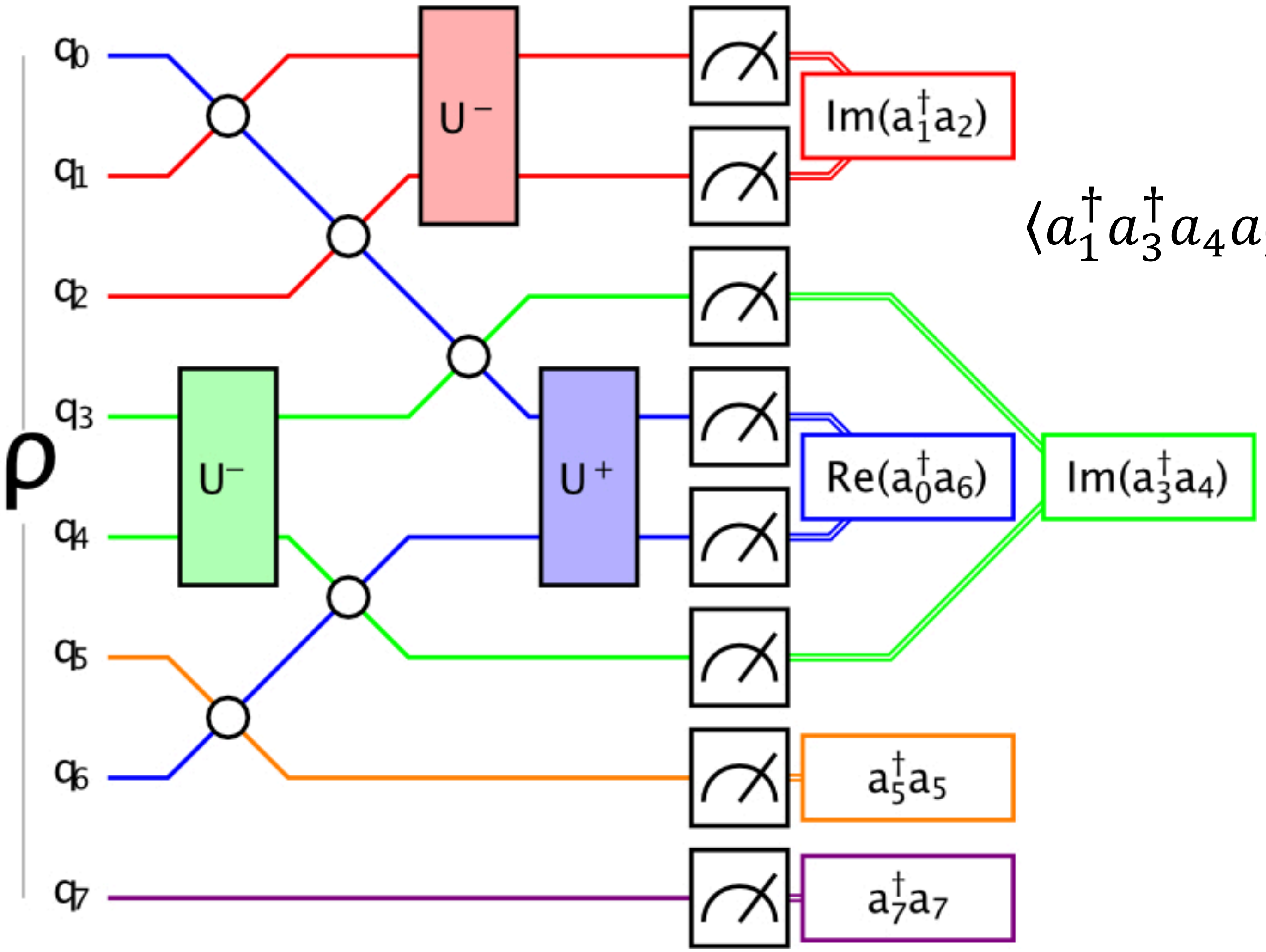
$$\mathbf{R}_{\text{corrected}} = \frac{\mathrm{Tr}(\mathbf{R}_{\text{ideal}})}{\mathrm{Tr}(\mathbf{R}_{\text{noisy}})} \cdot \mathbf{R}_{\text{noisy}}$$

Trial State



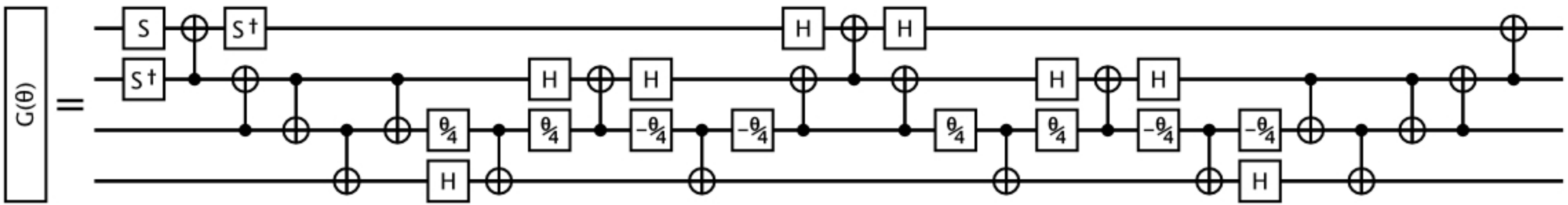
- The trial circuit is based on a (trotterised) Unitary Coupled Cluster ansatz
- Each "block" of the ansatz consists of a qubit routing step and a parameterised double-excitation
- The circuit is implemented using linear connectivity

Measurement



$$\langle a_1^\dagger a_3^\dagger a_4 a_2 \rangle = \langle \mathrm{Re}(a_1^\dagger a_2)\mathrm{Re}(a_3^\dagger a_4)\rangle + \langle \mathrm{Im}(a_1^\dagger a_2)\mathrm{Im}(a_3^\dagger a_4)\rangle$$

Trial State



- The parameterised double-excitation can be decomposed to 19 CNOT gates (assuming linear connectivity)
- The first 3 double-excitations can be simplified based on the initial states of the qubits

Methods

- Applying the Hamiltonian excites electrons
- Re-applying the Hamiltonian de-excites electrons
- Measurement of the overlap with the initial state (i.e. measurement of the second moment) contains information about the interaction between orbitals