



# Enhanced acceleration of unitary coupled-cluster calculation through Quantum Learning Machine

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# About Qubit

Started operations in Q2 - 2021

55+ team members in Paris & Boston

A portfolio of 6 drug discovery programs

A HPC-QC supercomputer 50pFlops AI & 40+ qubits

+\$25m raised to support novel developments



 QUANTONATION

XAnge

ΦMNES

bpifrance

i-Lab

**i-Nov**  
concours d'innovation

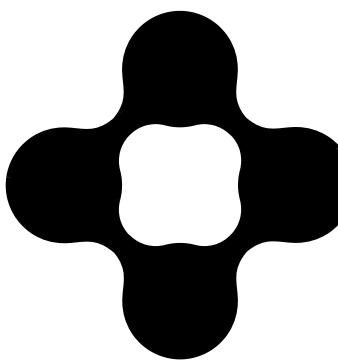


eit Health



European  
Innovation  
Council





## Objective Statement

Accelerate the UCC calculations for strong correlated system with **guaranteed « Chemical accuracy » (1kcal/mol) or ( $10^{-3}$  Hartree)**

## My Contribution

*Algorithms implementation (SSVQE, VQD), UCC methods - extension (Q-UCC // USCC), ...*

**Reduce Parameters**

**Reduce C-NOT gates**

**Reduce iterations /  
Qubits Reduction**

**Benchmarking molecules using MyQLM language - Eviden**



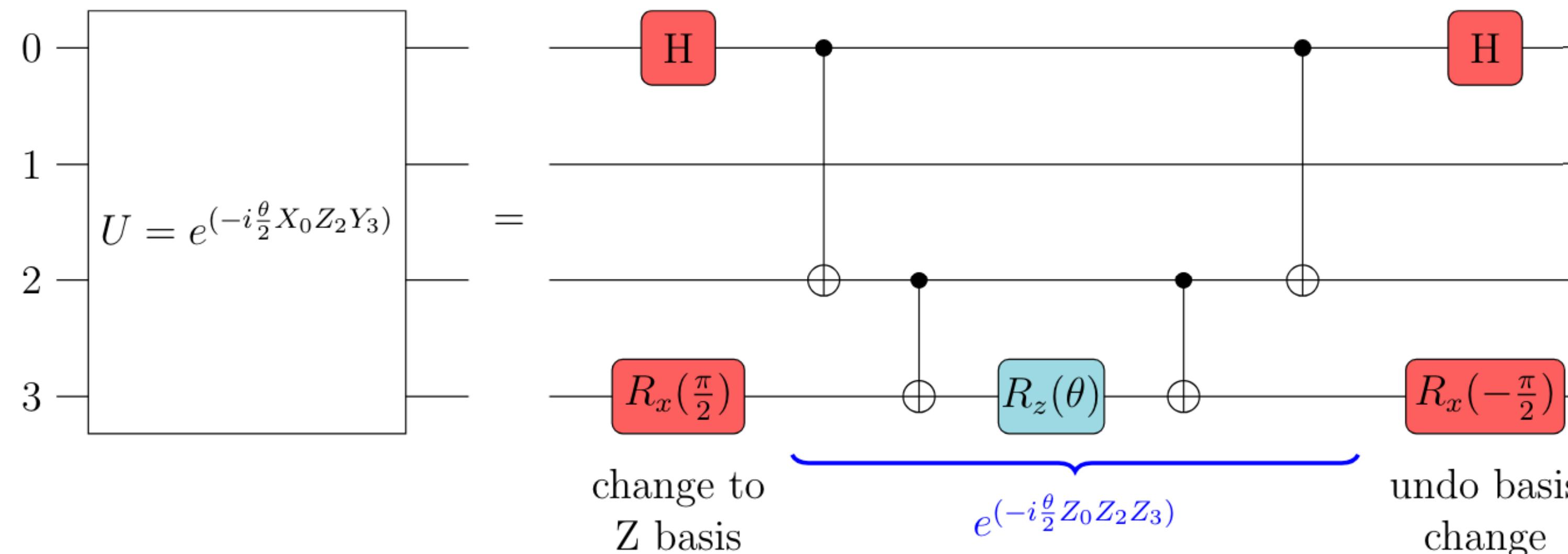
# Theoretical background

# Unitary Couple Cluster: Quantum Circuit Mapping

- UCCSD is given by the product of single and double fermionic evolution :

$$U_{UCCSD}(\theta) = \prod_{i,p} e^{\theta_i^p (a_i^\dagger a_p - a_p^\dagger a_i)} \prod_{i,j,p,q} e^{\theta_{ij}^{pq} (a_i^\dagger a_j^\dagger a_p a_q - a_q^\dagger a_p^\dagger a_j a_i)}$$

- Using Jordan-Wigner Transformation for qubit encoding

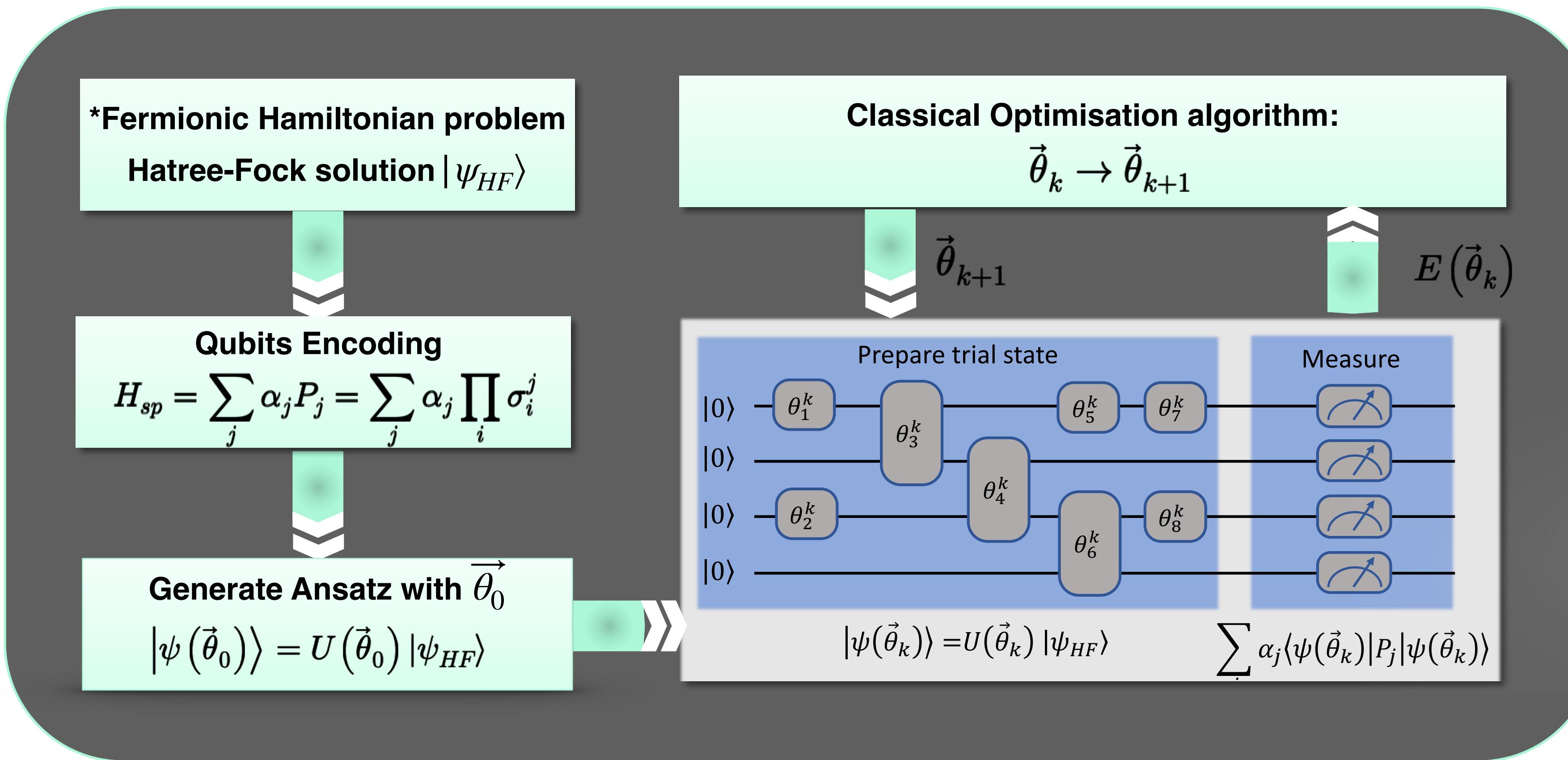


Circuit construction to perform rotation generated by a Pauli operator  $P=XIZY$

# Variational Quantum Eigensolver: UCC Ansatz

Variational Quantum Eigensolver (VQE) – UCC framework: finding eigenvalues of a Hamiltonian

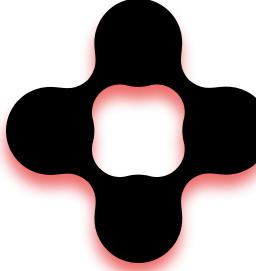
$$H = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$



# • Results •

• • •

PROPRIETARY



# Contribution

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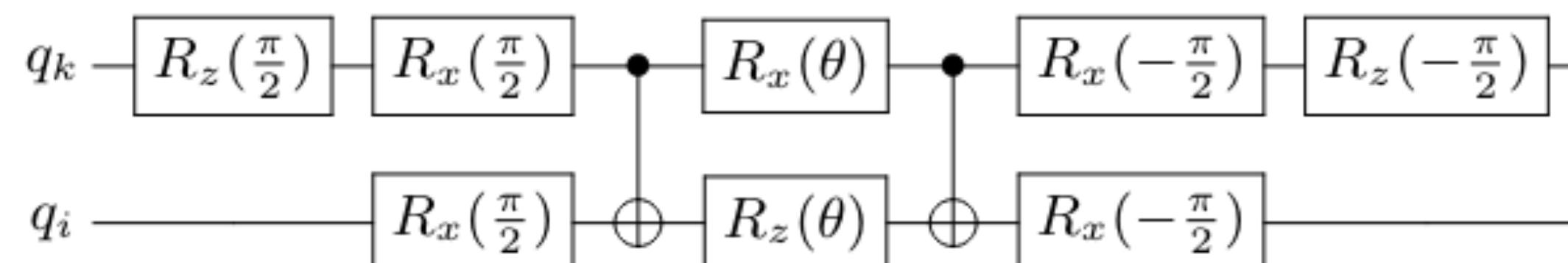
- 1. QUCC method – Reduction in the number of CNOT gates
- 2. CAS – Reduction in the number of Qubits
- 3. (CAS)-PMRS – Reduction in the number of iterations & high fidelity rate
- 4. USCC algorithm – Towards chemical accuracy and less parameters
- 5. VQD algorithm – Towards excited states measurement

# Qubit Unitary Coupled Cluster Single and Double

## Reduce Gate Complexity

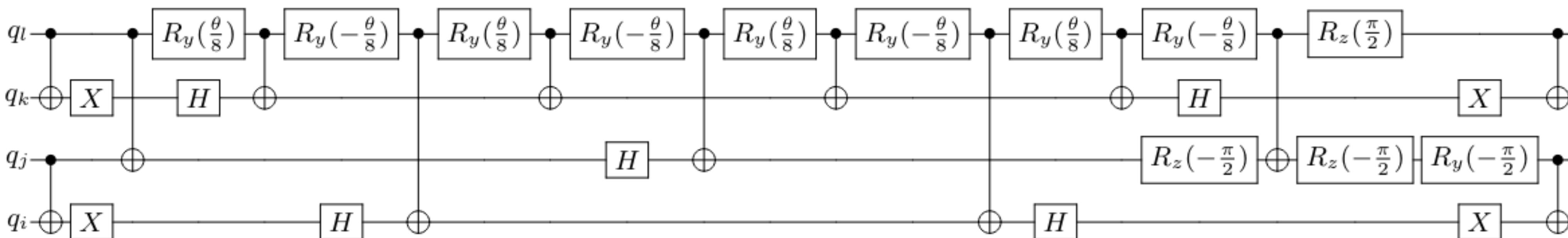
- Q-UCCSD is given by the product of single and double qubits evolution :

$$U_{\text{Q-UCCSD}}(\theta) = \prod_{k,i} e^{\theta_i^k (b_k^\dagger b_i - b_i^\dagger b_k)} \prod_{i,j,k,l} e^{\theta_{ij}^{kl} (b_l^\dagger b_k^\dagger b_j b_i - b_j^\dagger b_i^\dagger b_l b_k)}$$



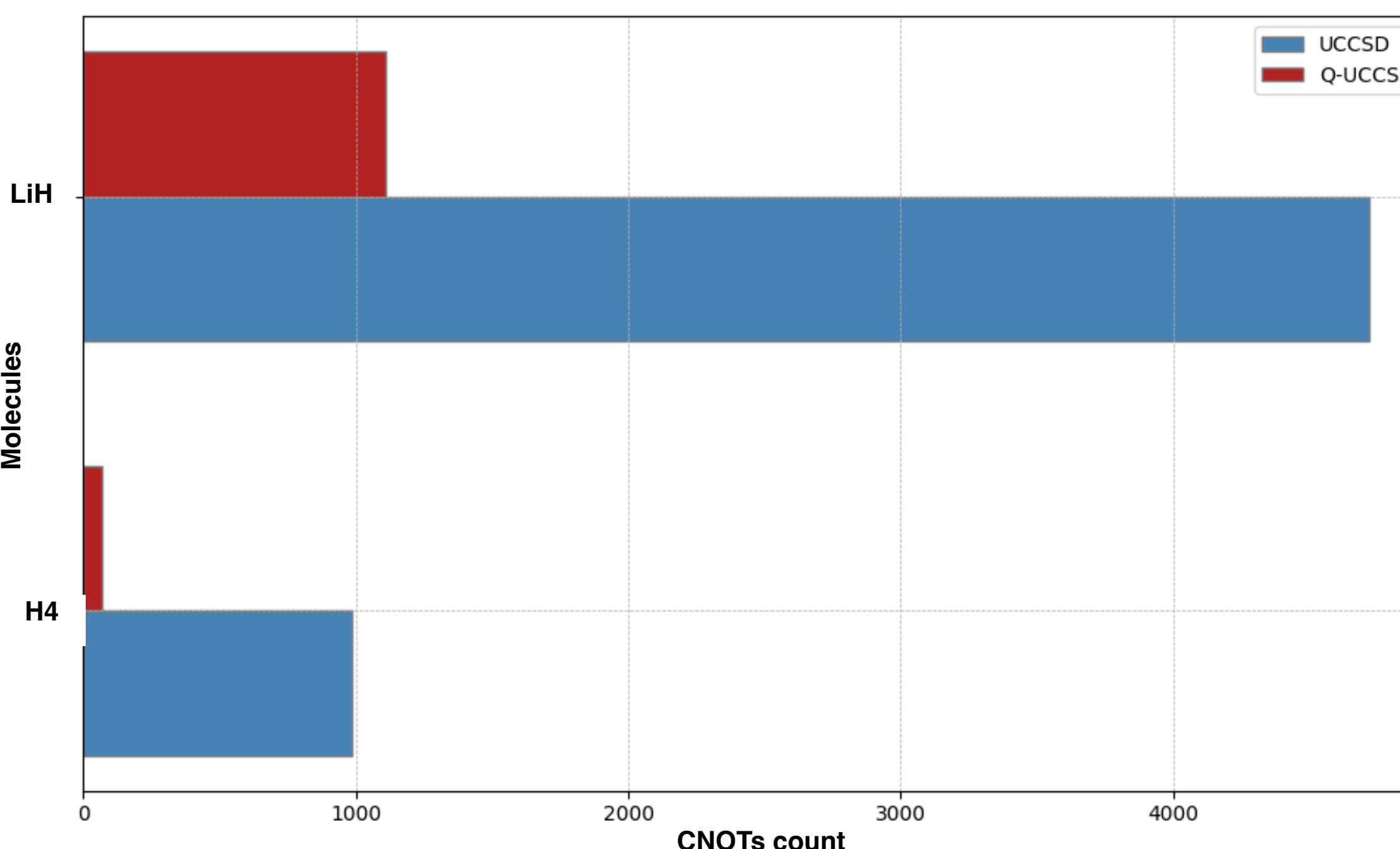
A circuit to implement a single qubit excitation evolution

Qubit excitation increase more CNOT-efficient than Fermion excitation evolutions

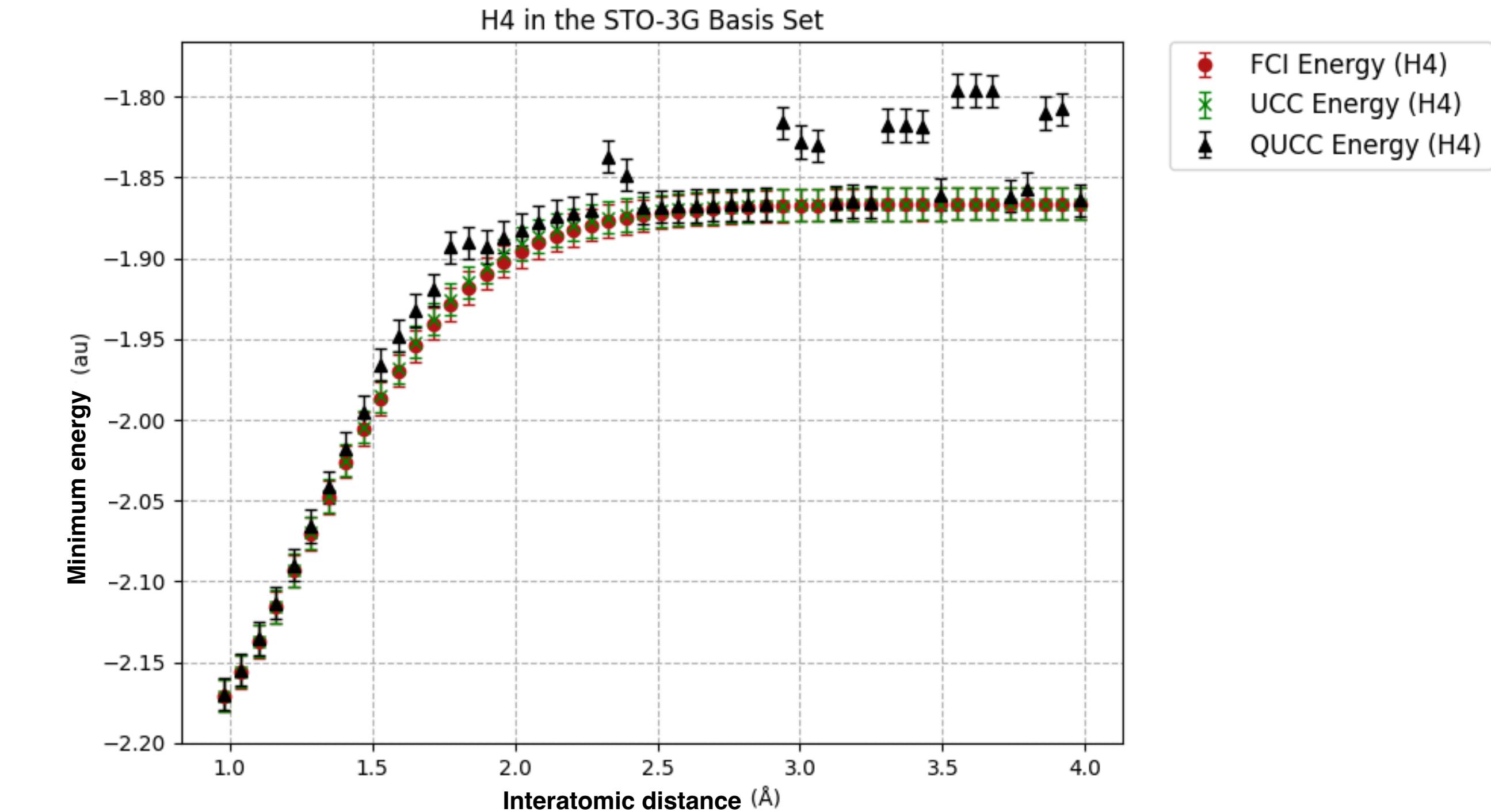


A circuit to implement a double qubit excitation evolution

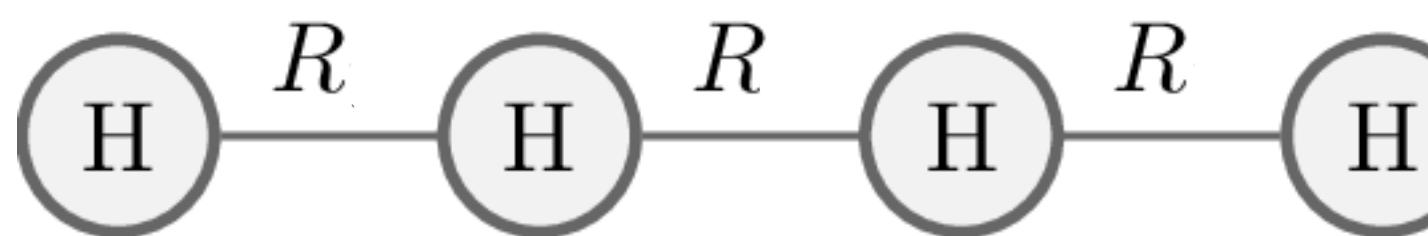
# Q-UCCSD versus UCCSD: Less CNOT-Gates

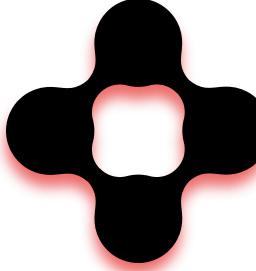


CNOT gates counts for UCCSD and QUCCSD using BFGS optimizer  
 $r_{H-H} = 0.75 \text{ \AA}$



The minimum VQE energies of H4 in linear geometry with different bond lengths calculated by QUCCSD - VQE compared to UCCSD-VQE - BFGS optimiser



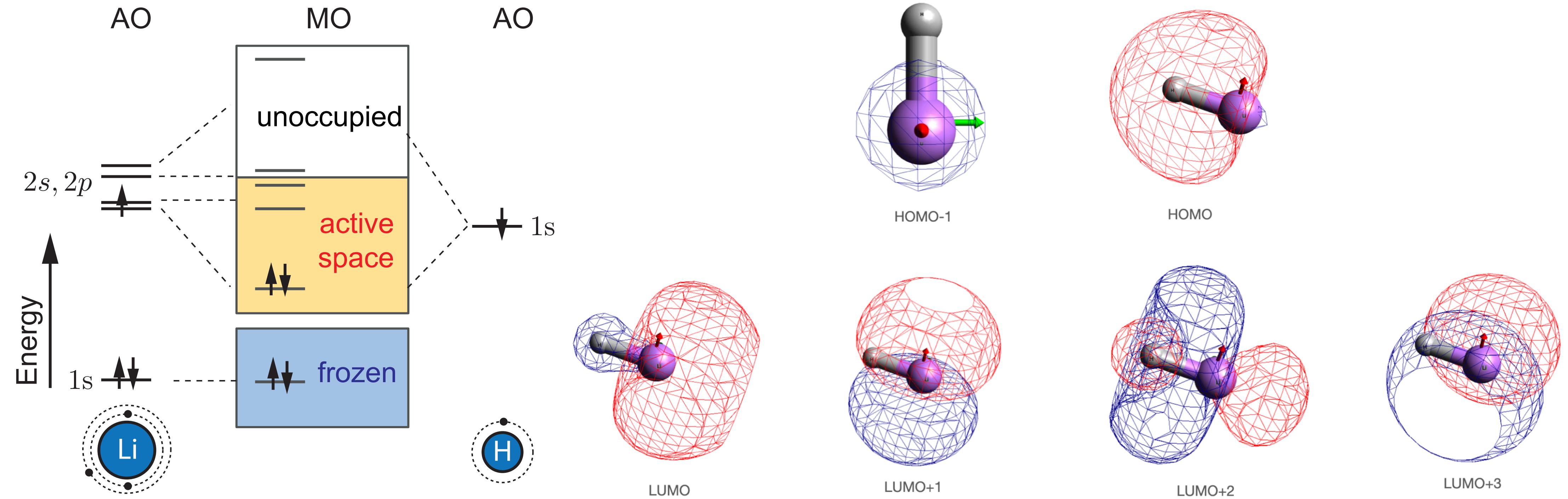


# Contribution

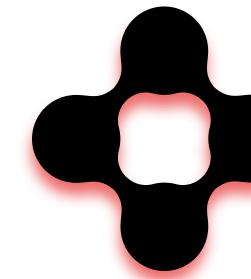
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1. QUCC method – Reduction in the number of CNOT gates
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3. (CAS)-PMRS – Reduction in the number of iterations & high fidelity rate
4. USCC algorithm – Towards chemical accuracy and less parameters
5. VQD algorithm – Towards excited states measurement

# Complete Active Space Selection (CAS)-Method: Reduce number of Qubits



**(Left)** LiH molecular orbitals (MO) formed out of atomic orbitals (AO) contributed by each element. The active space region is highlighted in yellow. **(Right)** Visualization of spatial orbitals in LiH molecule using STO-3G basis-set: 2 HOMOs and 4 LUMOs.



