Quantum Benchmarking Of Molecular Ground-State Energy Estimation

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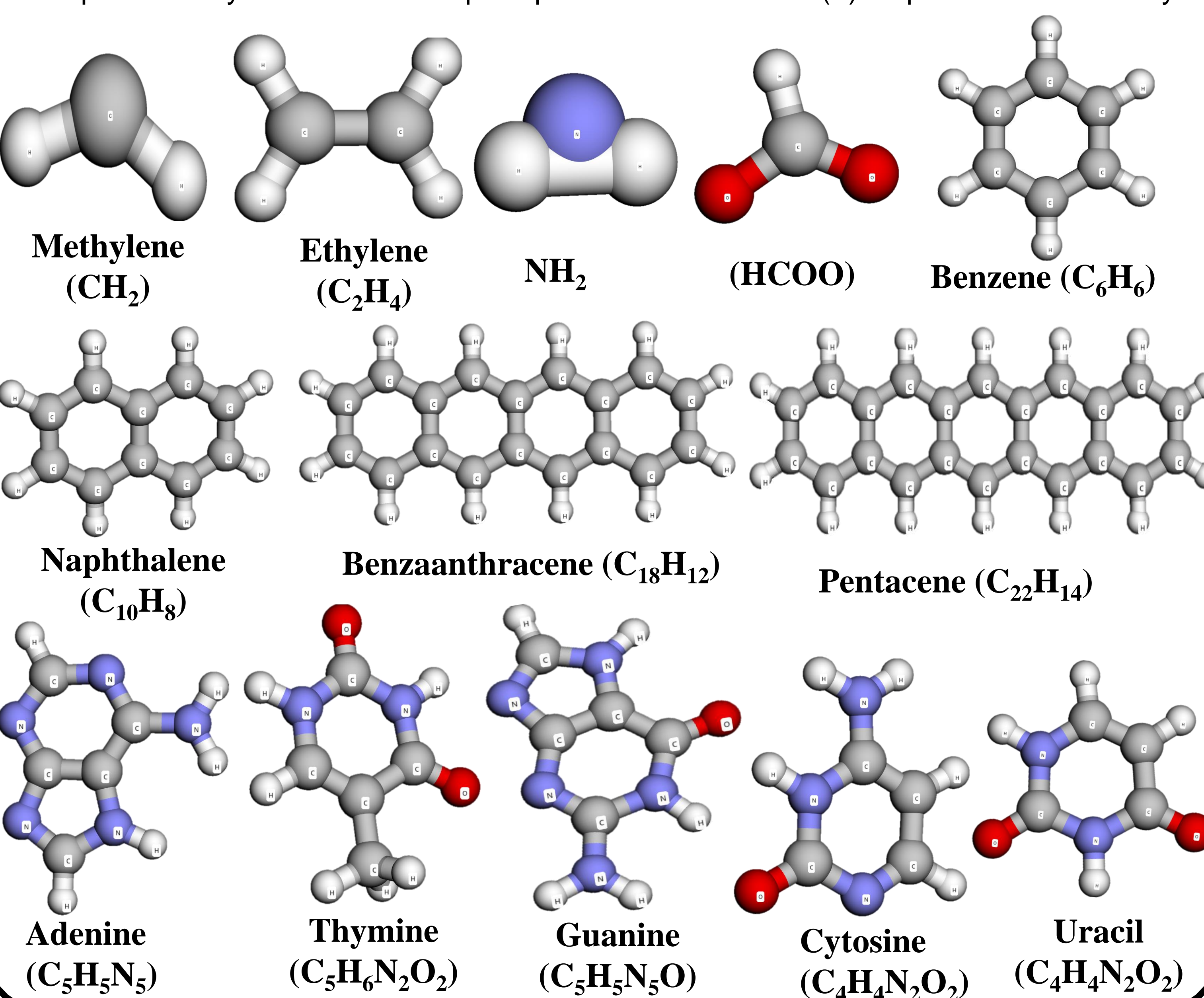
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Overview