# Contribution

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1. QUCC method – Reduction in the number of CNOT gates
2. CAS – Reduction in the number of Qubits
3. (CAS) + PMRS – **Reduction in the number of iterations & high fidelity rate**
4. USCC algorithm – Towards chemical accuracy and less parameters
5. VQD algorithm – Towards excited states measurement

# Parameter Shift-Rules (PMRS): Less iterations

- Gradient Descent step:  $\theta_{k+1} = \theta_k - \eta \nabla f(\theta_k)$

- Quantum circuit function:

$$f(x; \theta_i) = \langle x | U_i^\dagger(\theta_i) \hat{B} U_i(\theta_i) | x \rangle$$

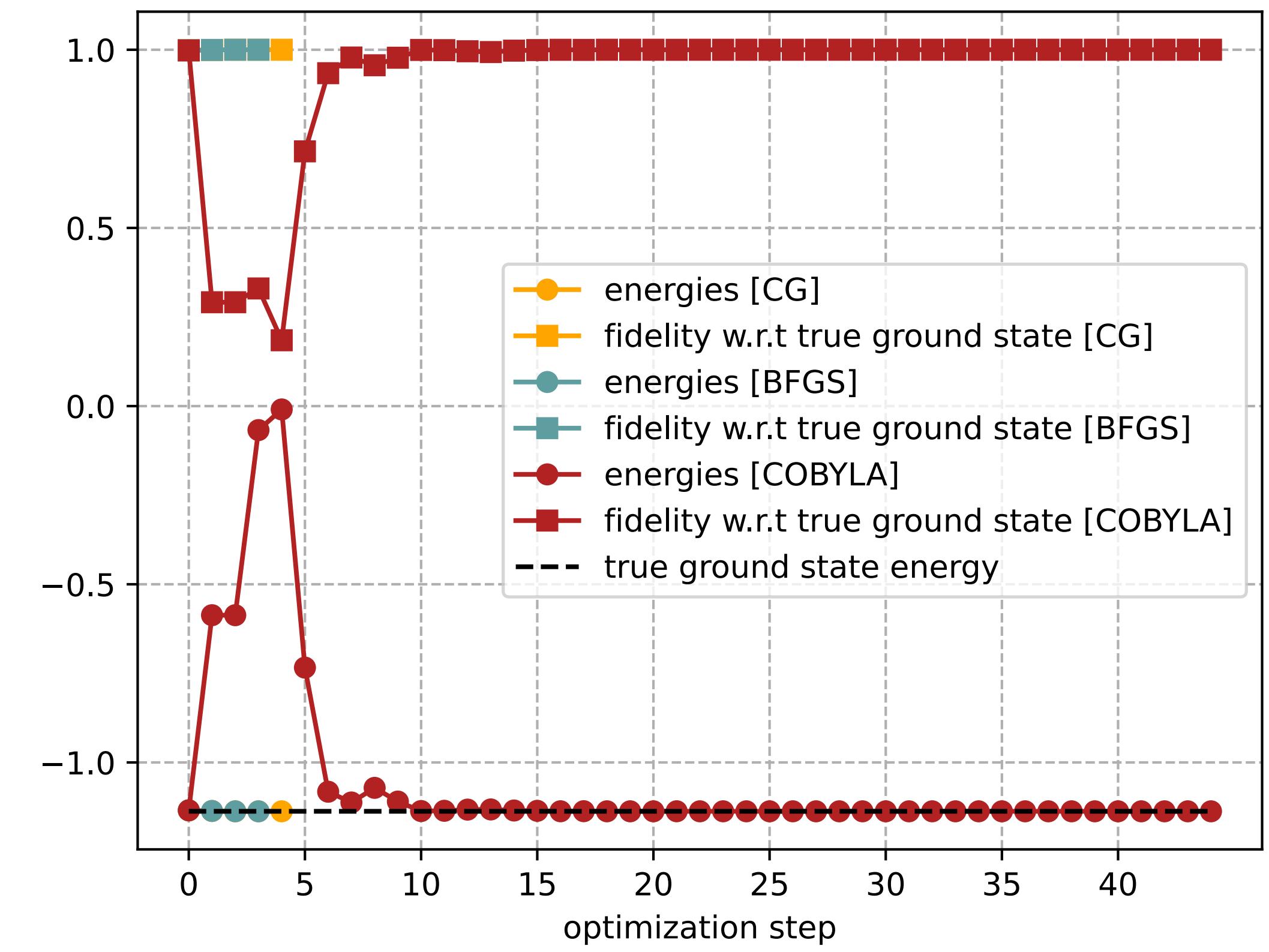
- Parameterized gates:

$$U_i(\theta_i) = \exp\left(-i \frac{\theta_i}{2} P_i\right)$$

- The gradient can be rewritten in terms of quantum functions:

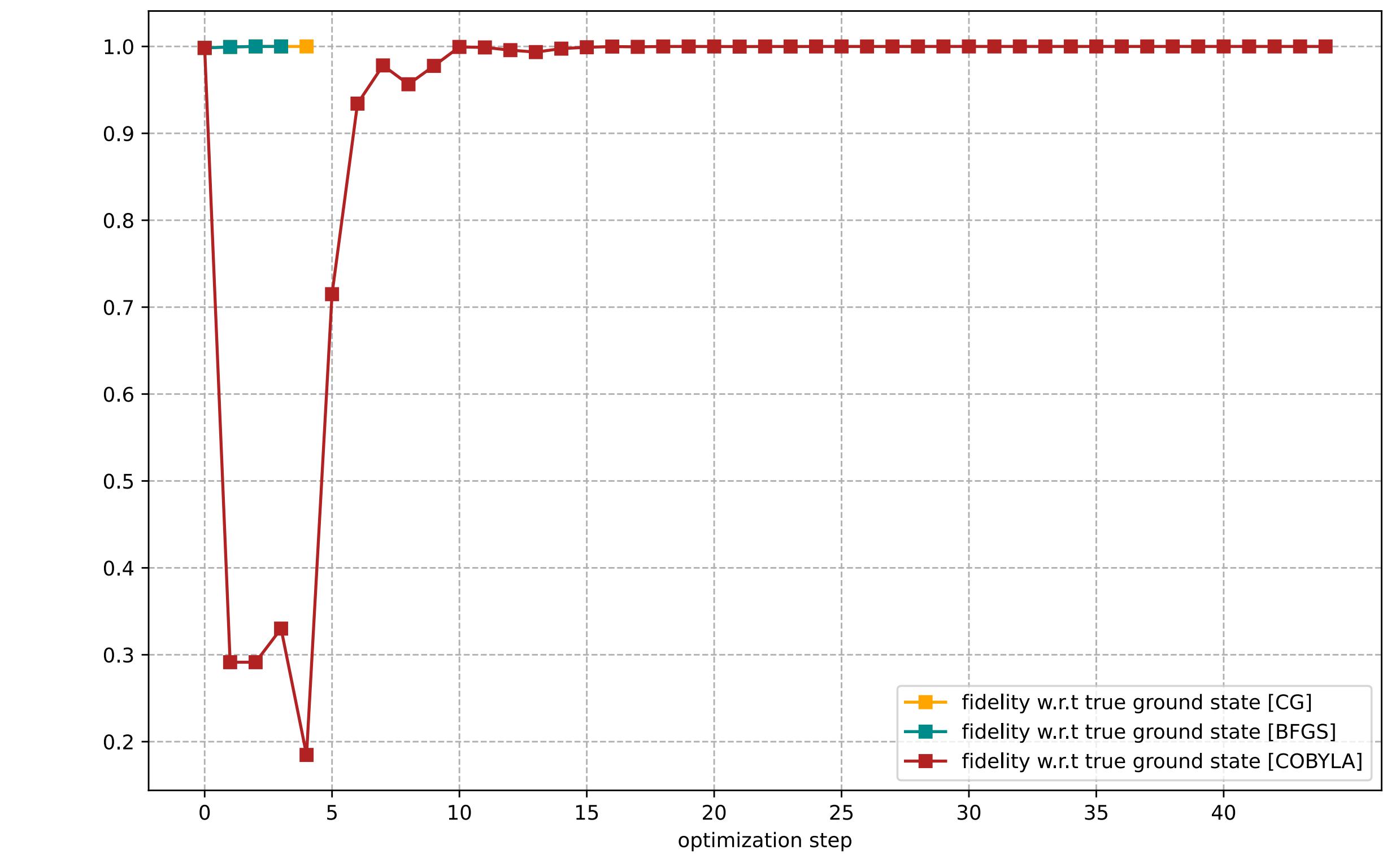
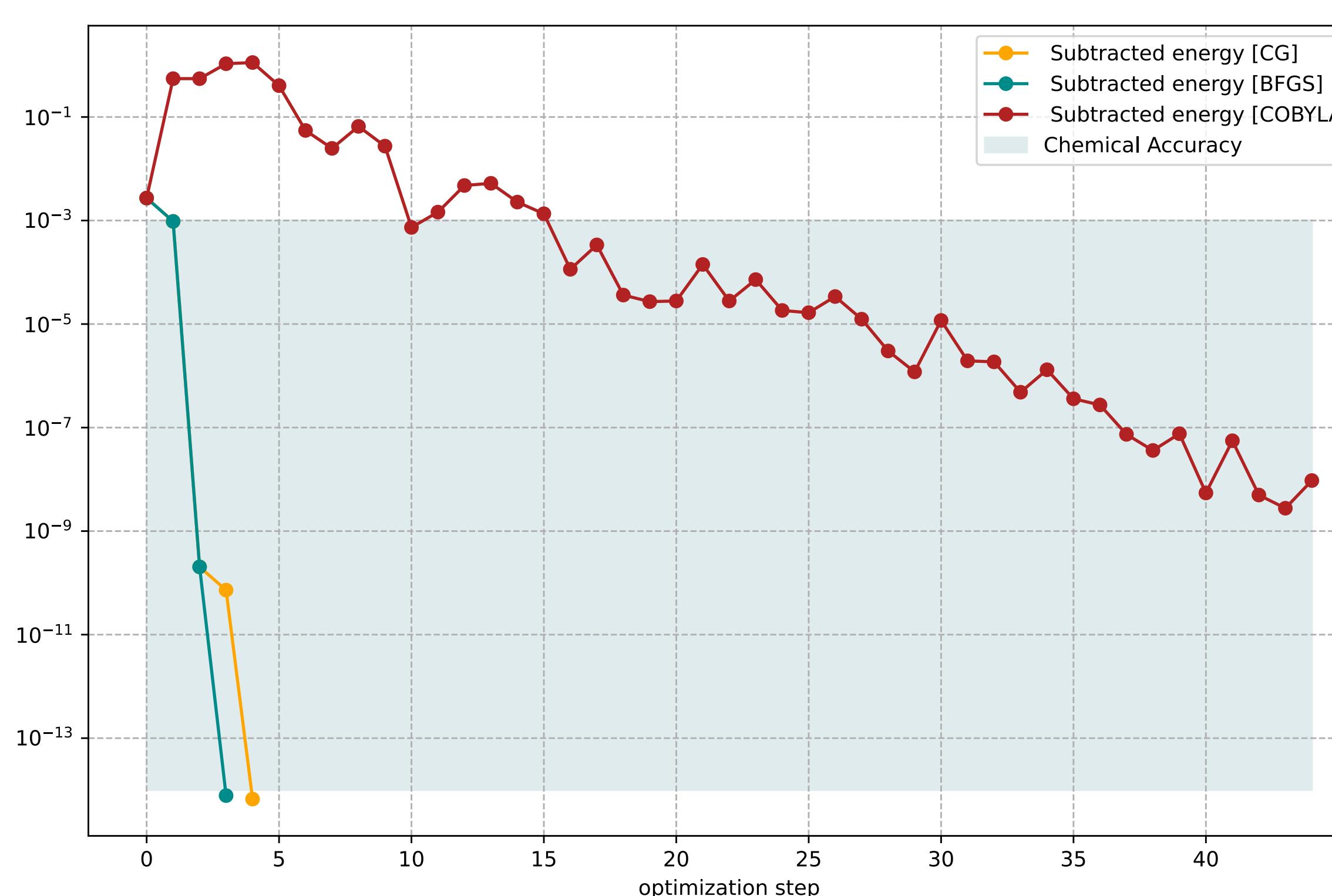
$$\nabla_\theta f(x; \theta) = \frac{1}{2} \left[ f\left(x; \theta + \frac{\pi}{2}\right) - f\left(x; \theta - \frac{\pi}{2}\right) \right]$$

PMRS application on H<sub>2</sub> molecule at r<sub>H-H</sub> = 0.75 Å, shows the energies (and fidelities) comparison between three optimizers: gradient based (CG and BFGS); free-gradient (COBYLA).



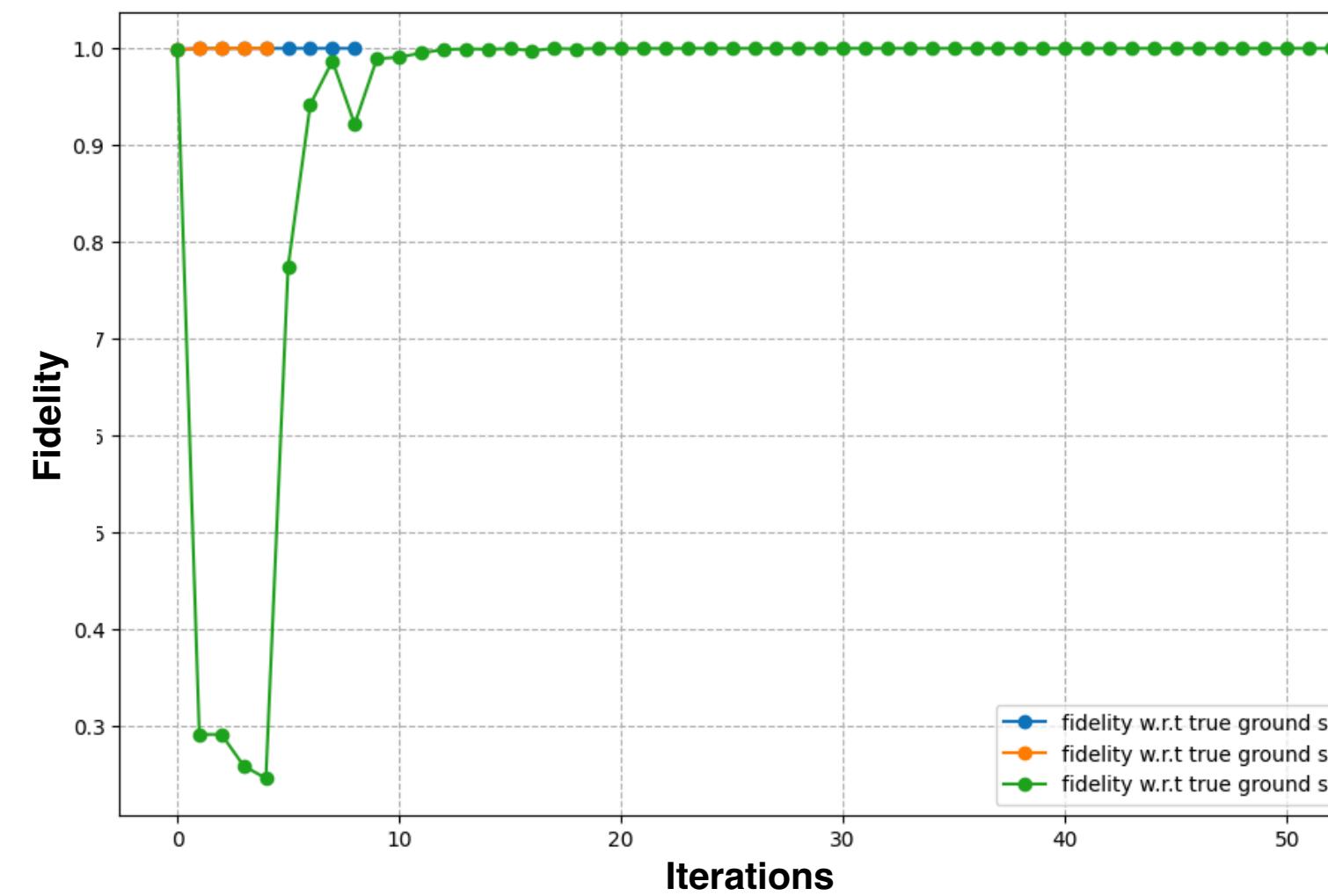
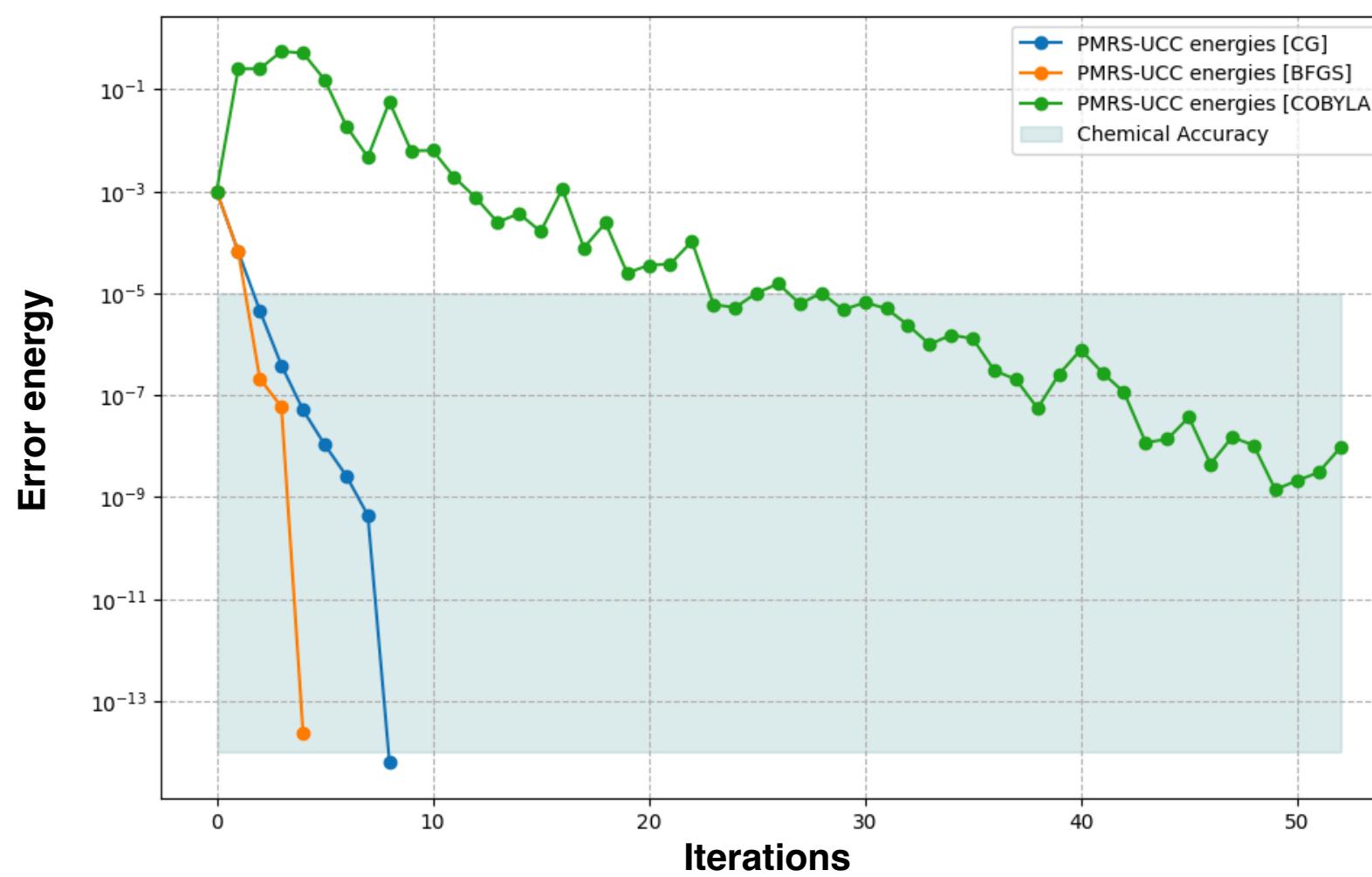
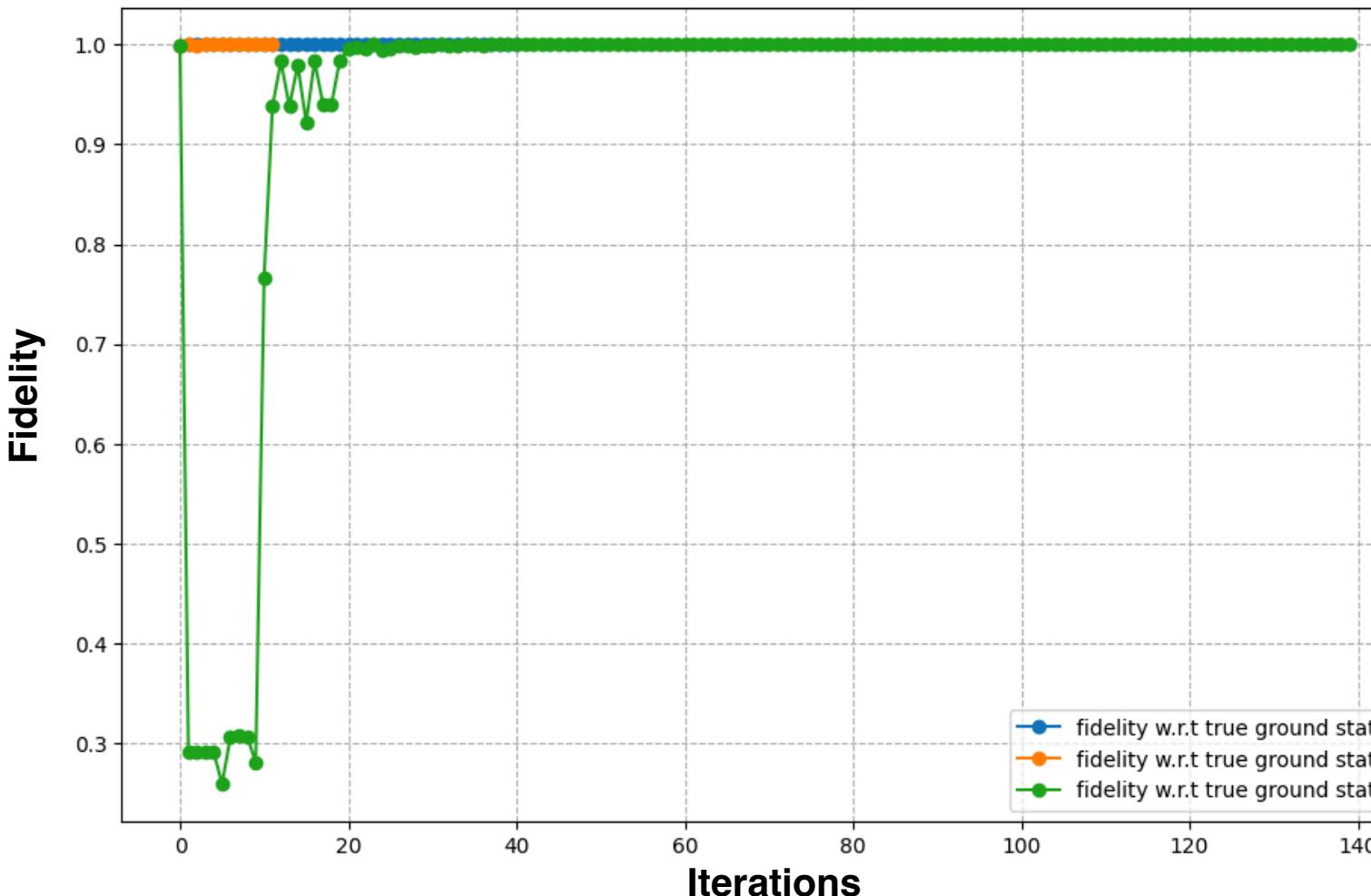
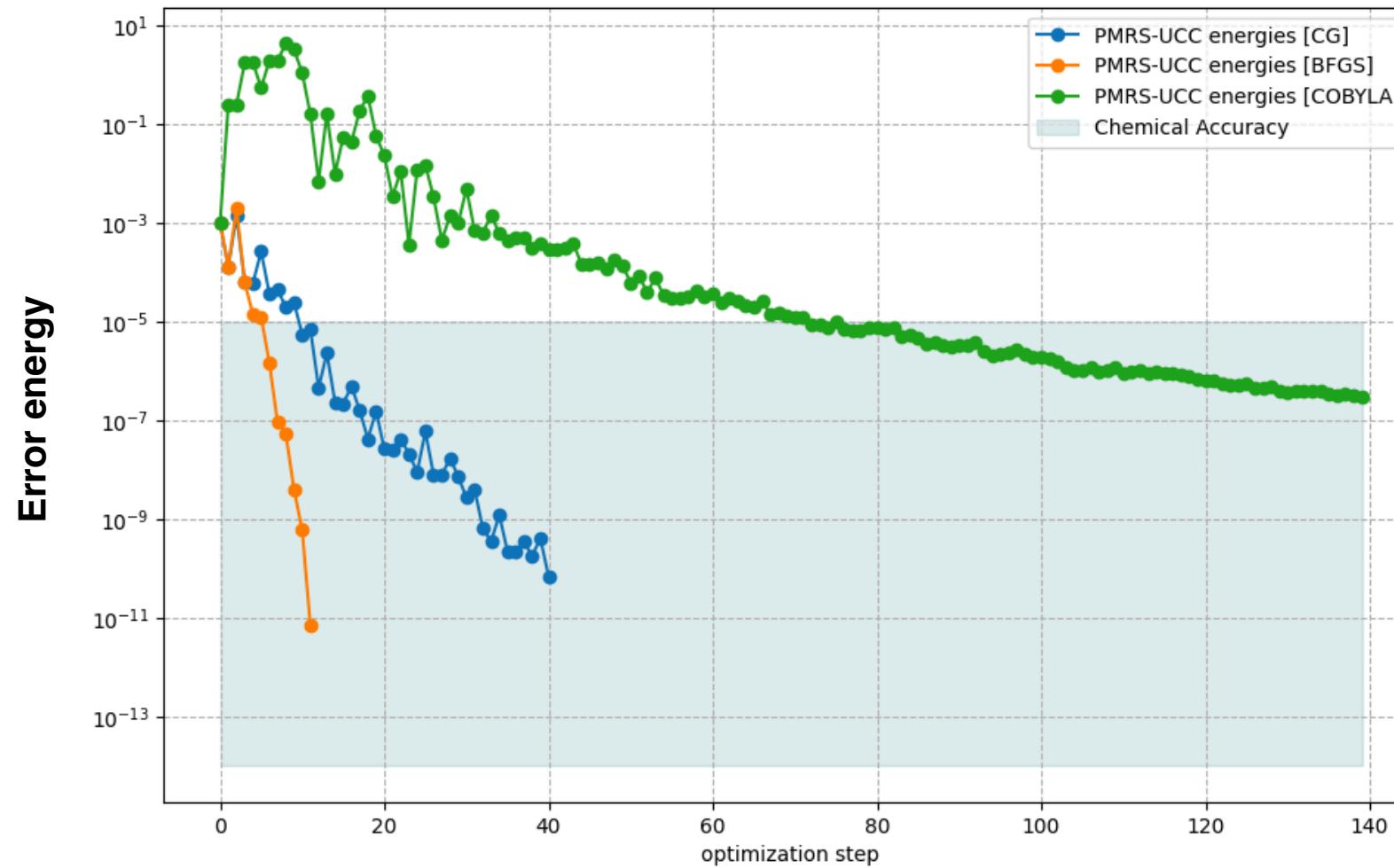


# Parameter Shift-Rules (PMRS): High Fidelity



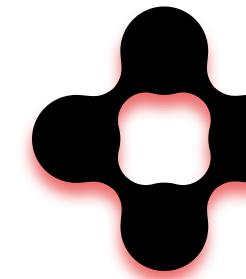
(Left) - PMRS Log scale energy & (Right) - Fidelity applied on  $\text{H}_2$  molecule at  $0.75\text{\AA}$  comparison between BFGS and L-BFGS optimizers between UCC and Q-UCC methods

# (CAS)- Parameter Shift-Rules (PMRS)



PMRS application on LiH molecule  
at 1.45 Å (12 qubits - STO-3G) -  
Non CAS

PMRS application on LiH molecule  
at 1.45 Å (Reduced to 6 qubits -  
STO-3G) - With CAS



# Contribution

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5. VQD algorithm – Towards excited states measurement

# Unitary Selective Couple Cluster (UsCC)

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## Algorithm 2 Unitary Selective Coupled-Cluster

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```
1: Step 1: Generate single and double excitations for a given molecule.  
2: for all single (S) and double (D) excitations  $[i, p]$  and  $[i, j, p, q]$  in UCCSD do  
3:   if  $h_1[i, p]$  and  $h_2[i, j, p, q]$  are larger than  $\epsilon_1$  then  
4:     add to ansatz  
5:   end if  
6: end for  
7: repeat  
8:   Step 2: Run VQE with the current ansatz to compute energy, update amplitudes for each excitation present in ansatz.  
9:   Step 3: For each single  $[i, p]$  or double  $[i, j, p, q]$  excitation present in ansatz using  $t_1$  and  $t_2$  values from the previous  
iteration and additional excitations  $[k, r]$  or  $[k, l, r, s]$ , generate triple and quadruple excitations with the following coeffi-  
cients:  
10:     $t_1[i, p] \cdot h_2[j, k, q, r]$   
11:     $h_1[i, p] \cdot t_2[j, k, q, r]$   
12:     $t_2[i, j, p, q] \cdot h_1[k, r]$   
13:     $h_2[i, j, p, q] \cdot t_1[k, r]$   
14:     $t_2[i, j, p, q] \cdot h_2[k, l, r, s]$   
15:   Step 4: For each excitation, if the absolute value of the largest coefficient computed in step 3 is larger than  $\epsilon_n$  on  
iteration  $n$ , add this excitation to ansatz.  
16: until termination condition
```

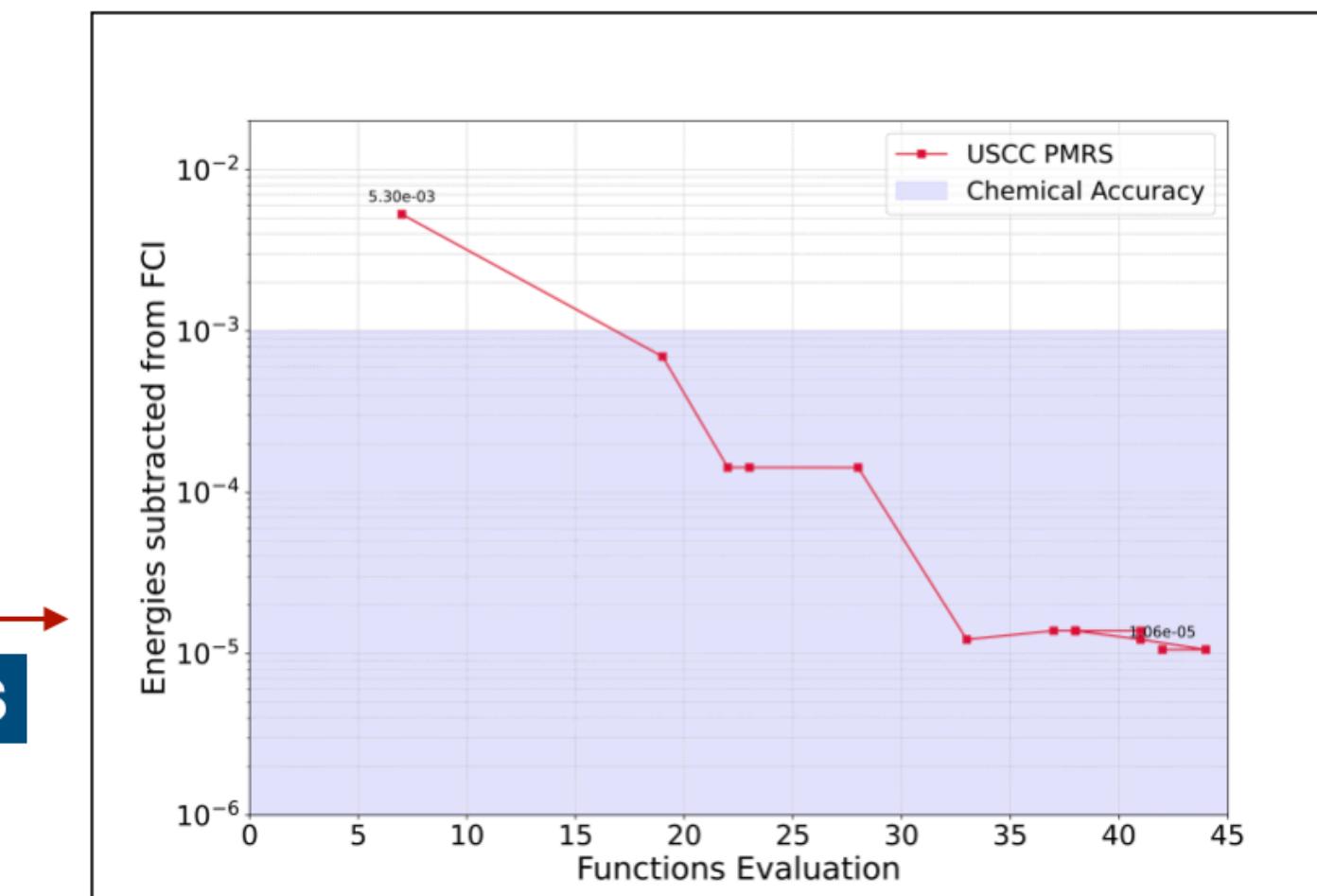
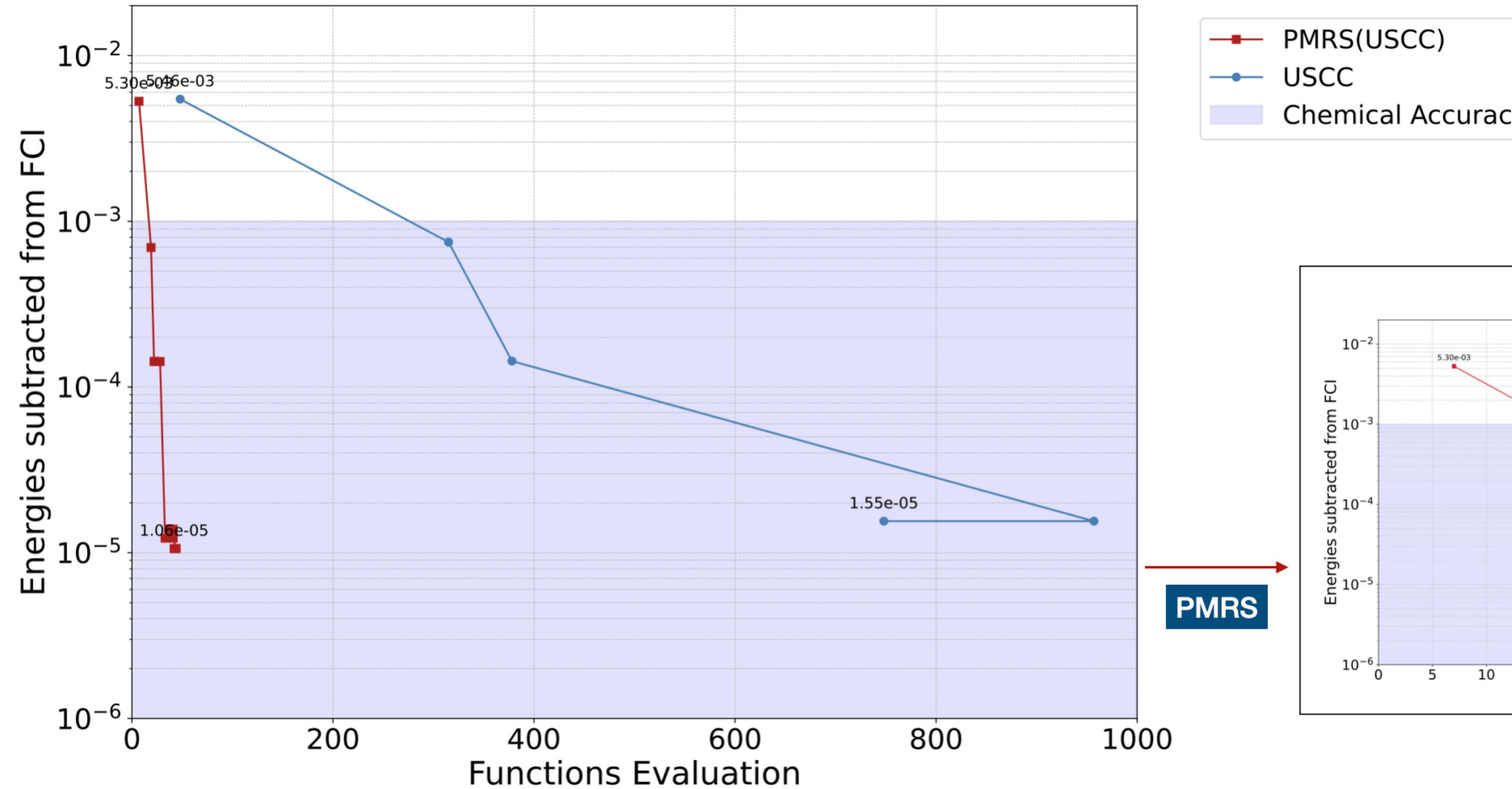
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### Reference:Unitary Selective Coupled-Cluster Method

[Dmitry A. Fedorov](#), [Yuri Alexeev](#), [Stephen K. Gray](#), [Matthew Otten](#)

# (PMRS) - Unitary Selective Couple Cluster (UsCC)

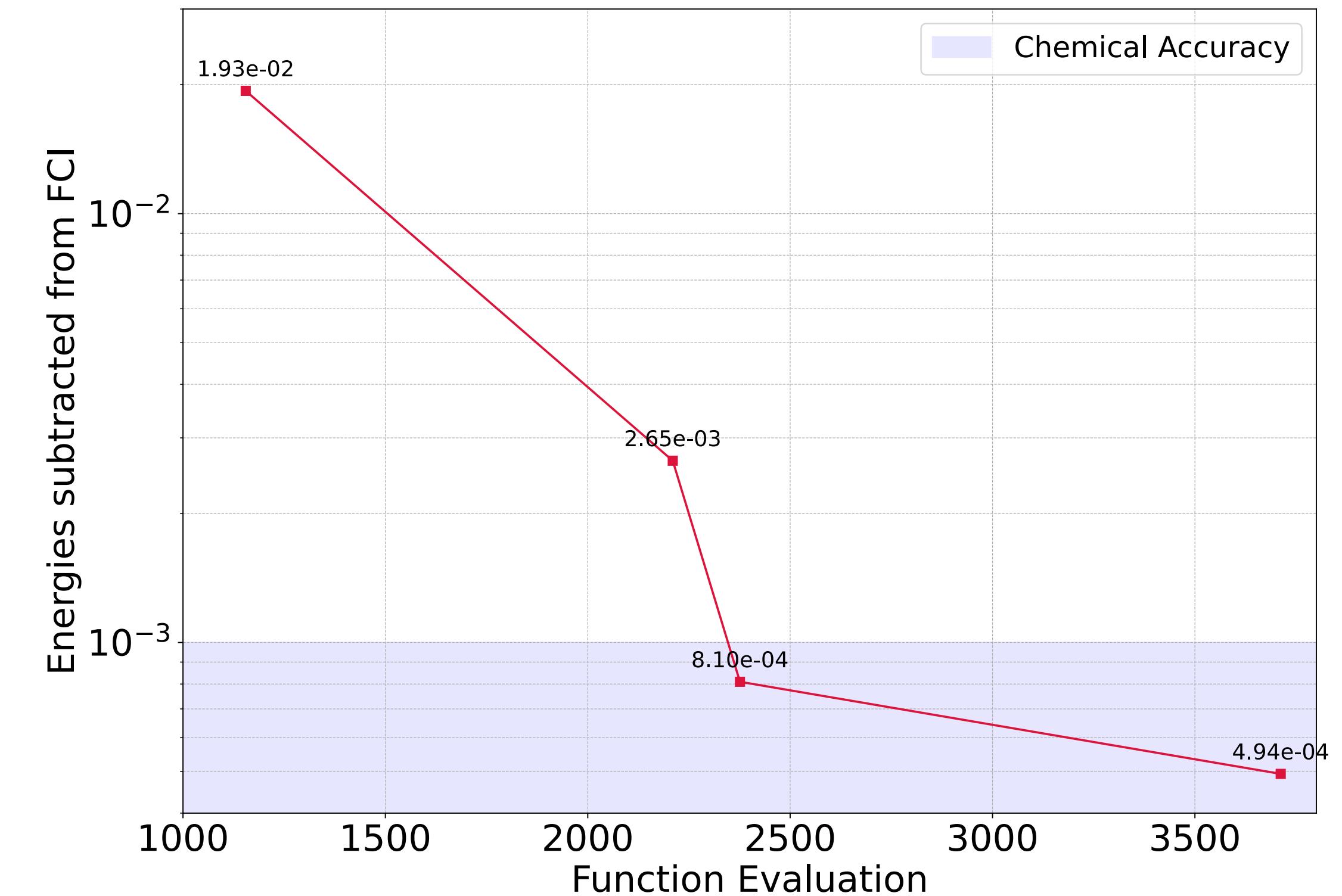
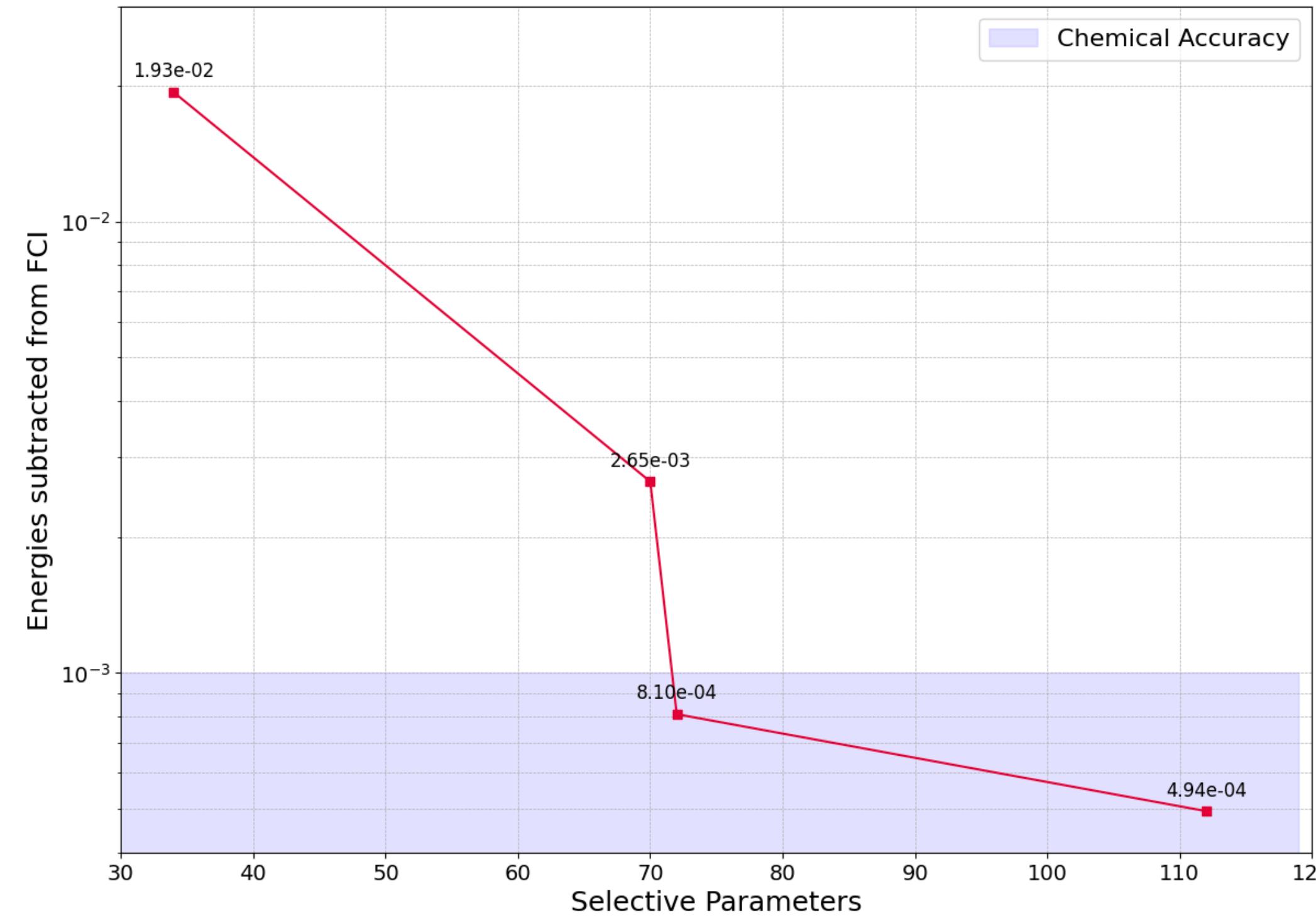
## Less Functions Evaluation + Chemical Accuracy



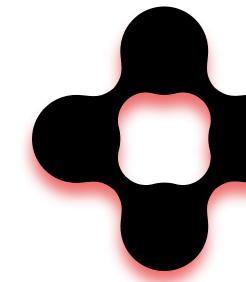
Test UsCCSDTQ-VQE and PMRS-UsCCSDTQ-VQE on LiH 12 qubits in term of Function Evaluation. BFGS optimizer, tolerance  $10^{-6}$  (Hartree), STO-3G basis set is used

# Unitary Selective Couple Cluster (UsCC)

## Toward bigger molecules



Test UsCCSDTQ-VQE on H<sub>4</sub> molecule (16 qubits). BFGS optimizer, tolerance  $10^{-6}$  (Hartee), 6-31G basis set is used.



# Contribution

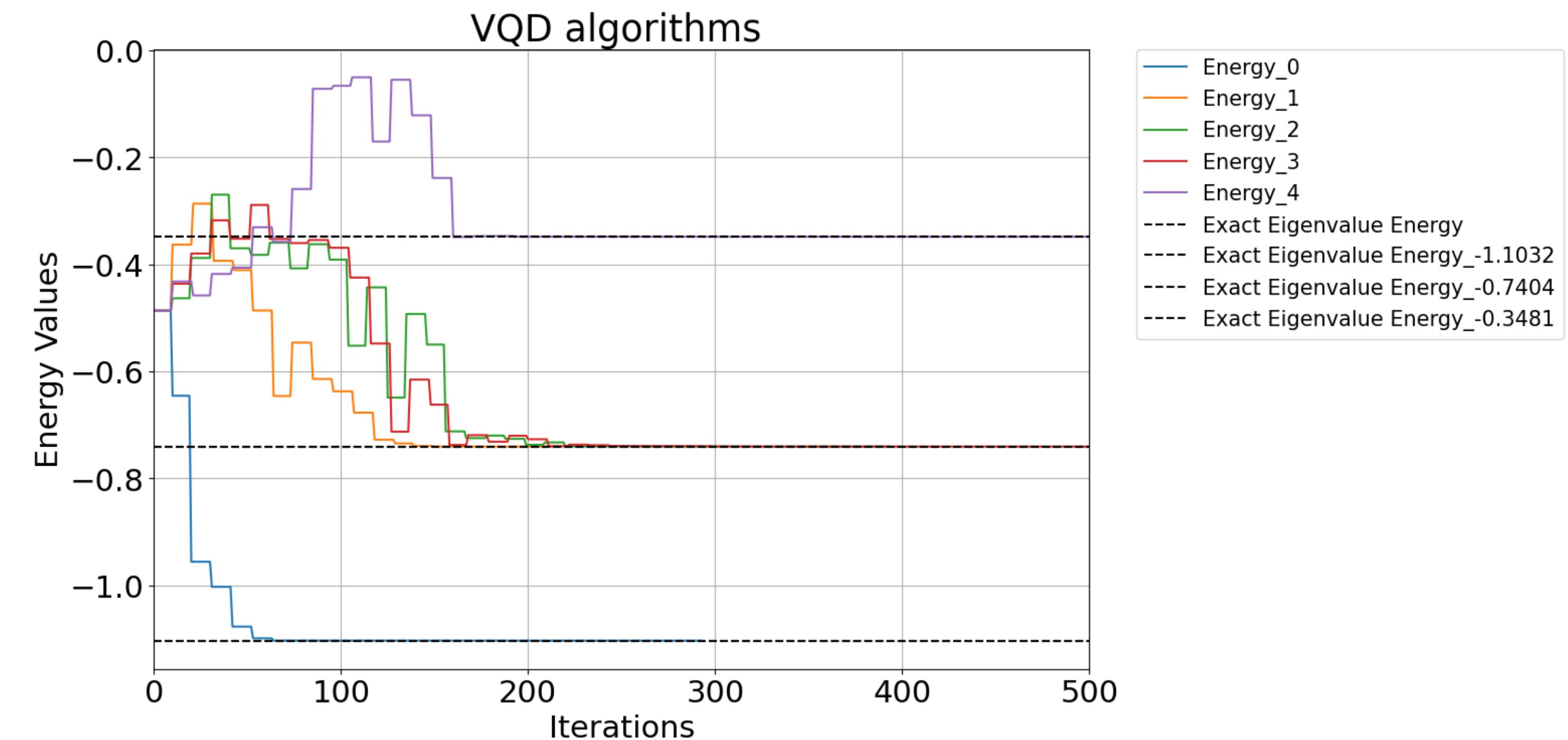
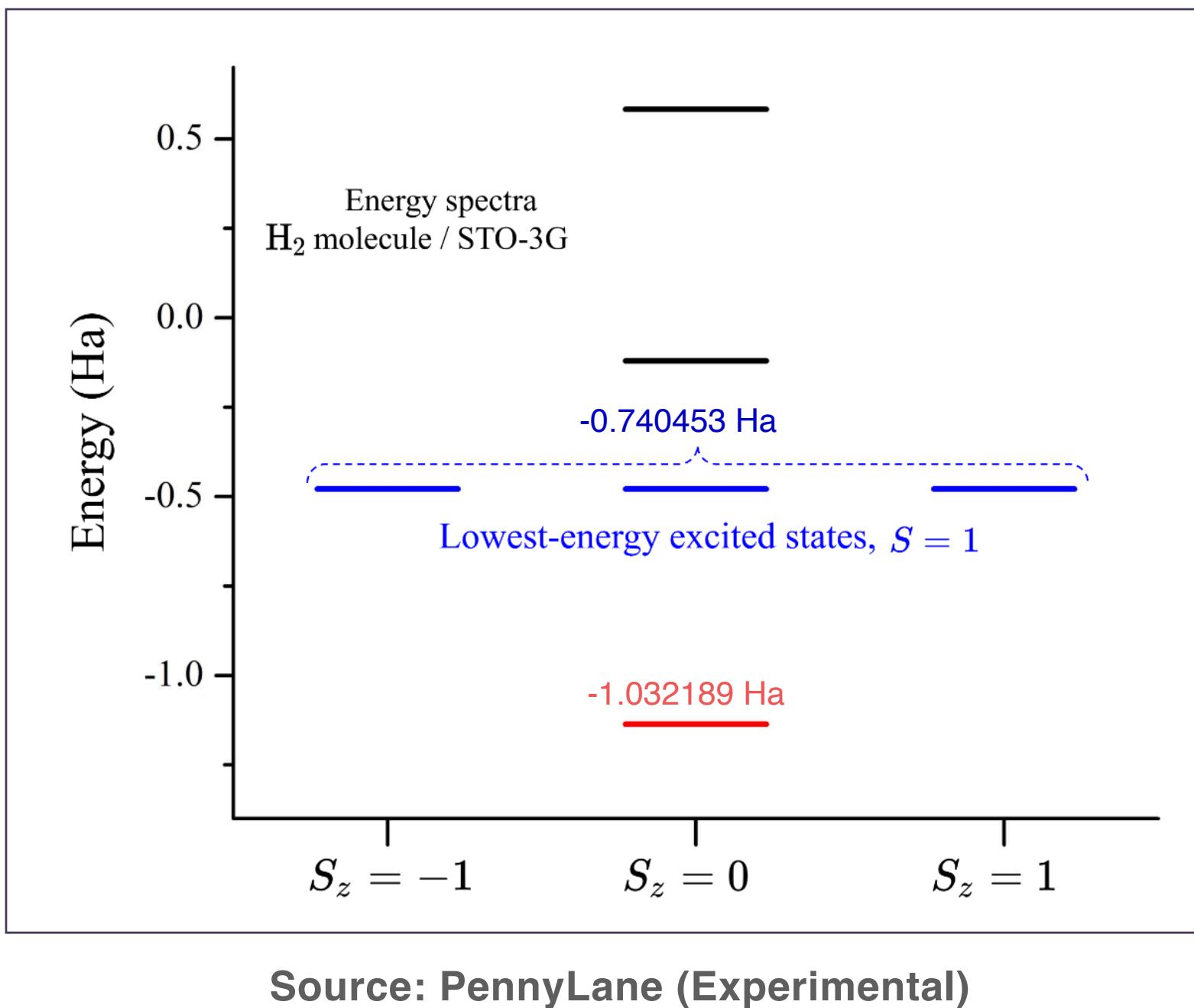
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# Variational Quantum Deflation: Towards excited states

**Cost function:**

$$F(\boldsymbol{\theta}_k) = \langle \psi(\boldsymbol{\theta}_k) | H | \psi(\boldsymbol{\theta}_k) \rangle + \sum_{i=0}^{k-1} \beta_i |\langle \psi(\boldsymbol{\theta}_k) | \psi(\boldsymbol{\theta}_i) \rangle|^2$$

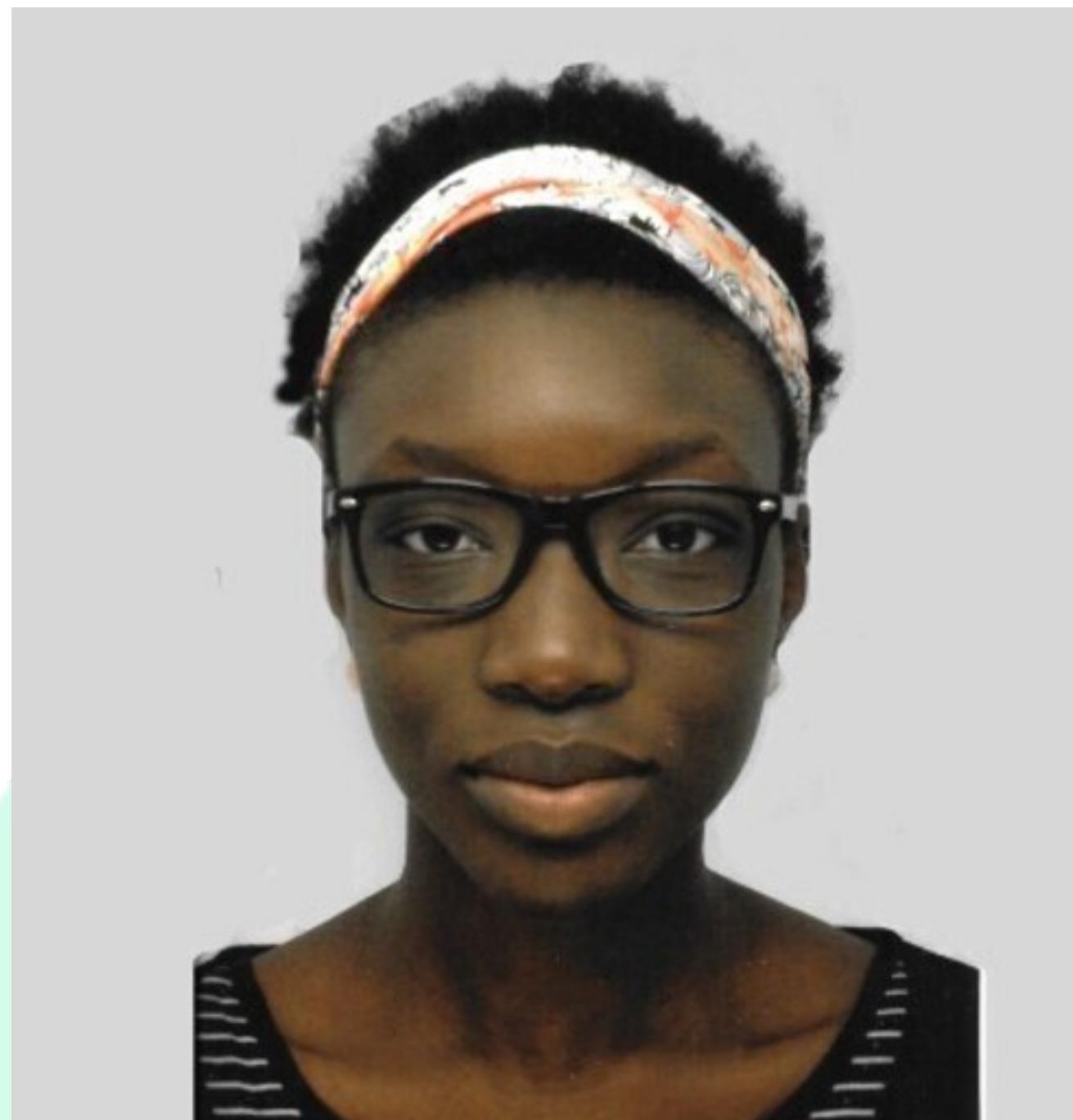


Variational Quantum Deflation (VQD) for at  $r_{\text{H}-\text{H}} = 0.75\text{\AA}$ , with UCCGSD ansatz. Target up to k=4 excited state with BFGS Optimiser

# I CONCLUSION

- Explore tools to accelerate the Unitary Coupled Cluster calculations such as CAS method and PMRS
- Targeting at bigger molecules and balancing cost with UsCC method - achieve better chemical accuracy over UCC method