- Ground-state energy estimation (GSEE) and excited-state energy estimation (ESEE) are at the core of predicting and controlling chemical reactions, with huge impact in various technologies.
- Classical algorithms for GSEE scale exponentially with system size and are elusive to even the most powerful supercomputers for useful system sizes.
- Quantum computation (QC) emerges as a powerful alternative with a potentially linear scaling. Results of QC algorithms must be benchmarked on reliable data.
- The Variational Quantum Eigen solver (VQE) is a hybrid quantum-classical algorithm for approximating molecular ground-state energies on near-term quantum devices.
- We demonstrate VQE for **DNA bases** (adenine, thymine, guanine, cytosine, uracil), **small organic functional groups** (NH_2, COOH), simple **hydrocarbons** (methylene (CH_2), ethylene (C_2H_4)), and **aromatic hydrocarbons** (benzene (C_6H_6), naphthalene ($C_{10}H_8$), benz[a]anthracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$)), using quantum software on both CPU and GPU devices. **While we cannot draw conclusions on energy accuracy, we prove the GPU acceleration of VQE.**
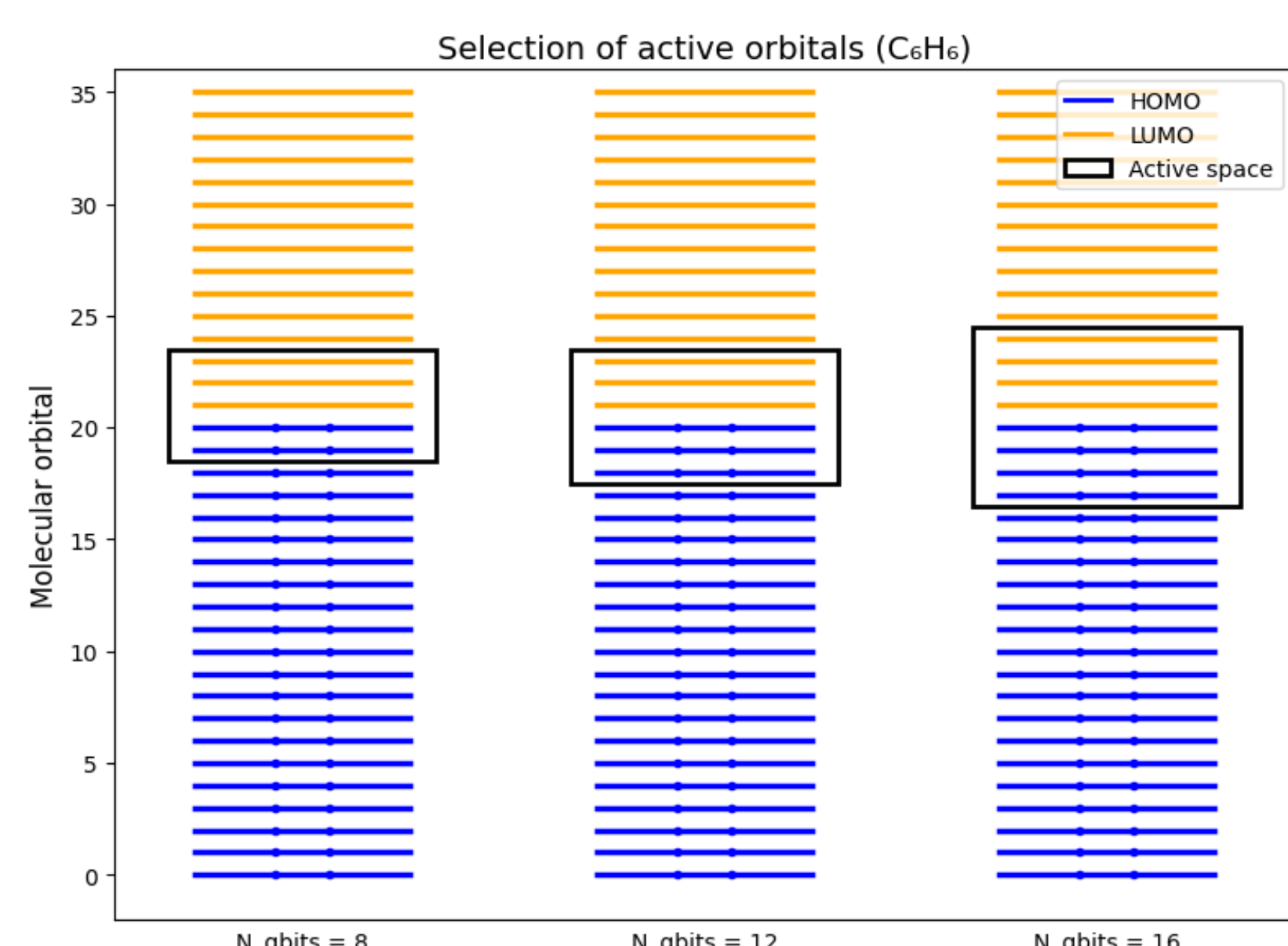
Classical algorithms: Molecular Structure

- Geometry obtained from the Computational Chemistry Comparison and Benchmark Database (CCCBDB) [3].
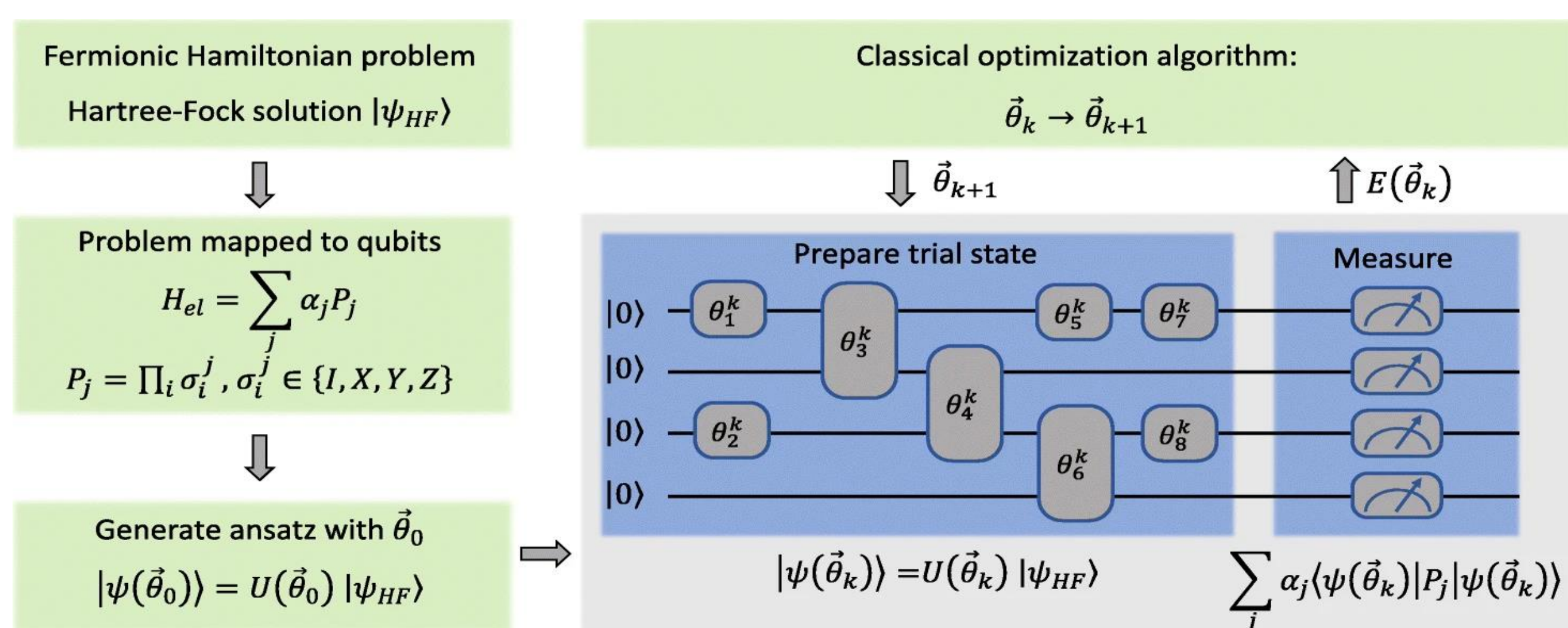- Experimentally determined and pre-optimized at the CCSD(T)/cc-pVDZ level of theory.