- Implement algorithms aims at targeting the excited state energy with high fidelity rate
- Acquire a proficient skills in coding in MyQLM simulator

# ❖ ACKNOWLEDGMENT

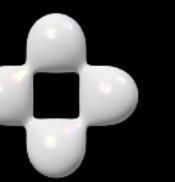




# APPENDIX SLIDES



# Our team of 55+ experts turns our founders' cutting-edge research & vision into reality



Pr Jay Ponder  
**Co-Founder**  
Expert in biochemistry.  
Former chair Gordon conferences.  
Lead developer Tinker.



Pr J.-P. Piquemal  
**Co-Founder & CSO**  
Expert in Quantum Chemistry & HPC computations.  
RSC fellow / project lead Tinker-HP.  
Atos Fourier Prize Laureate.



Pr Pengyu Ren  
**Co-Founder**  
Expert in multiscale modeling of proteins and nucleic acids.  
Lead developer Amoeba



Pr Matthieu Montes  
**Co-Founder**  
Expert in drug discovery.  
8 patents.  
1 compound at clinical stage.



Dr Louis Lagardère  
**Co-Founder**  
Expert in HPC computations.  
Lead developer Tinker-HP.  
Atos Fourier Prize Laureate.



Robert Marino, PhD  
**CEO**  
Serial entrepreneur  
Founded Europe's largest deeptech accelerator



Marion Pierfitte, MBA  
**COO**  
Biopharma | Product Launch & GTM Strategy | Digital Health | INSEAD



Jérôme Foret, PhD  
**Chief Platform Officer**  
20+ years of experience in software development.  
2 startups founded in AI.



Éric Nicolai  
**Head of Med. Chem.**  
30+ years in drug discovery, BMS, Sanofi, Cerep



Sara Dolcetti  
**VP Business Dev, Boston**  
15+ years of experience in BD & Licensing.



Léa El Khouri, PhD  
**Head comp chemistry**  
ABFE expert, worked on SAMPL challenge



Sarada Loock  
**Head Of MarCom**  
15+ years of experience in marketing & communication.

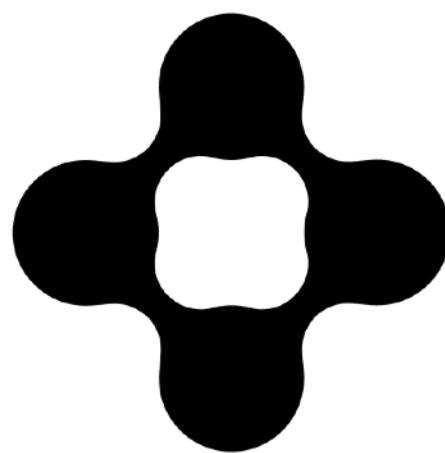


Alberto Peruzzo, PhD  
**Team Lead Quantum Computing**  
15+ years world leading research in field of quantum computing

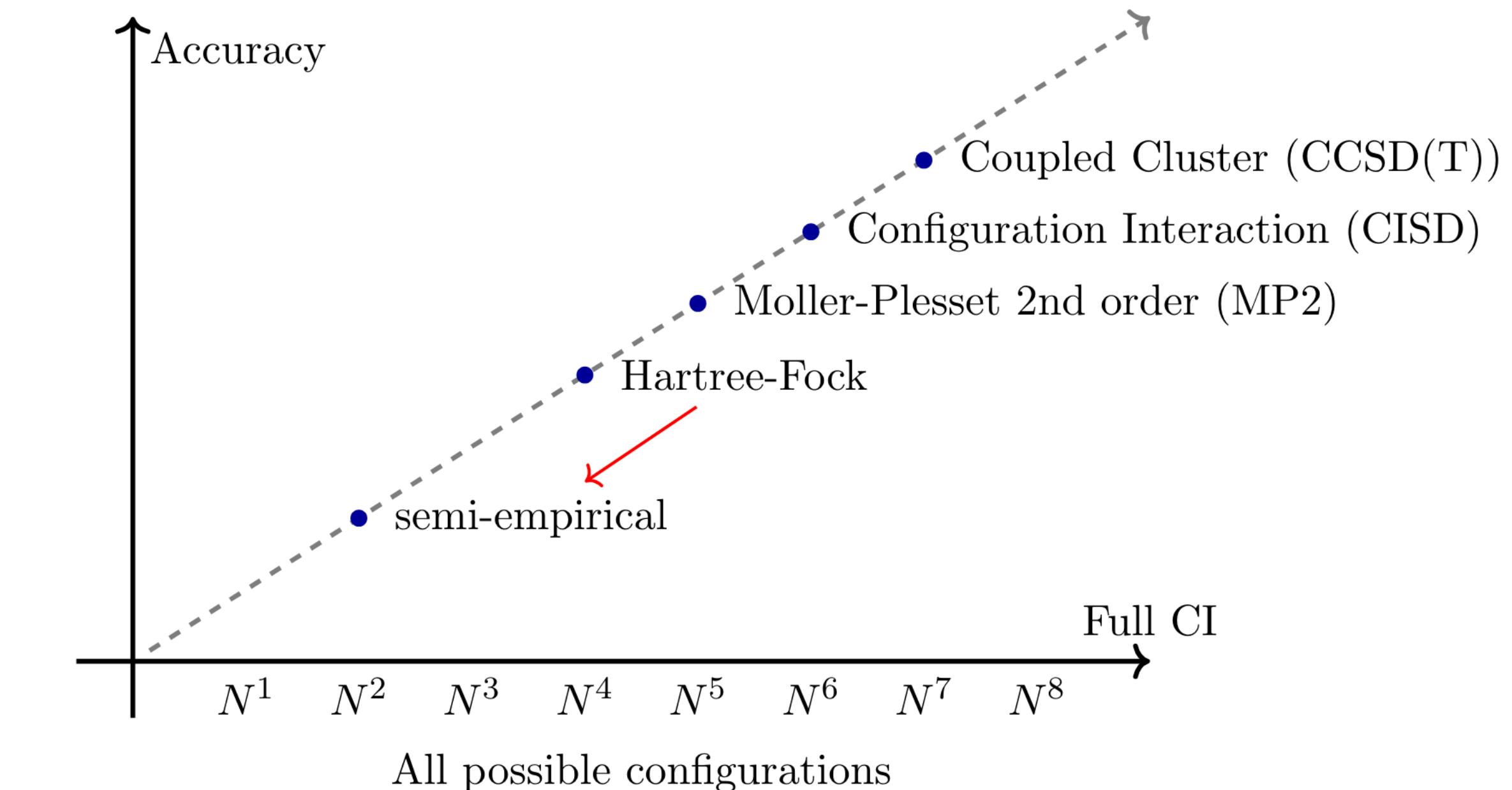
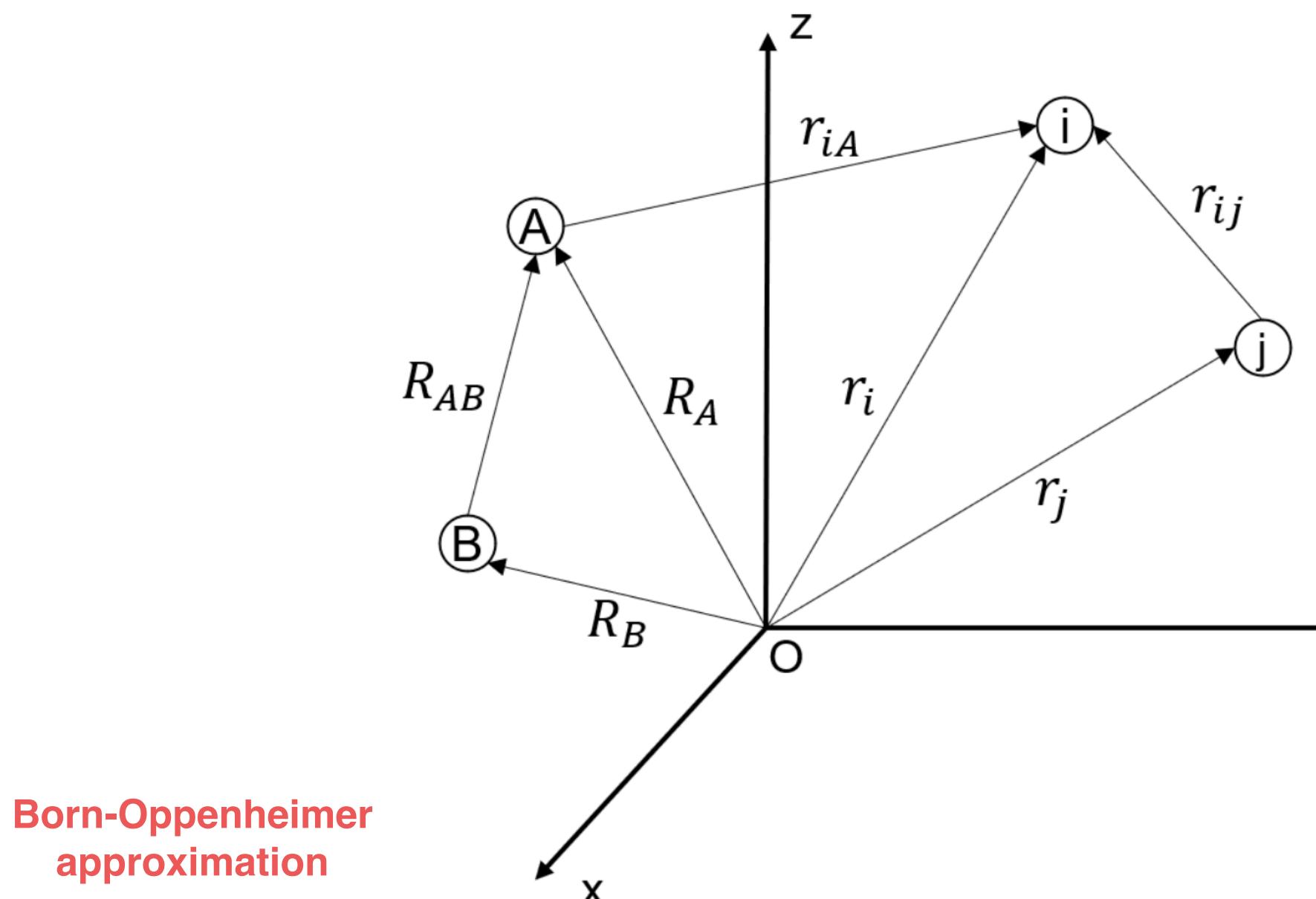


Boris Sattarov  
**Lead AI Generative Modelling**  
Ex DeFabritiis lab, ex 99 and beyond.



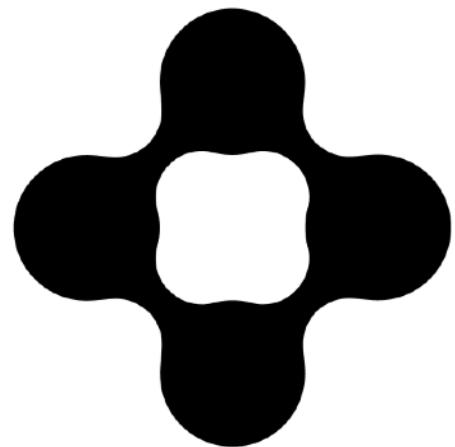


# Classical approach - First quantized Hamiltonian

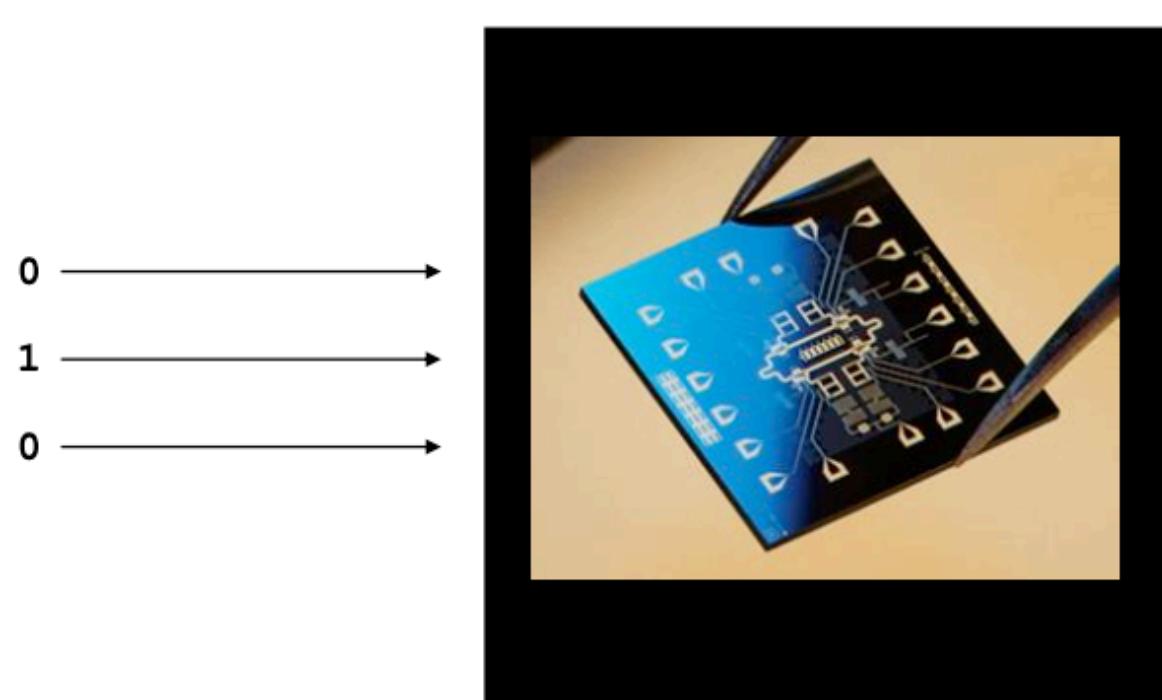
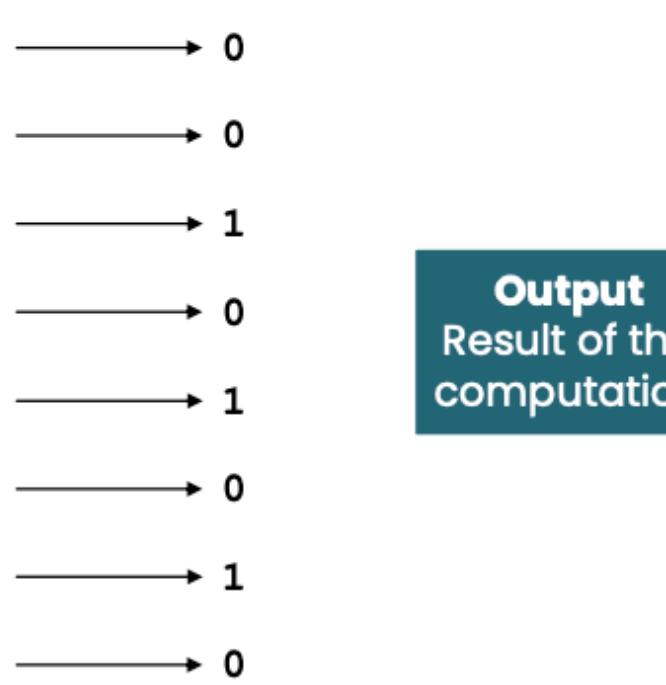
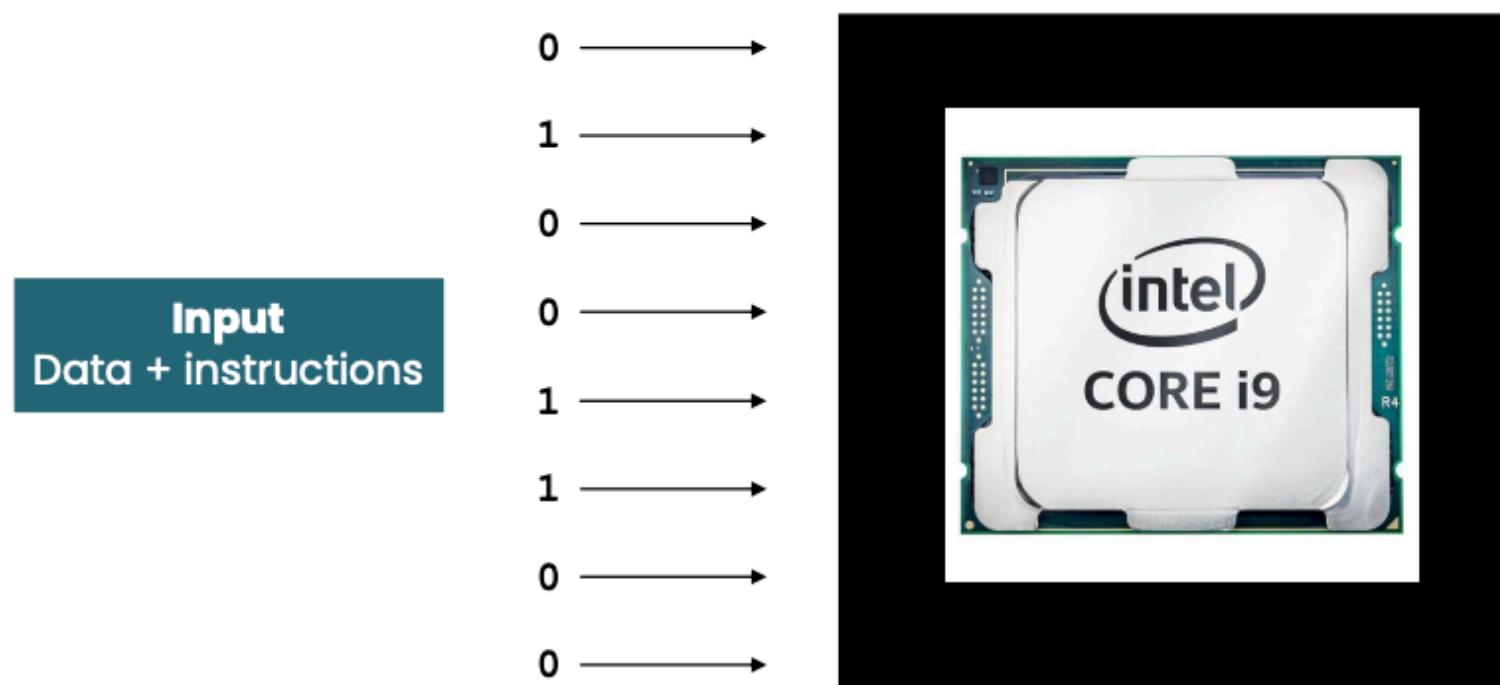


$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_a}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}.$$

We want to reach to FCI exact energy but requires much less computational resources !!!



# A classical / quantum processor



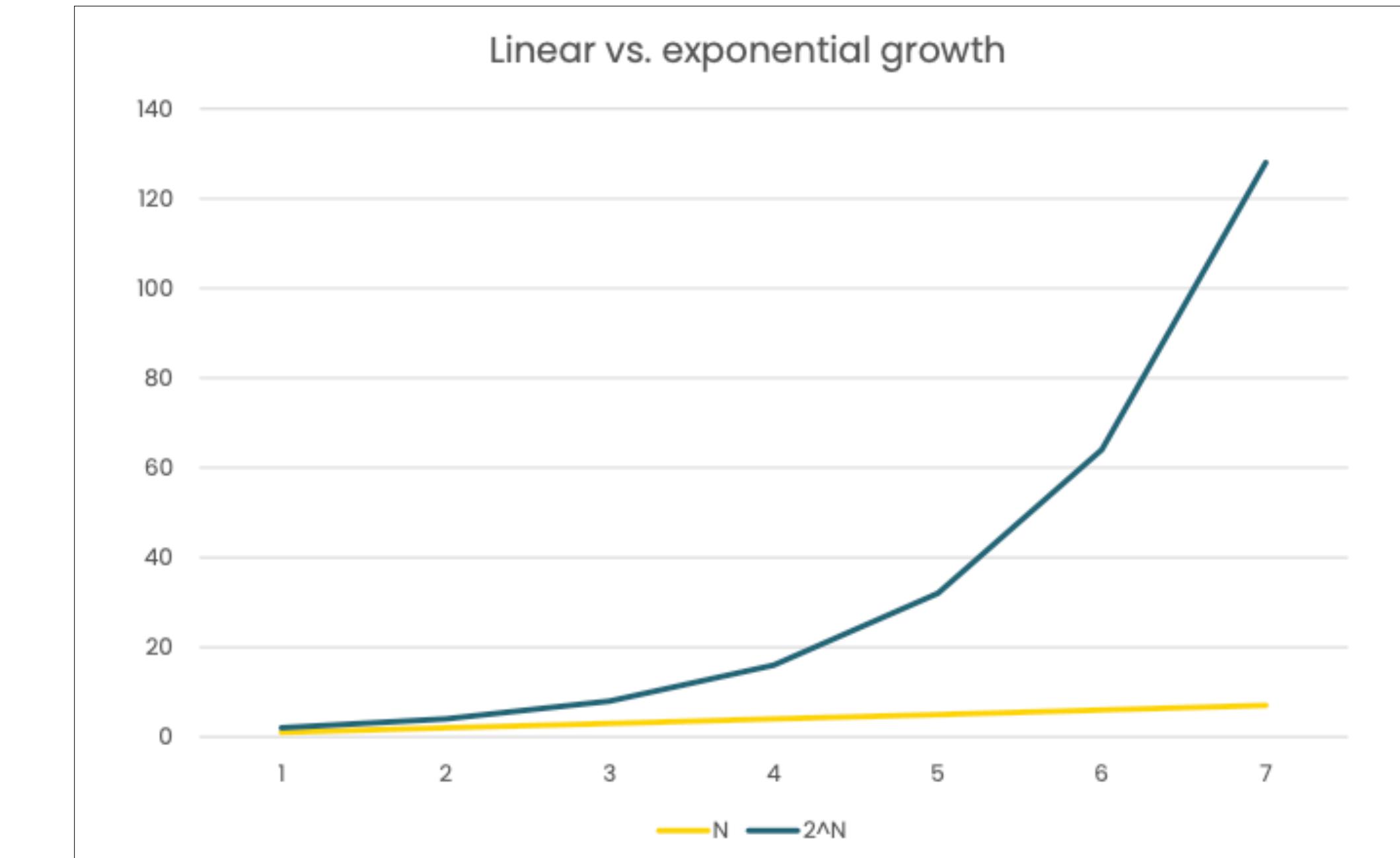
000 with some probability  
001 with some probability  
010 with some probability  
011 with some probability  
100 with some probability  
101 with some probability  
110 with some probability  
111 with some probability

**Input**  
Data + instructions

3 qubits

**Output**  
Result of the computation

$2^3 = 8$  different results



To describe the state of exponential computing power

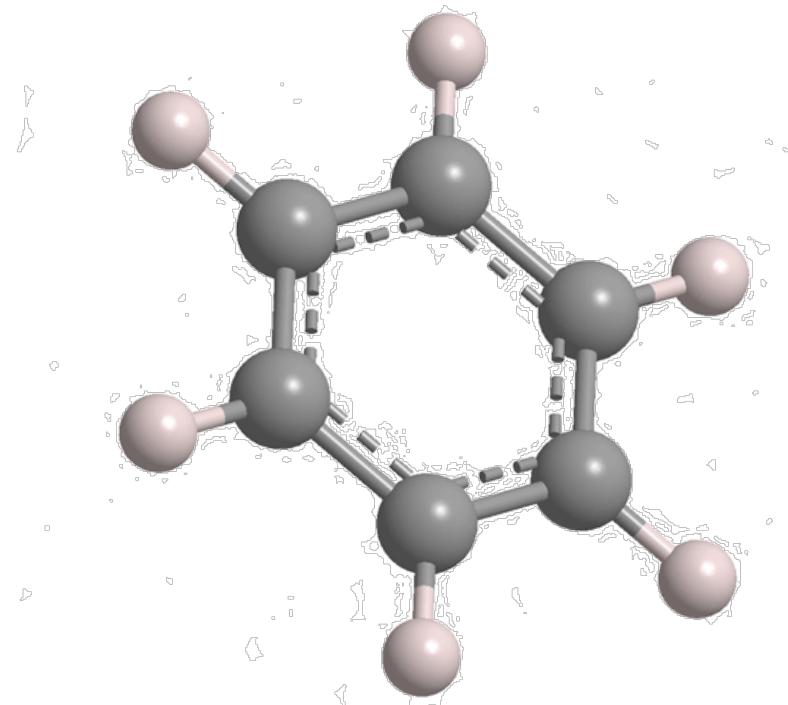
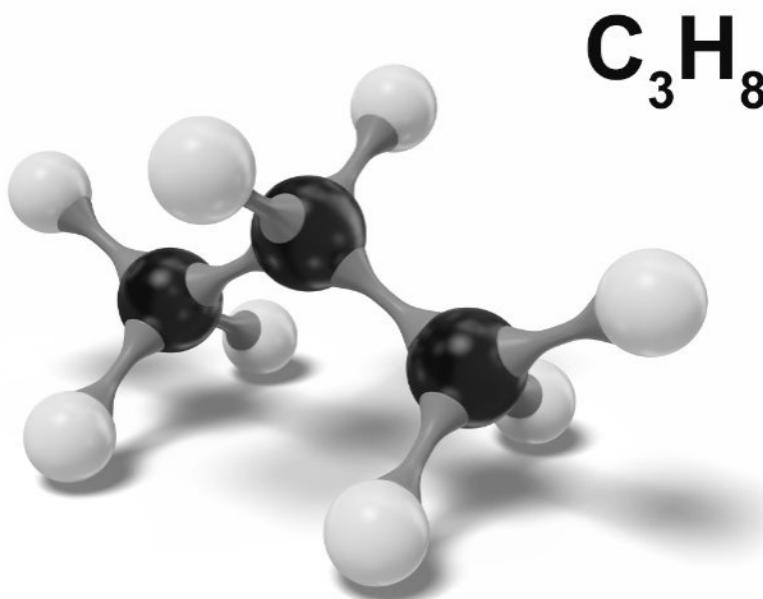
A CPU with N bits:

A QPU with N qubits:

➤ Need only N parameters

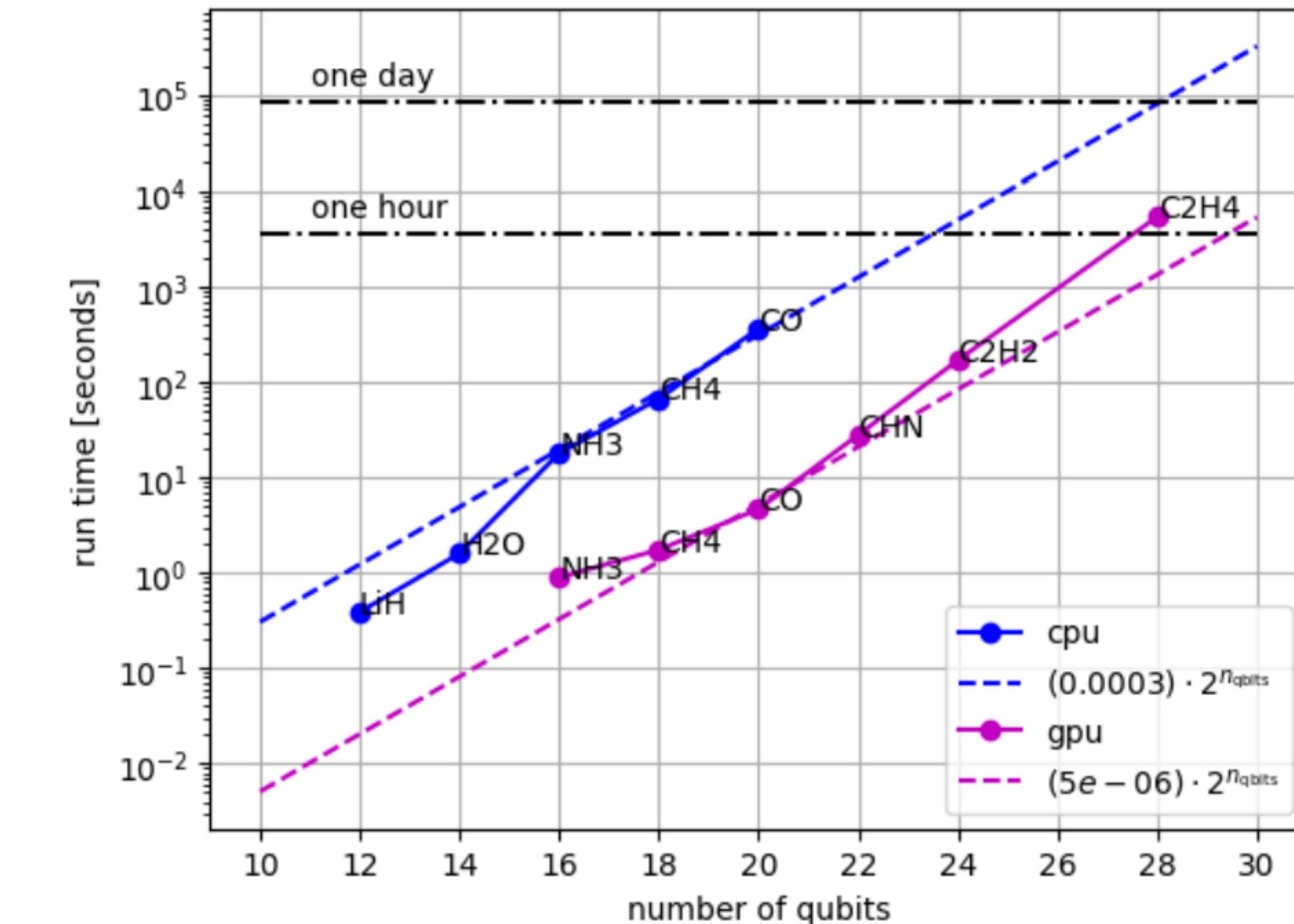
➤ Need  $2^N$  parameters

# Quantum Resources: Number of qubits increases

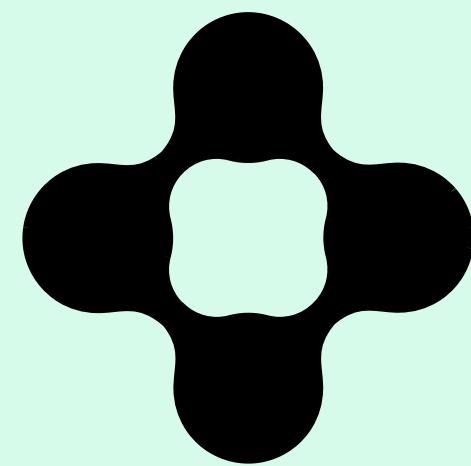
**Benzene****Propane**

➤ 42 electrons over 36 spatial orbitals = 72 qubits  
Quantum Memory needed

➤ 26 electrons over 23 spatial orbitals = 46 qubits

**Figure 1:** Timings (in seconds), using both CPUs and GPUs resources, for the evaluation of increasing size molecular Hamiltonians

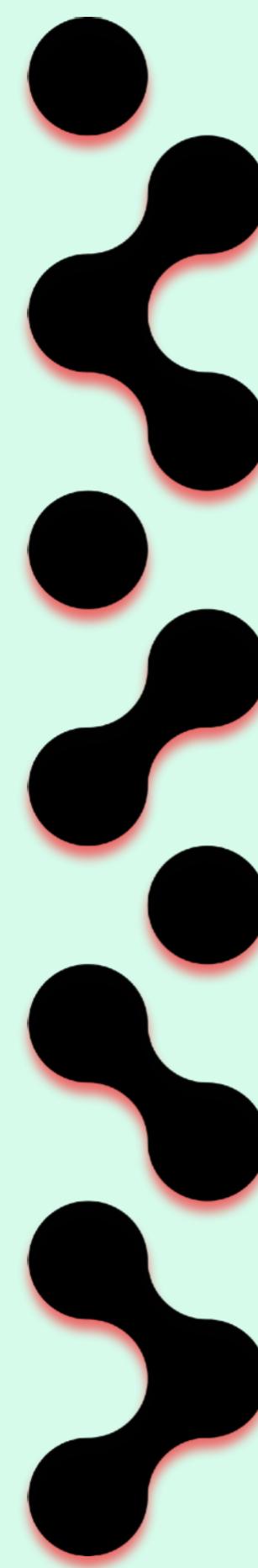
\* Large-scaled molecules (i.e the number of qubits increases). A quantum state represented by N qubits can encode  $2^N$  DOFs => Exponential Scaling



# Quantum approach: From fermions to qubits

## Second-quantized Hamiltonian

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