Methylene (CH_2) · **Ethylene (C_2H_4)** · **NH_2** · **(HCOO)** · **Benzene (C_6H_6)**

Naphthalene ($C_{10}H_8$) · **Benzaanthracene ($C_{18}H_{12}$)** · **Pentacene ($C_{22}H_{14}$)**

Adenine ($C_5H_5N_5$) · **Thymine ($C_5H_6N_2O_2$)** · **Guanine ($C_5H_5N_5O$)** · **Cytosine ($C_4H_4N_2O_2$)** · **Uracil ($C_4H_4N_2O_2$)**

Methodology

- We use the CUDA Quantum (CUDA-Q) framework, enabling simulations on both CPU and GPU backends.
- Within the `6-31G` and `cc-pVDZ` basis set for the molecular Hamiltonian, we downsize the active space by freezing "core" orbitals and restricting the simulation to chemically relevant "reactive" orbitals, thus balancing computational cost with chemical accuracy.
- The molecular Hamiltonian is constructed via PySCF and OpenFermion libraries, and the UCCSD ansatz is implemented as the variational circuit within CUDA-Q.
- We systematically evaluate energy convergence, qubit and parameter counts, and computational runtimes across various active space configurations.

Selection of active orbitals (C_6H_6)
- HOMO
- LUMO
- Active space

VQE Scheme

Fermionic Hamiltonian problem
Hartree-Fock solution $|\psi_{HF}\rangle$

↓

Problem mapped to qubits
$H_{el} = \sum_j \alpha_j P_j$
$P_j = \prod_i \sigma_i^j, \sigma_i^j \in \{I, X, Y, Z\}$

↓

Generate ansatz with $\vec{\theta}_0$
$|\psi(\vec{\theta}_0)\rangle = U(\vec{\theta}_0)|\psi_{HF}\rangle$

Classical optimization algorithm:
$\vec{\theta}_k \to \vec{\theta}_{k+1}$
↓ $\vec{\theta}_{k+1}$ ⇑ $E(\vec{\theta}_k)$

Prepare trial state | Measure

$|\psi(\vec{\theta}_k)\rangle = U(\vec{\theta}_k)|\psi_{HF}\rangle$
$\sum_j \alpha_j \langle \psi(\vec{\theta}_k)|P_j|\psi(\vec{\theta}_k)\rangle$

Overview of the Variational Quantum Eigensolver (VQE) workflow. The electronic structure problem is first mapped from fermionic operators to qubit-based Pauli operators. An initial trial wavefunction is prepared using a parameterized quantum circuit (ansatz) based on the Hartree-Fock reference. Expectation values of the Hamiltonian are measured on a quantum device, and the energy is evaluated classically. A classical optimizer updates the parameters iteratively to minimize the energy, forming a hybrid quantum-classical optimization loop.