**Double excitation operator**

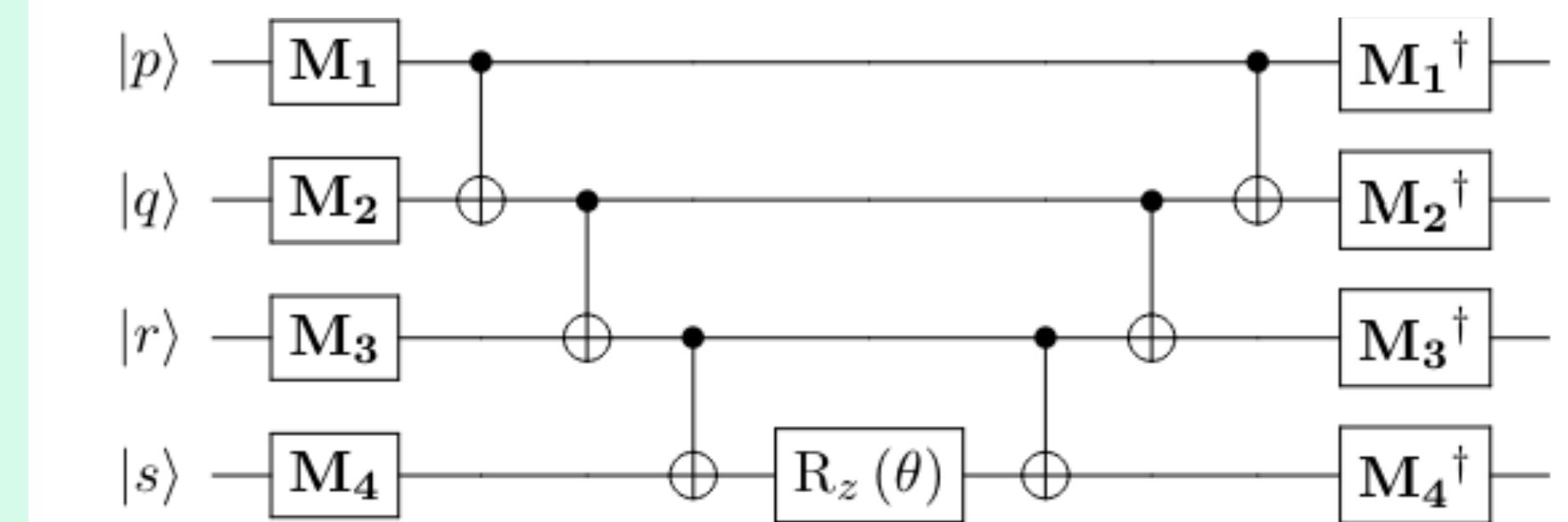
$$h_{pqrs} (a_p^\dagger a_q^\dagger a_r a_s + a_s^\dagger a_r^\dagger a_p a_q)$$

**Pauli Representation**

$$\left( \bigotimes_{k=s+1}^{r-1} \sigma_k^z \right) \left( \bigotimes_{k=q+1}^{p-1} \sigma_k^z \right)$$

$$\begin{bmatrix} \Re\{h_{pqrs}\} \\ \Im\{h_{pqrs}\} \end{bmatrix} = \frac{1}{8} \begin{bmatrix} \sigma_s^x \sigma_r^x \sigma_q^x \sigma_p^x - \sigma_s^x \sigma_r^x \sigma_q^y \sigma_p^y \\ + \sigma_s^x \sigma_r^y \sigma_q^x \sigma_p^y + \sigma_s^y \sigma_r^x \sigma_q^y \sigma_p^x \\ - \sigma_s^x \sigma_r^y \sigma_q^y \sigma_p^y - \sigma_s^y \sigma_r^x \sigma_q^y \sigma_p^y \\ + \sigma_s^x \sigma_r^y \sigma_q^y \sigma_p^x - \sigma_s^y \sigma_r^y \sigma_q^y \sigma_p^y \\ \sigma_s^y \sigma_r^x \sigma_q^x \sigma_p^x + \sigma_s^x \sigma_r^y \sigma_q^x \sigma_p^x \\ - \sigma_s^x \sigma_r^x \sigma_q^y \sigma_p^x - \sigma_s^x \sigma_r^y \sigma_q^y \sigma_p^y \\ - \sigma_s^y \sigma_r^x \sigma_q^y \sigma_p^y + \sigma_s^y \sigma_r^y \sigma_q^x \sigma_p^y \\ + \sigma_s^y \sigma_r^y \sigma_q^x \sigma_p^y + \sigma_s^y \sigma_r^y \sigma_q^y \sigma_p^x \end{bmatrix}$$

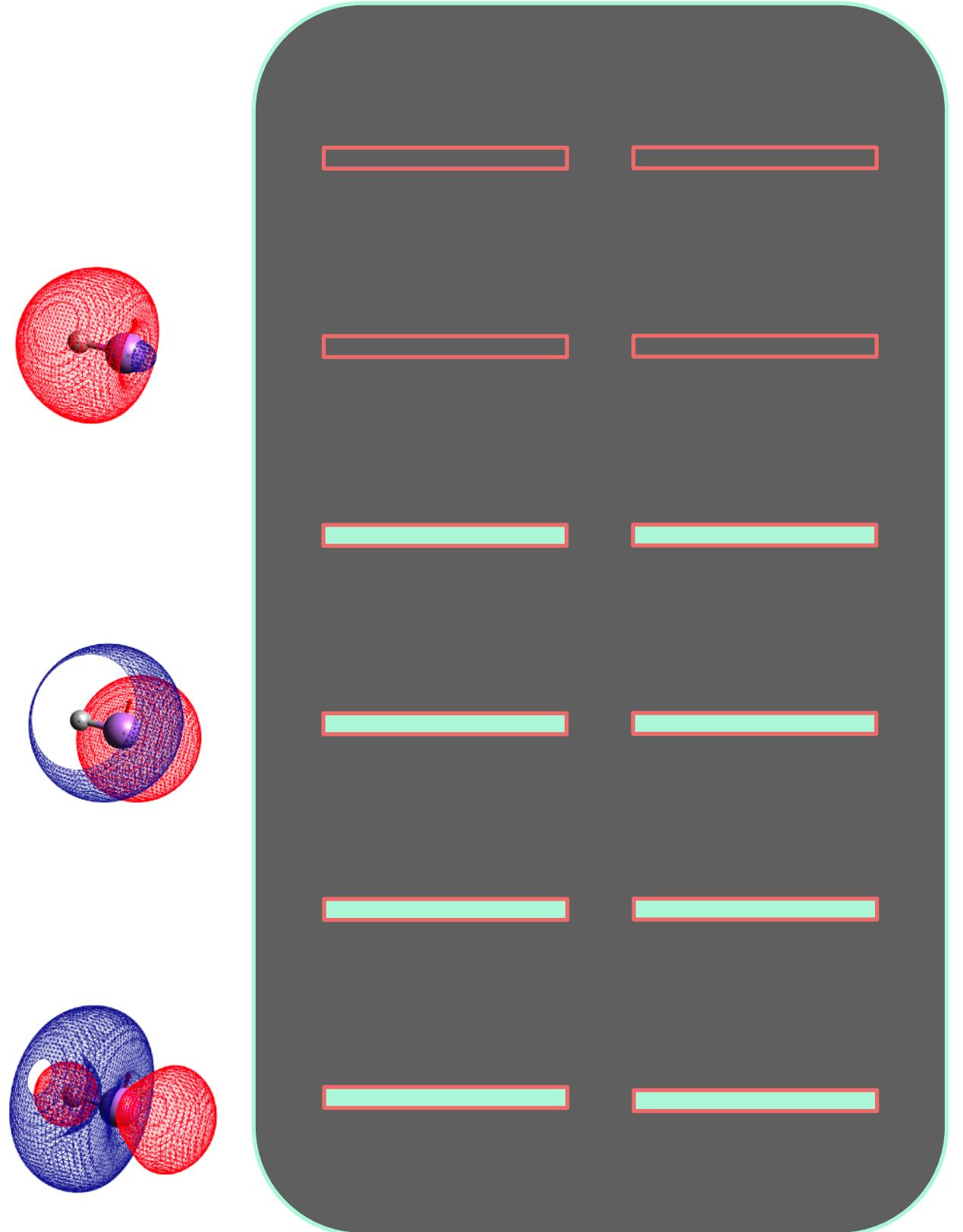
**Quantum Circuit**



# Second Quantization: From fermions to qubits

## Fermion

$$\{a_p, a_q\} = \{a_p^\dagger, a_q^\dagger\} = 0 \text{ and } \{a_p, a_q^\dagger\} = \delta_{pq}$$



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

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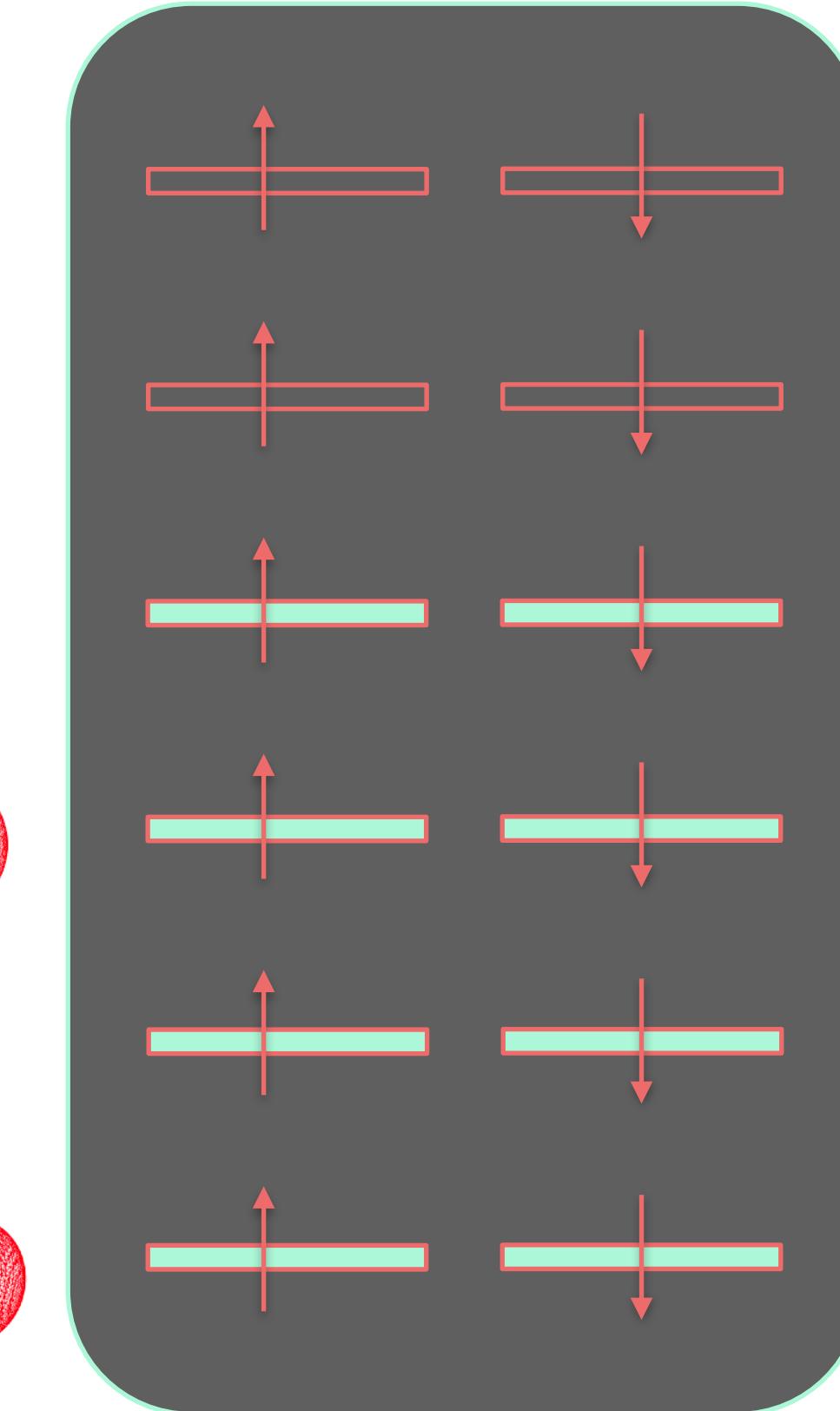
Jordan-Wigner Transformation

$$a_j = \frac{1}{2} (\sigma_j^x + i\sigma_j^y) \prod_{i=0}^{j-1} \sigma_i^z$$

$$a_j^\dagger = \frac{1}{2} (\sigma_j^x - i\sigma_j^y) \prod_{i=0}^{j-1} \sigma_i^z$$

## Spin

$$\forall i \neq j, a_i a_j^\dagger = -a_j^\dagger a_i$$



$$H_{sp} = \sum_j \alpha_j P_j = \sum_j \alpha_j \prod_i \sigma_i^j$$

# Ansatz construction: Unitary Coupled Cluster

A initial state wave-function:

$$|\psi(\theta)\rangle = e^{T(\theta) - T^\dagger(\theta)} |\psi_{\text{HF}}\rangle$$

	Single excitations	Double excitations	Triple / Quadruple excitations	
Virtual	— —	— —	— +	↑↓ ↑
Occupied	— +	— —	— —	↓ +
HF	+ —	+ +	+ +	↑ +
	excited determinants			

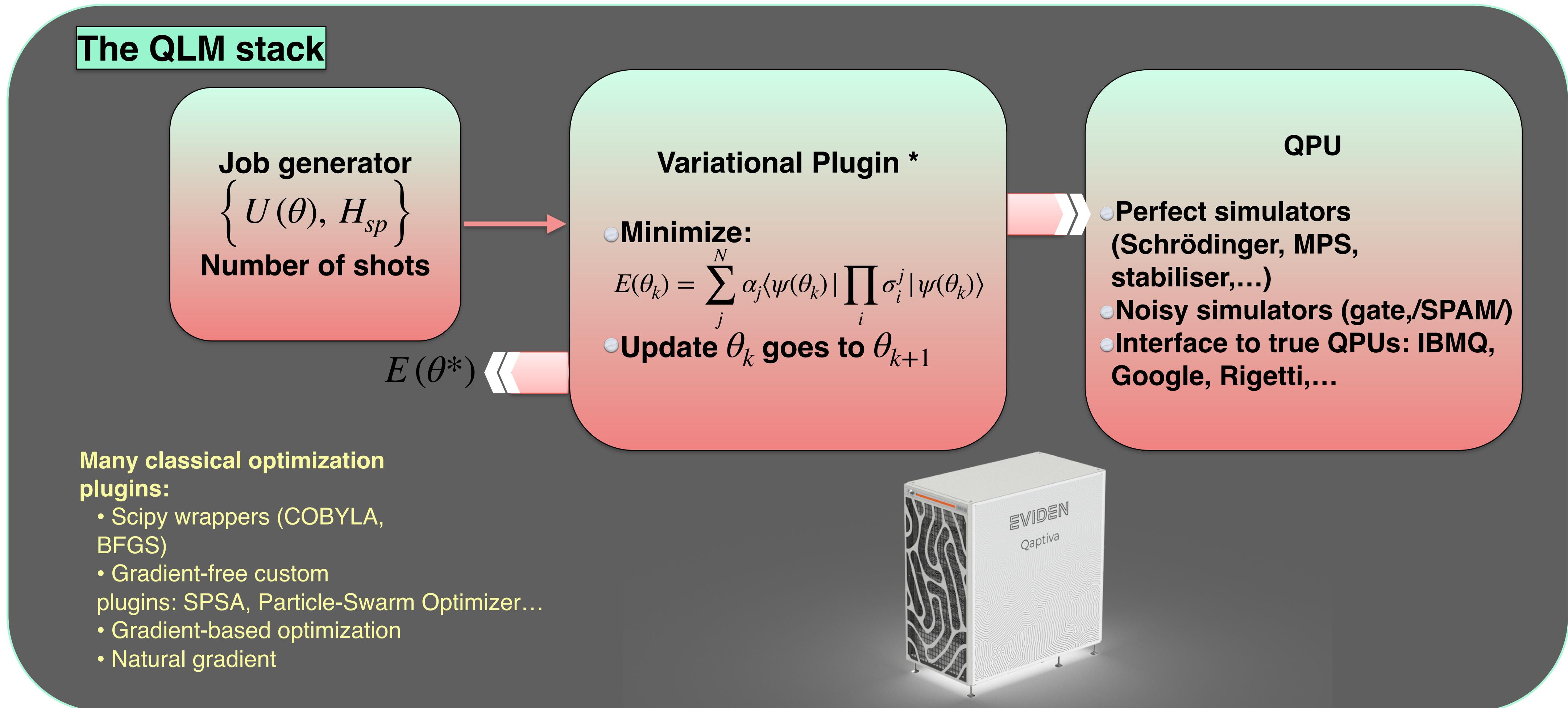
Excitation operators (S,D,T,Q):

$$\begin{aligned} \hat{T}_{UCCSDTQ} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 \\ &= \sum_{i \in \text{occ}, p \in \text{virt}} \theta_i^p \hat{a}_i^\dagger \hat{a}_p \\ &+ \sum_{i,j \in \text{occ}, p,q \in \text{virt}} \theta_{ij}^{pq} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_p \hat{a}_q \\ &+ \sum_{i,j,k \in \text{occ}, p,q,r \in \text{virt}} \theta_{ijk}^{pqr} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_p \hat{a}_q \hat{a}_r \\ &+ \sum_{i,j,k,l \in \text{occ}, p,q,r,s \in \text{virt}} \theta_{ijkl}^{pqrs} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_p \hat{a}_q \hat{a}_r \hat{a}_s \end{aligned}$$

Trotter decomposition:

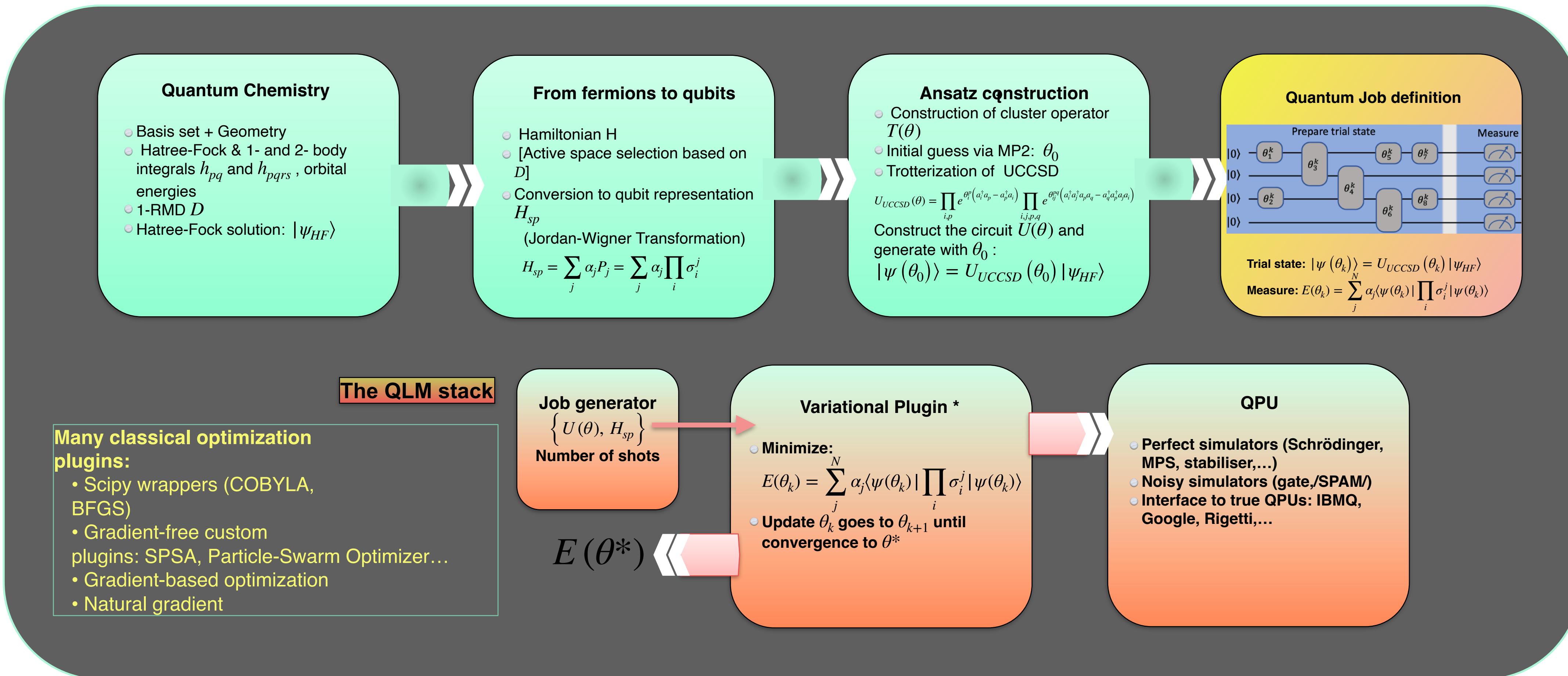
$$U(\theta) = \left[ \prod_{\gamma} e^{\frac{\theta_{\gamma}}{t} (T_{\gamma} - T_{\gamma}^\dagger)} \right]^t + \mathcal{O}\left(\frac{1}{t}\right)$$

# Quantum Learning Machine (QLM) - Workflow



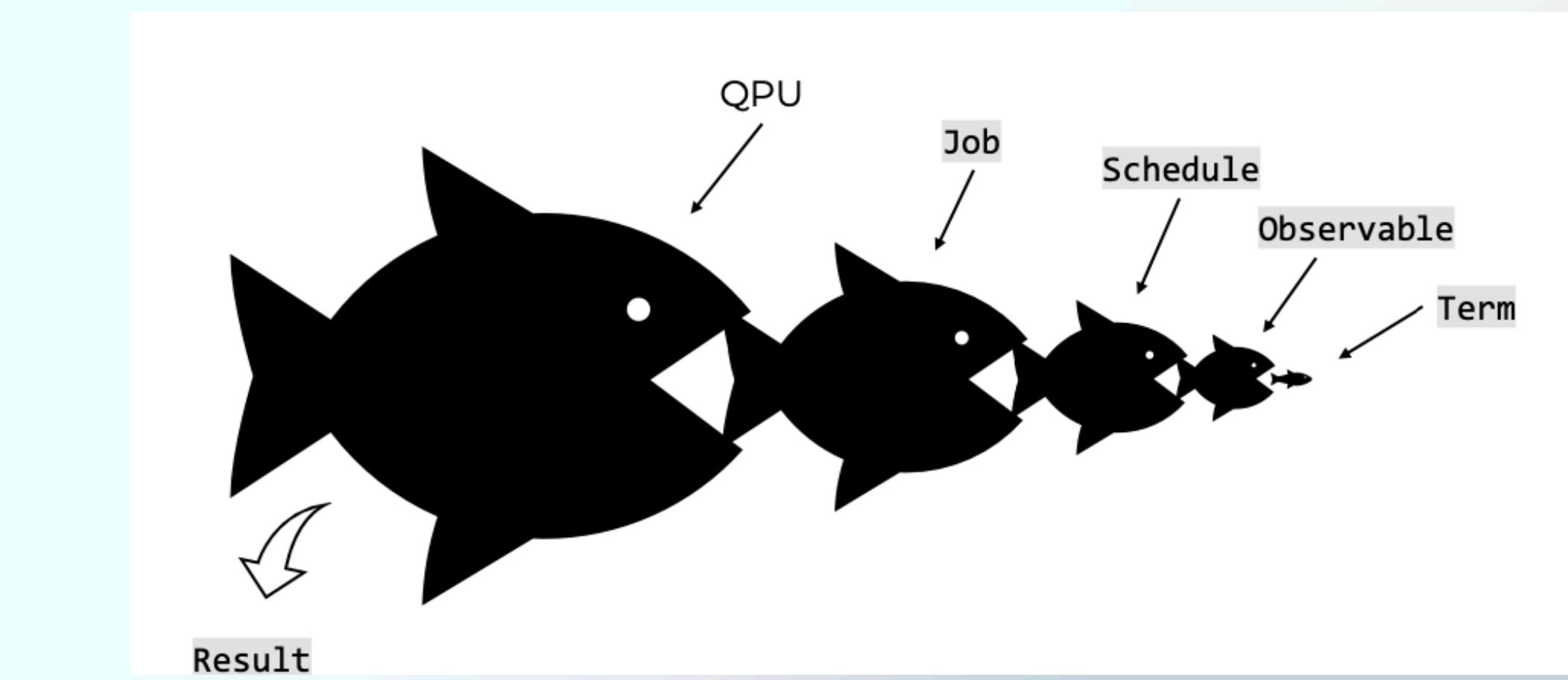
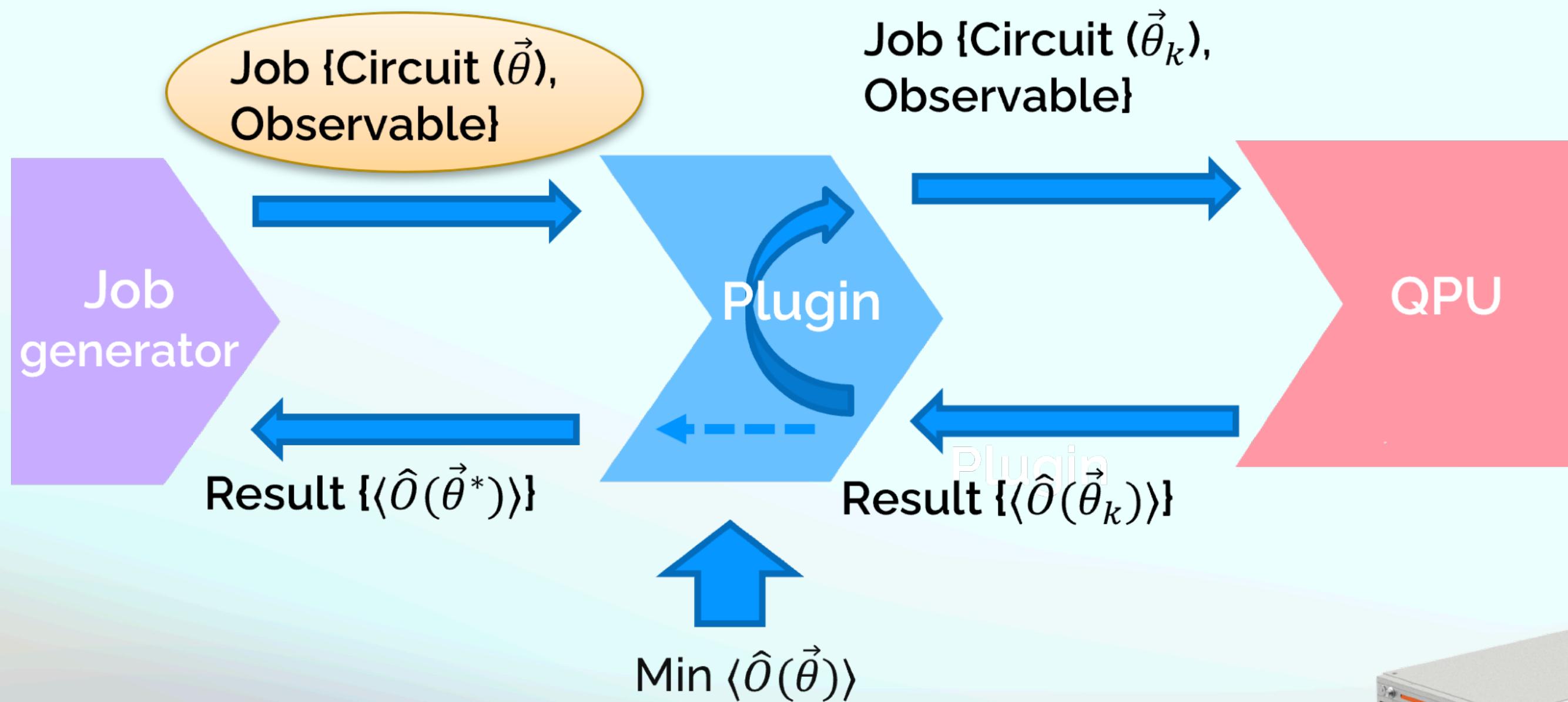
# Variational Quantum Eigensolver: UCC Ansatz

Variational Quantum Eigensolver (VQE) – QLM framework: finding eigenvalues of a Hamiltonian



\* Each plugin has a well-defined role such as compiling the circuit to a given gateset, rewriting it to comply with a given connectivity (see "Compilation plugins"), or generating all the elementary jobs required to compute the expectation value of a general observable (see "Observable Splitter plugin").

# Quantum Learning Machine (QLM) - Workflow



# Variational Quantum Simulation

qat.plugins

```
# Resource Hamiltonian
t = Variable("t", float)
Parameters ▶ t1 = Variable("t_1", float)
t2 = Variable("t_2", float)
tf = 3.0
drive = [(heaviside(t, 0., t1), Observable(2, pauli_terms=[Term(1, "X", [0]), Term(1, "X", [1])])),  
         (heaviside(t, t1, t2), Observable(2, pauli_terms=[Term(1, "ZZ", [0, 1])])),  
         (heaviside(t, t2, tf), Observable(2, pauli_terms=[Term(1, "X", [0]), Term(1, "X", [1])]))]
Schedule ▶ schedule = Schedule(drive=drive, tmax=tf)

# Target Hamiltonian
H_target = Observable(2, pauli_terms=[Term(1, 'XZ', [0, 1])])

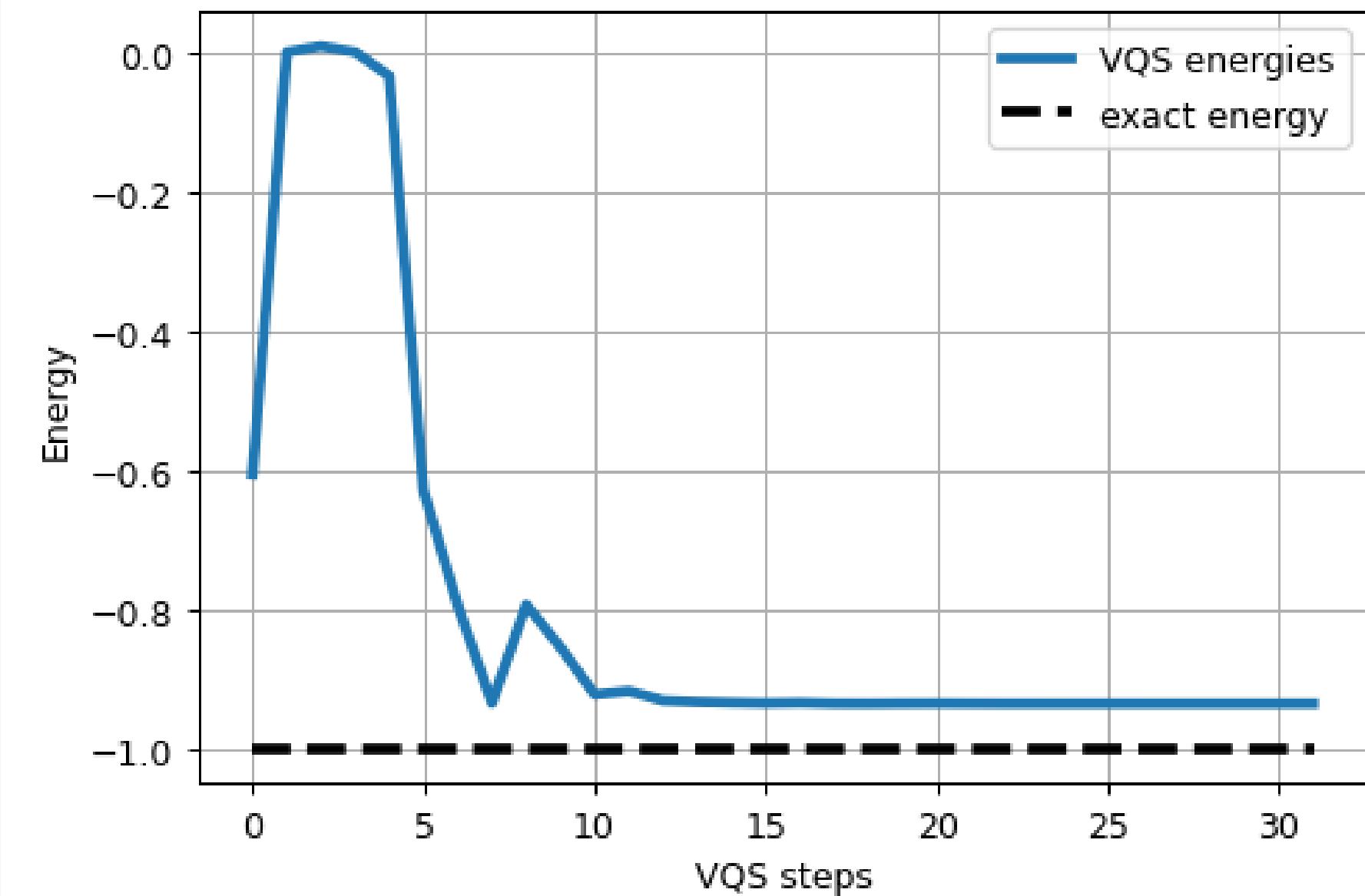
# Parametric job
job = schedule.to_job(job_type="OBS", observable=H_target)

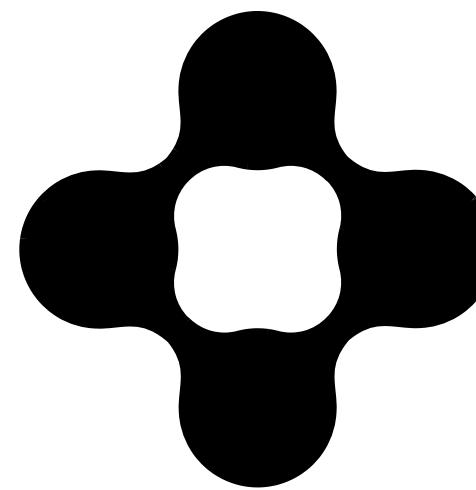
# Description of the stack
Noise model ▶ hardware_model = HardwareModel(jump_operators=[Observable(2, pauli_terms=[(Term(.1, 'Z', [0]))])])
gpu = AnalogQPU(hardware_model=hardware_model)
Plugin ▶ optimizer_scipy = ScipyMinimizePlugin(method="COBYLA", x0=[0.4, 1.2])
stack = optimizer_scipy | gpu

# Simulation
Execution ▶ res = stack.submit(job)
print("<H_target> =", res.value)

<H target> = -0.9361429660408287
```

Optimized parameters:  
[0.7410633260759264, 1.4773270772097082]





# Subspace-search variational quantum eigensolver for excited states

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## Algorithm 1 Subspace-search variational quantum eigensolver

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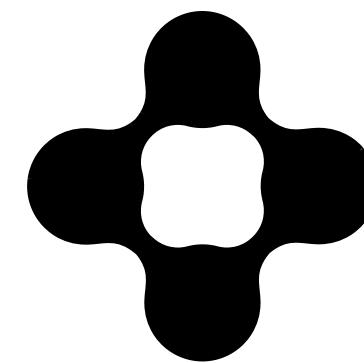
- 1: **Input:** Ansatz circuit  $U(\boldsymbol{\theta})$ , input states  $\{\varphi_j\}_{j=0}^k$ , orthogonal ( $\varphi_i|\varphi_j = \delta_{ij}$ )
- 2: **Step 1:** Construct ansatz circuit  $U(\boldsymbol{\theta})$  and choose input states  $\{\varphi_j\}_{j=0}^k$  which are mutually orthogonal ( $\varphi_i|\varphi_j = \delta_{ij}$ ).
- 3: **Step 2:** Minimize

$$\mathcal{L}_1(\boldsymbol{\theta}) = \sum_{j=0}^k \langle \varphi_j | U^\dagger(\boldsymbol{\theta}) H U(\boldsymbol{\theta}) | \varphi_j \rangle.$$

We denote the optimal  $\boldsymbol{\theta}$  by  $\boldsymbol{\theta}^*$ .

- 4: **Step 3:** Construct another parametrized quantum circuit  $V(\boldsymbol{\phi})$  that only acts on the space spanned by  $\{\varphi_j\}_{j=0}^k$ .
- 5: **Step 4:** Choose an arbitrary index  $s \in \{0, \dots, k\}$ , and maximize

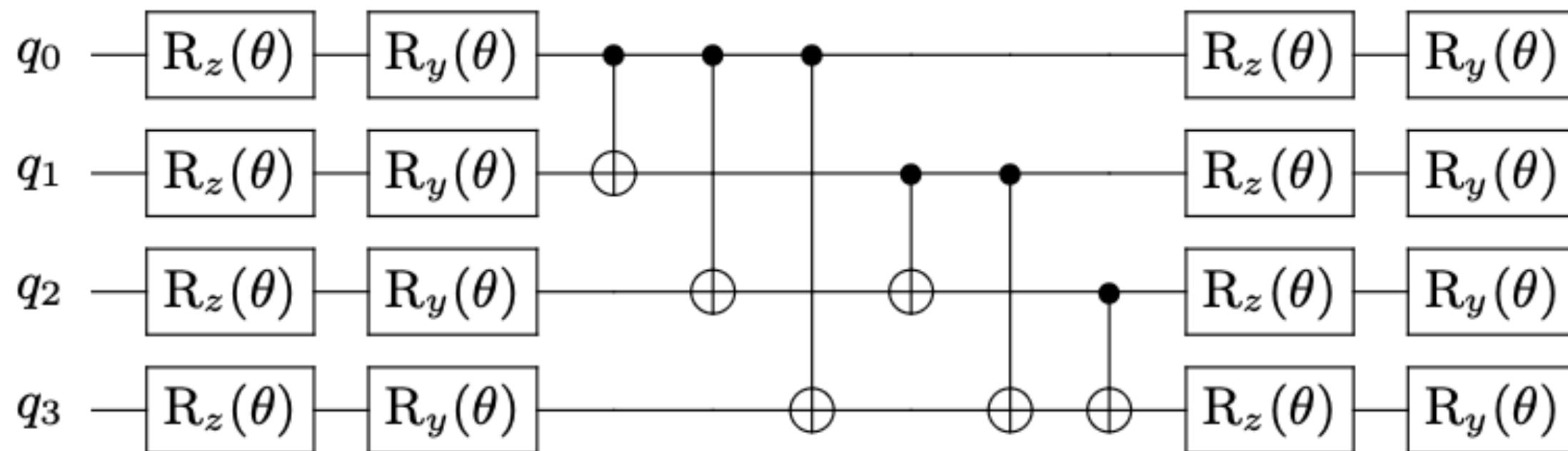
$$\mathcal{L}_2(\boldsymbol{\phi}) = \langle \varphi_s | V^\dagger(\boldsymbol{\phi}) U^\dagger(\boldsymbol{\theta}^*) H U(\boldsymbol{\theta}^*) V(\boldsymbol{\phi}) | \varphi_s \rangle.$$



# SSVQE - ansatz & Applied for Ising Model

Total operator of the parameterised variational ansatz is

$$U(\boldsymbol{\theta}) = [U_{\text{rot}}(\boldsymbol{\theta})][U_{\text{ent}}][U_{\text{pre}}(\boldsymbol{\theta})].$$

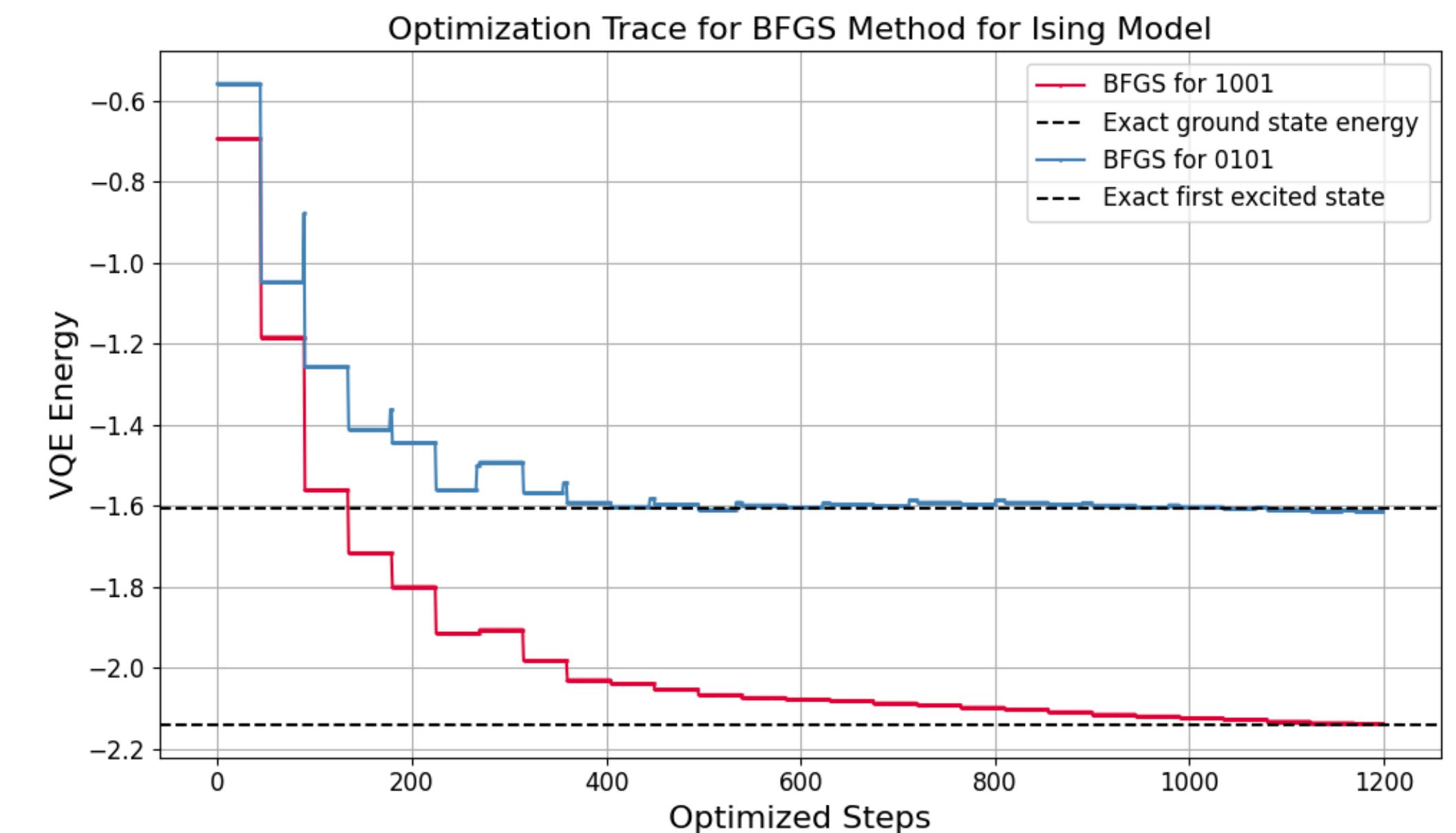


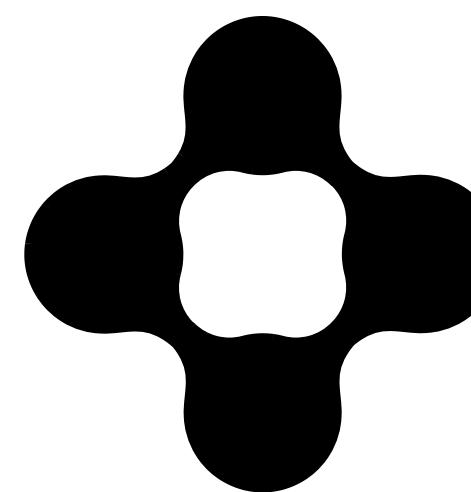
"Hardware-efficient ansatz" - the entanglement pattern with 6 CX gates and depth = 1 is shown.



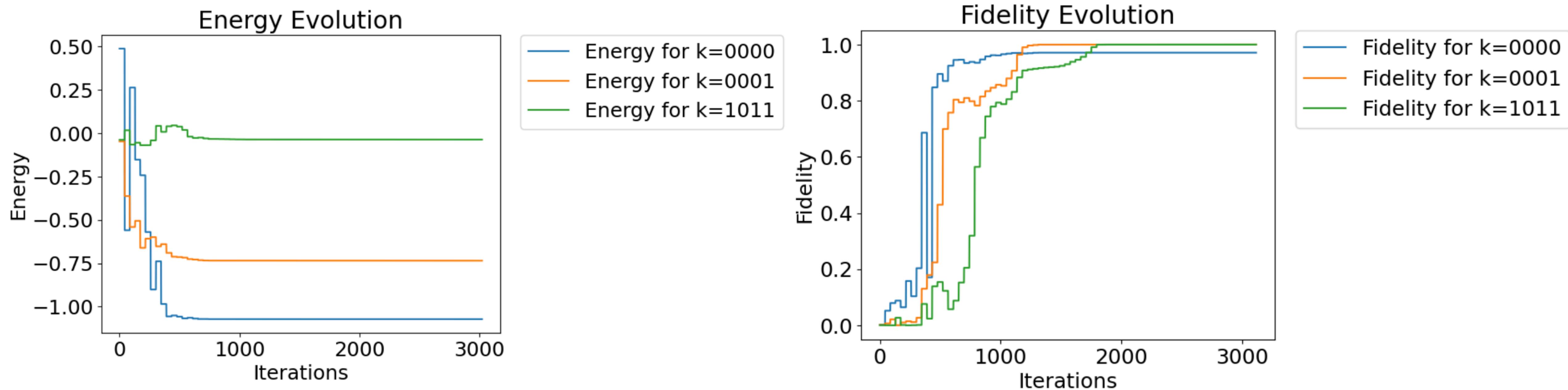
**Ising Model (N=4)**

$$H_{\text{Ising}} = \sum_{i=1}^N a_i X_i + \sum_{i=1}^N \sum_{j=1}^{i-1} J_{ij} Z_i Z_j$$

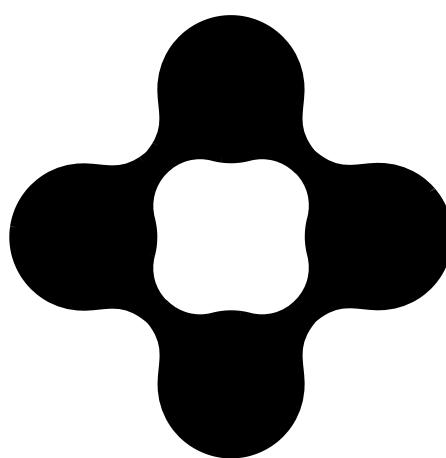




# SSVQE - Result



The energy levels of the Hamiltonian of H<sub>2</sub> in the STO-3G basis set: four qubits.  
The fidelity is close to one



# Complete Active Space Selection (CAS)

**Less optimised steps & variational parameters**

## The anti-hermitian operator UCC

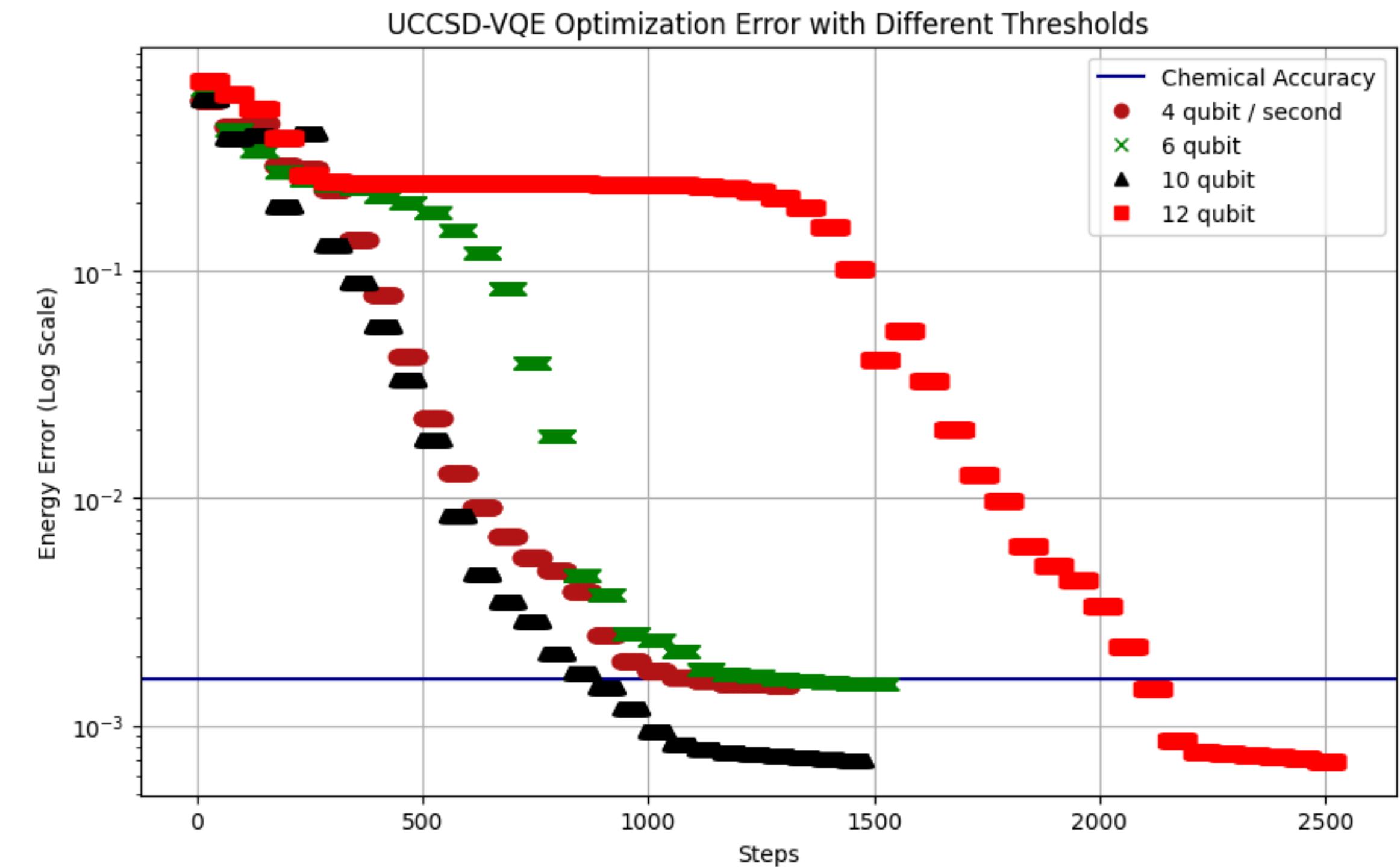
$$\forall p, q, r, s \in \mathcal{I}'^2 \times \mathcal{O}'^2,$$

$$T_{\text{UCCSD}}^{(\text{CAS})} = \sum_{p \in \mathcal{O}', r \in \mathcal{I}'} \theta_p^r (\hat{a}_p^\dagger \hat{a}_r - \hat{a}_r^\dagger \hat{a}_p) + \sum_{p, q \in \mathcal{O}', r, s \in \mathcal{I}'} \theta_{pq}^{rs} (\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s - \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_p \hat{a}_q)$$

## The Møller-Plesset second-order (MP2) as initial guess:

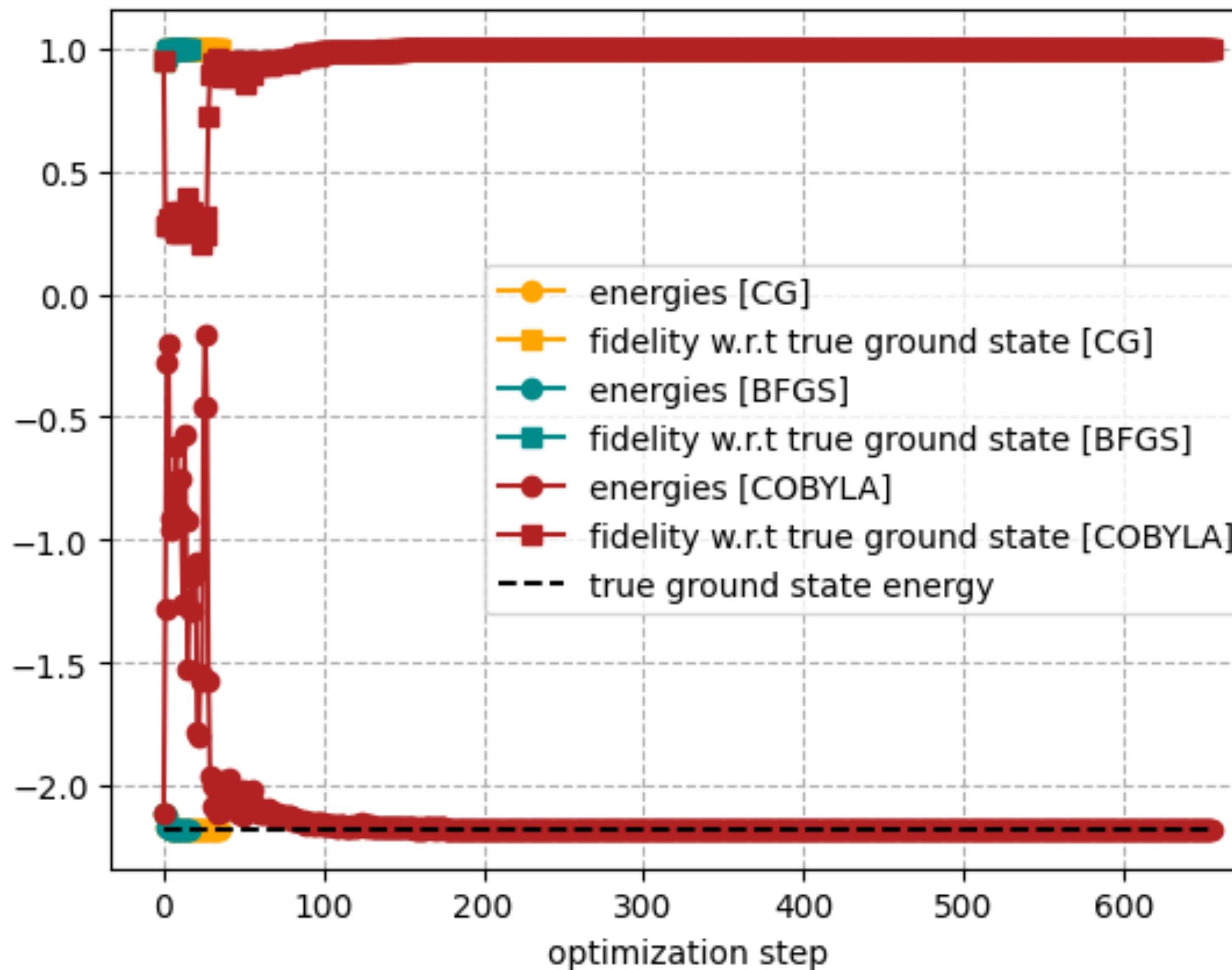
$$\forall p, r \in \mathcal{I}' \times \mathcal{O}' \quad \theta_p^r = 0$$

$$\forall p, q, r, s \in \mathcal{I}'^2 \times \mathcal{O}'^2 \quad \theta_{pq}^{rs} = \frac{h_{pqrs} - h_{pq}}{\epsilon_r + \epsilon_s - \epsilon_p - \epsilon_q}$$



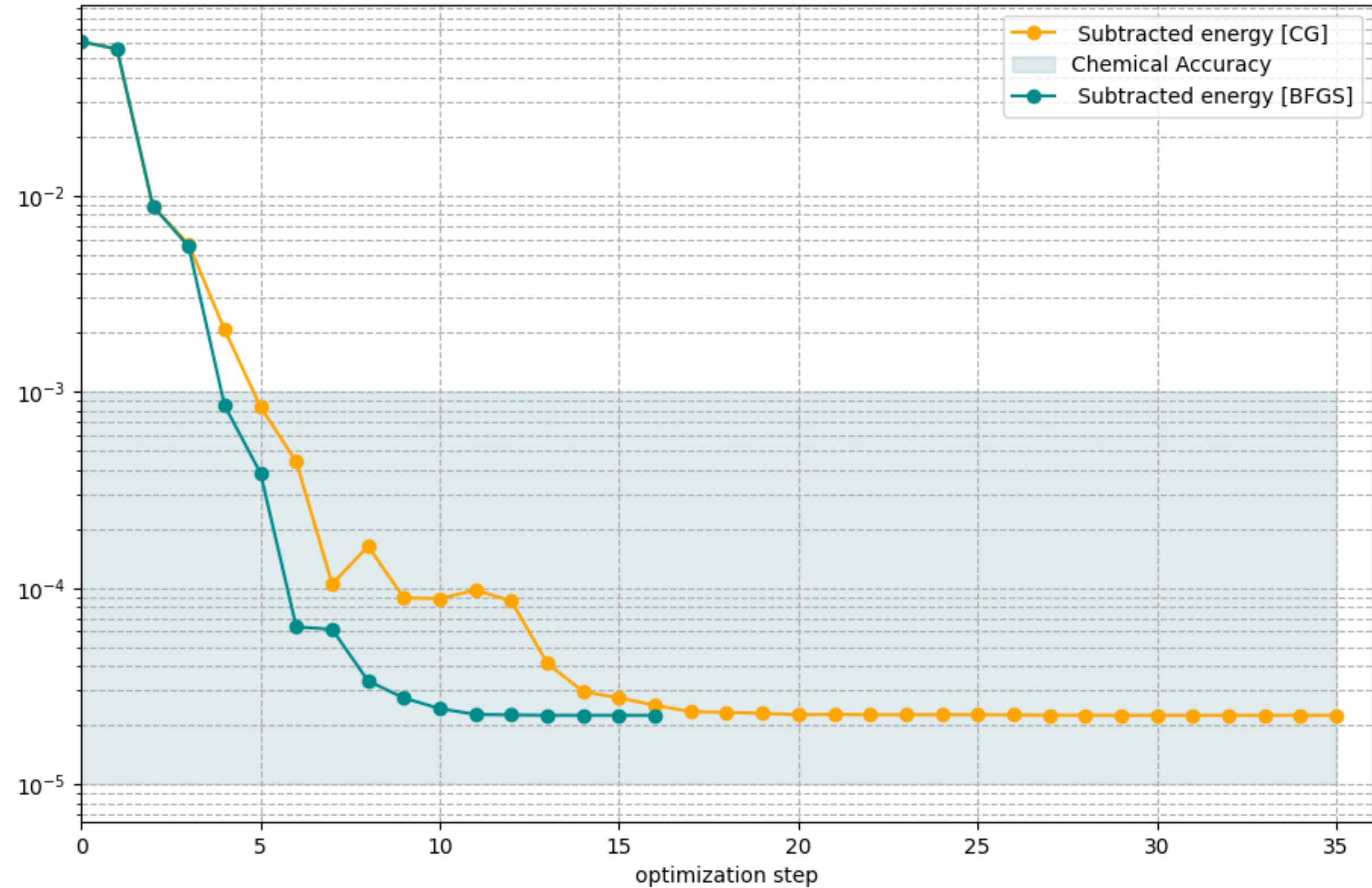
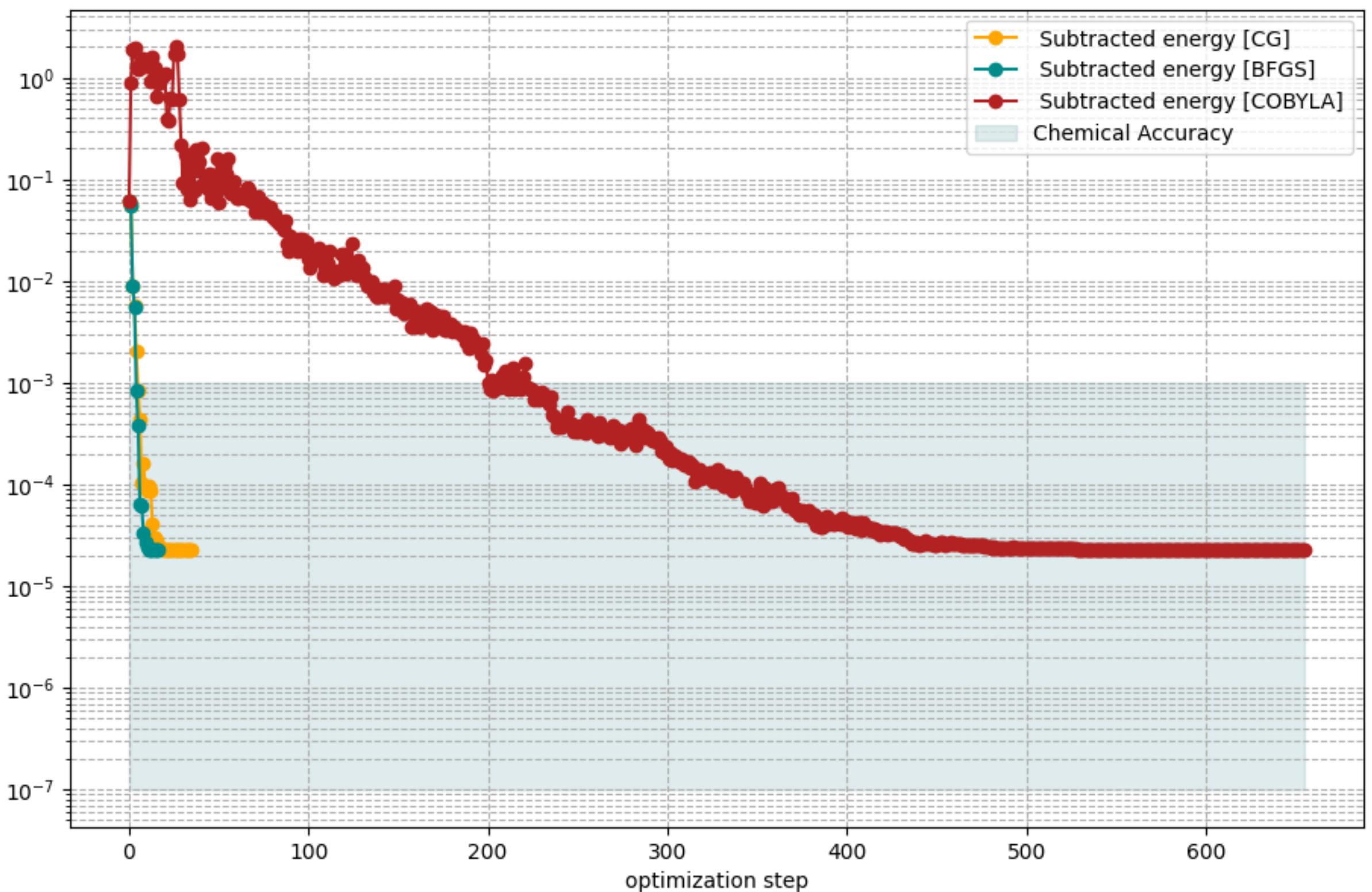
CAS study UCC-VQE: LiH molecule (6-31G basis set) at  $r_{\text{Li-H}} = 1.45\text{\AA}$ , using BFGS optimizers. The size of the qubits represents the number of active spin-orbitals. The blue line indicates the chemical accuracy.

# Parameter Shift-Rules (PMRS) - H4

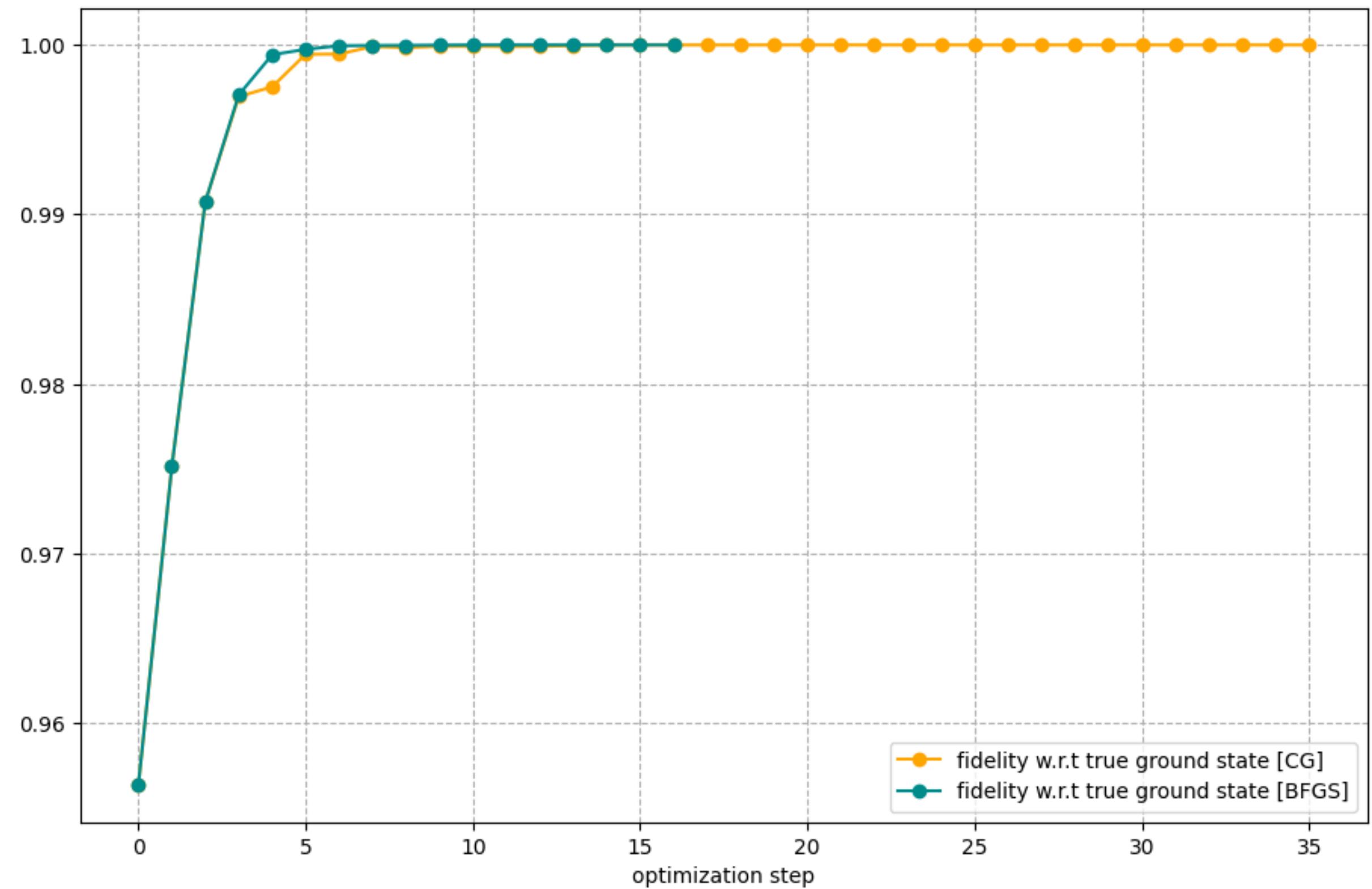
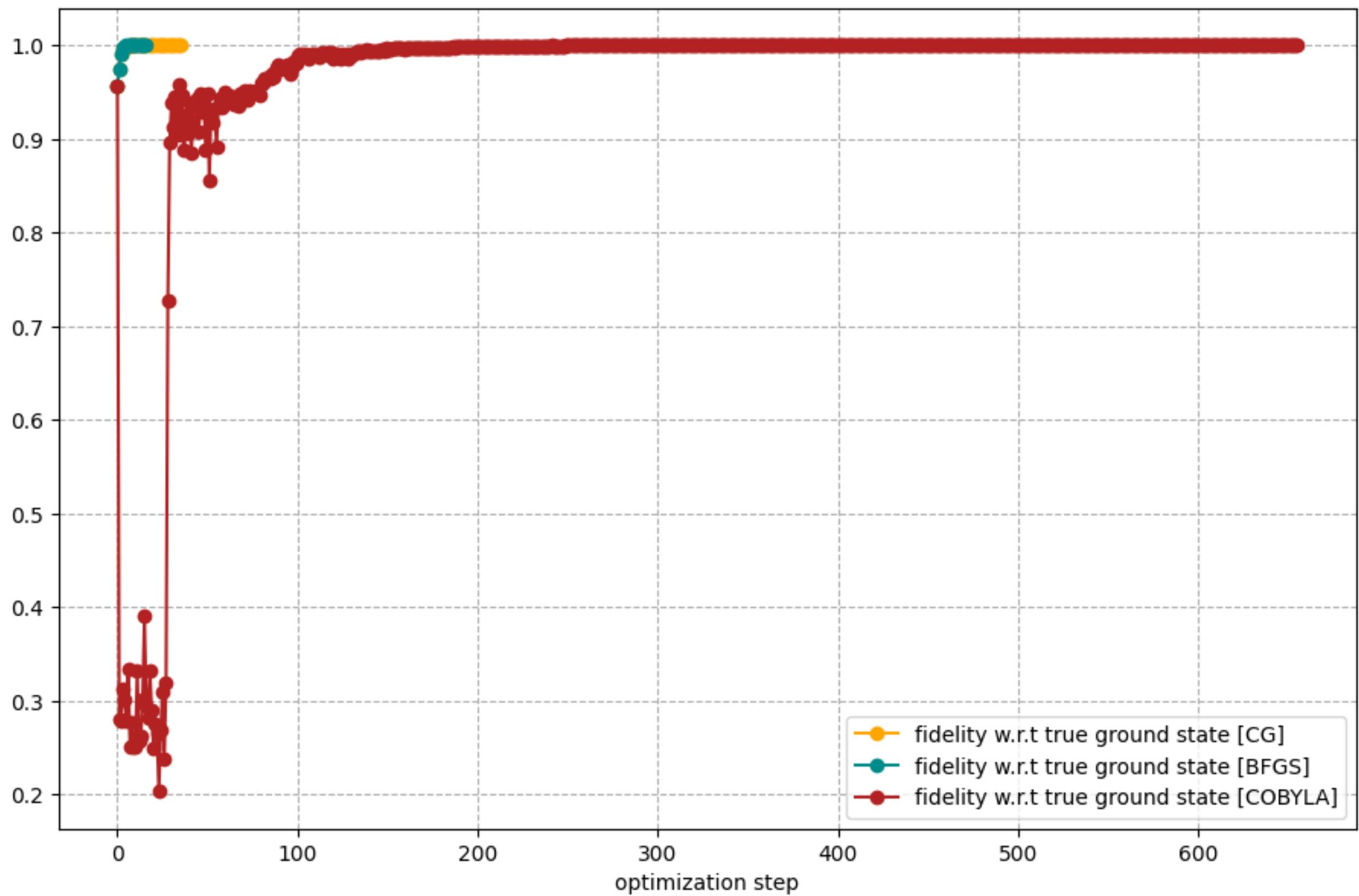


PMRS application on H4 molecule at  $0.84 \text{ \AA}$  shows the energies (and fidelities) comparison between three optimizers: gradient based (CG and BFGS); free-gradient (COBYLA).

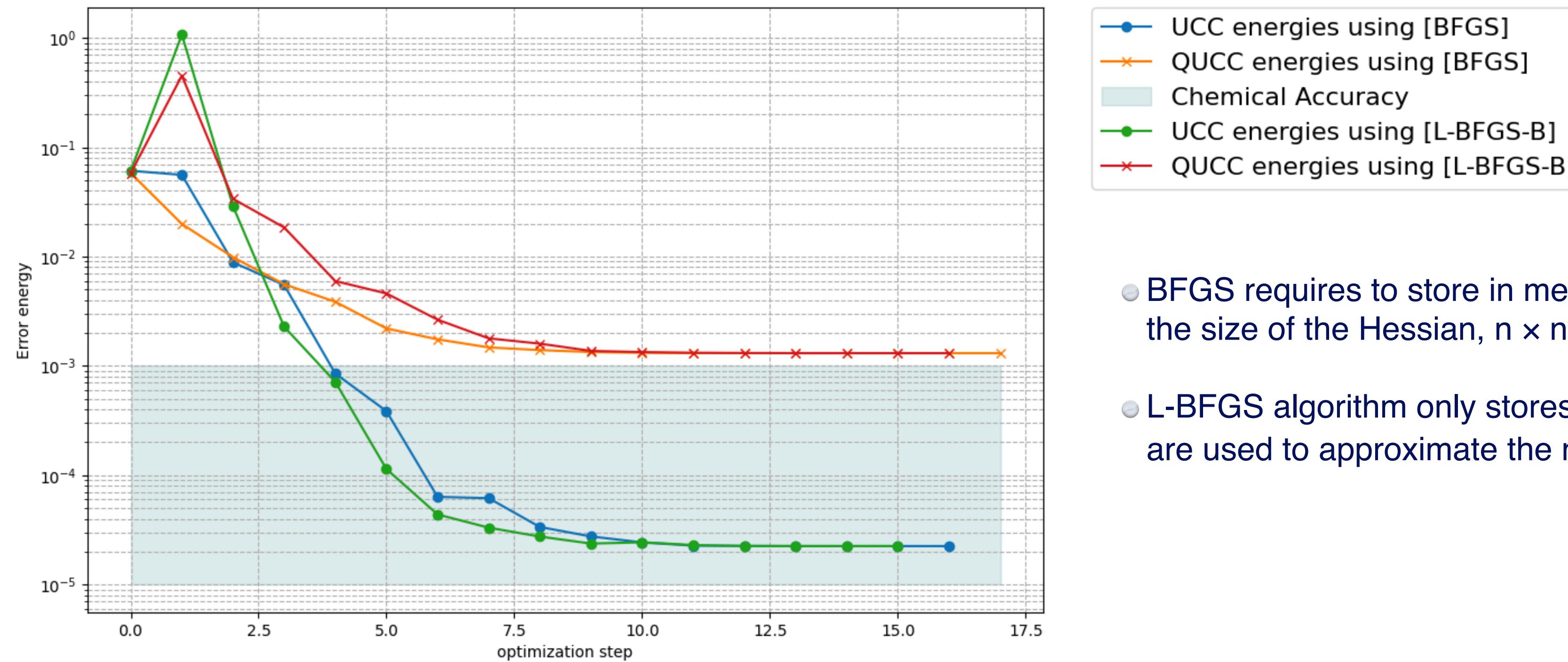
# Parameter Shift-Rules (PMRS) - H4: Error scale



# Parameter Shift-Rules (PMRS) - H4: Fidelity



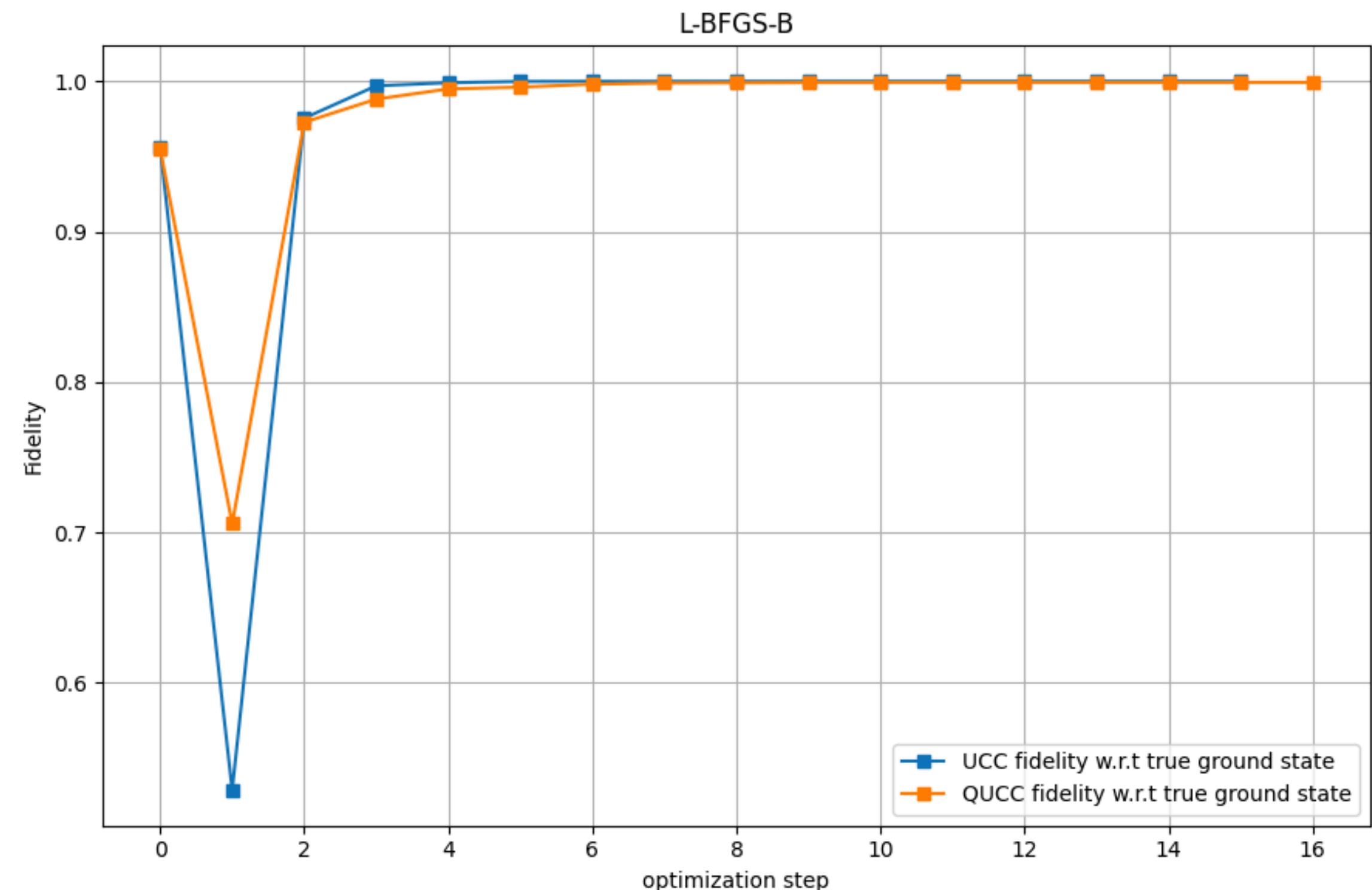
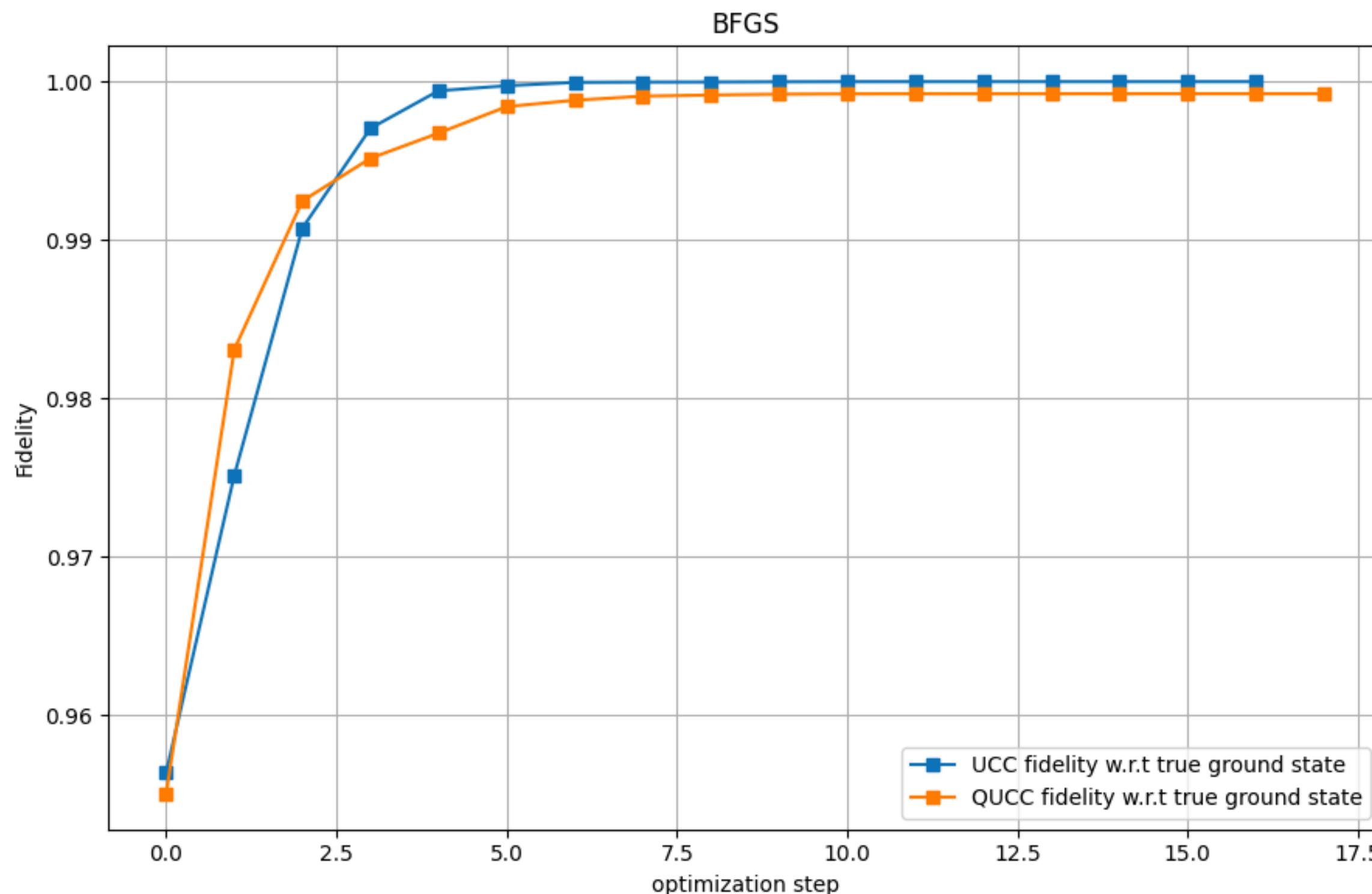
# Parameter Shift-Rules (PMRS): Optimizers



- BFGS requires to store in memory a matrix of the size of the Hessian,  $n \times n$ ,
- L-BFGS algorithm only stores a few vectors that are used to approximate the matrix  $H_k^{-1}$

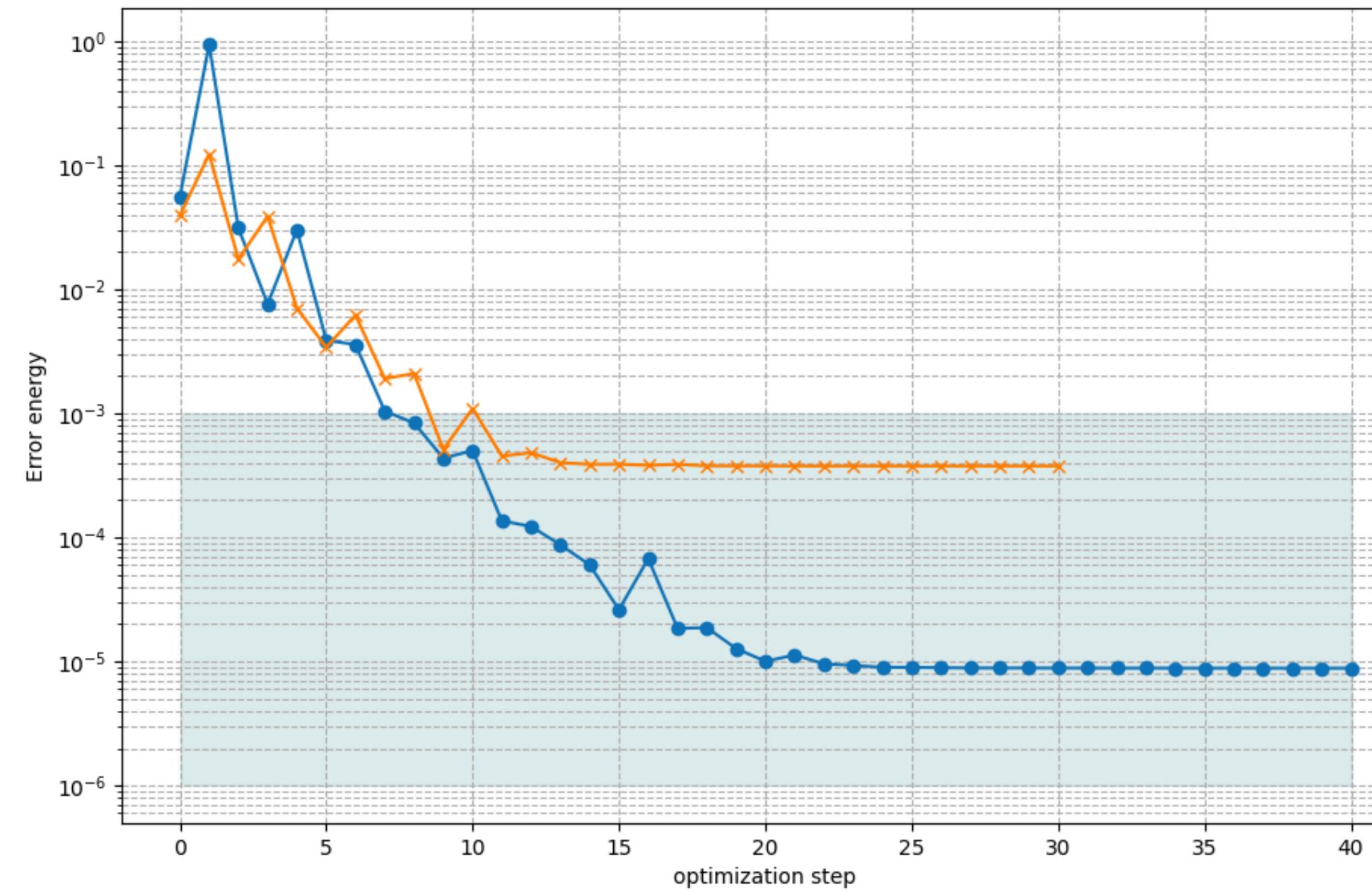
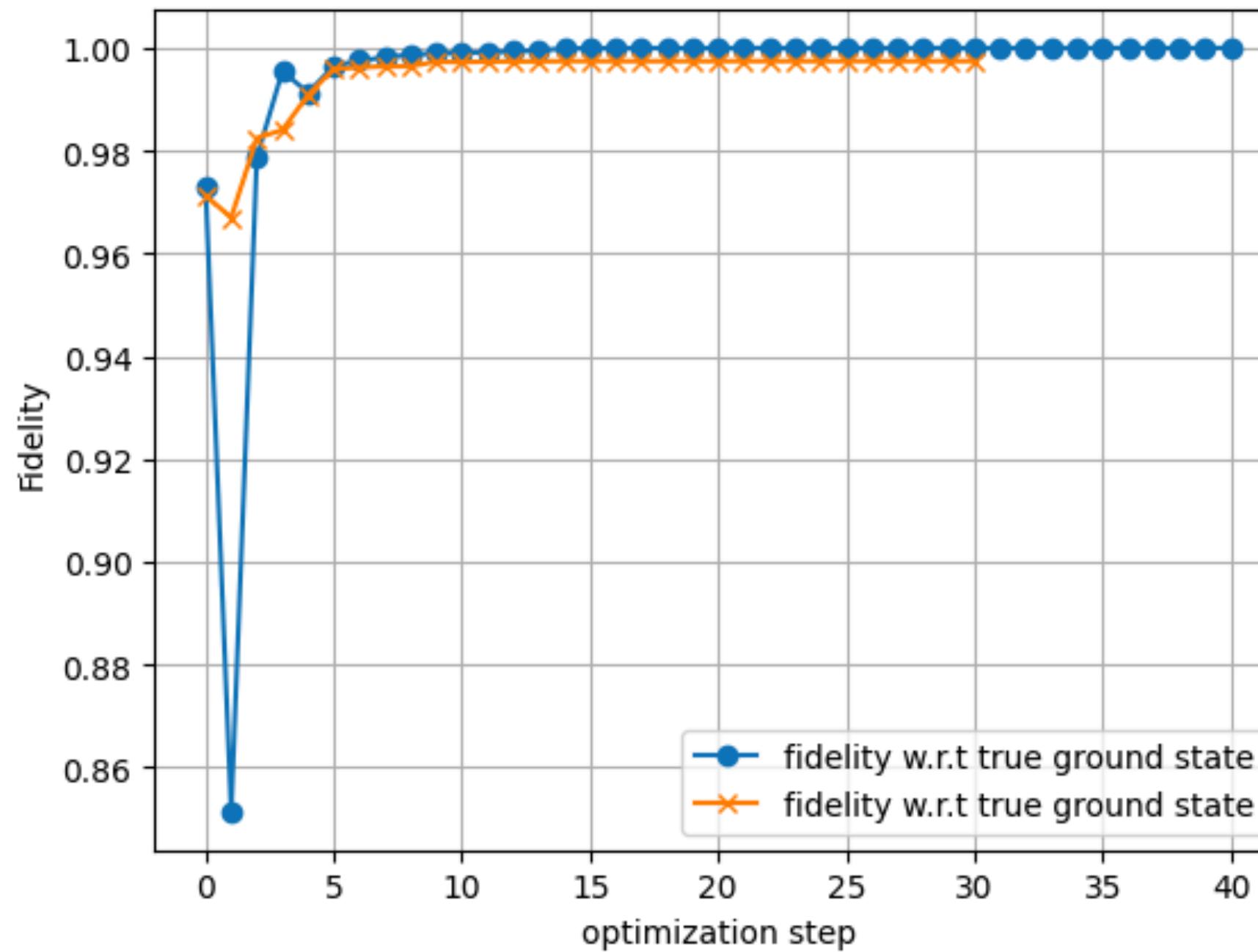
PMRS application on H4 molecule at  $0.85\text{\AA}$  comparison between BFGS and L-BFGS optimizers measure the shows the energy convergence, error is between UCC(QUCC) energies and FCI.

# Parameter Shift-Rules (PMRS): High Fidelity



PMRS - fidelity  $\text{H}_4$  molecule at  $0.85\text{\AA}$  comparison between BFGS and L-BFGS optimizers between UCC and Q-UCC methods

# Parameter Shift-Rules (PMRS) - MP2 terms |



| PMRS application on LiH molecule at  $1.45\text{\AA}$  (BFGS): (left figure) shows the fidelity obtained from UCC simulations comparing MP2 initial guess with two choices (right figure): full MP2 (includes single excitations in the optimization process), and "MP2 reduced" eliminates them