Molecular Hamiltonian

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}\right) + \sum_{i<j}\frac{1}{r_{ij}}$$
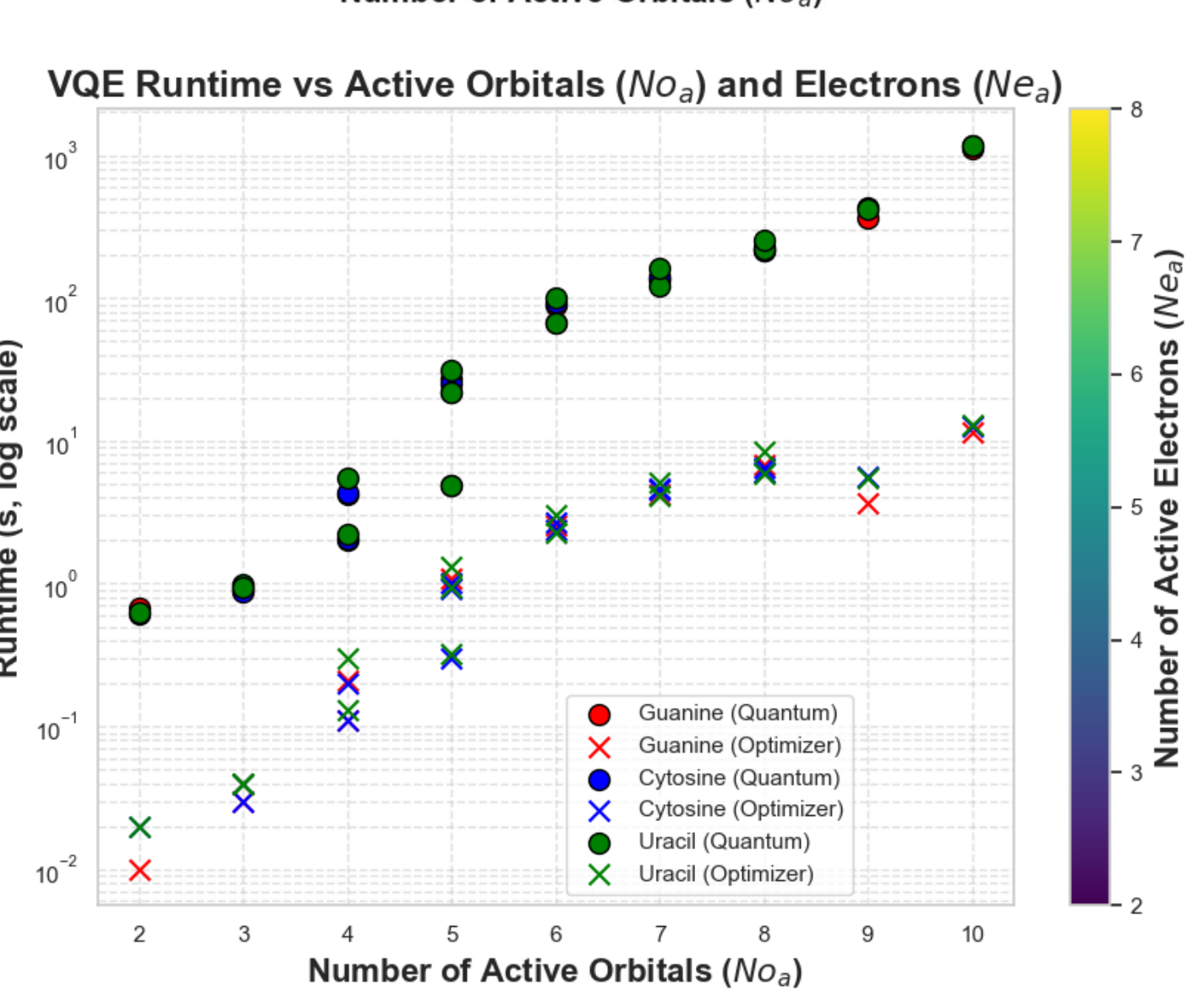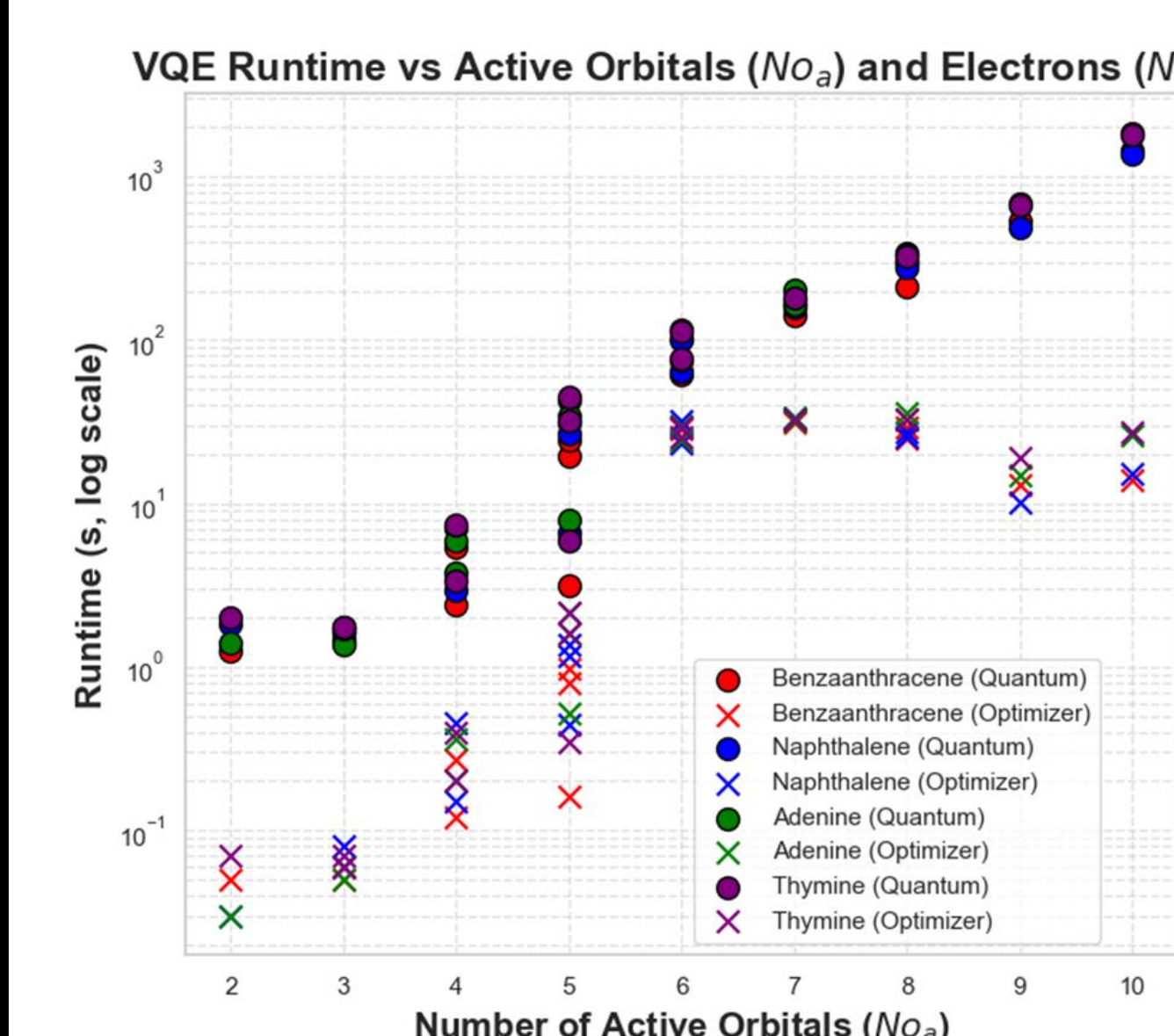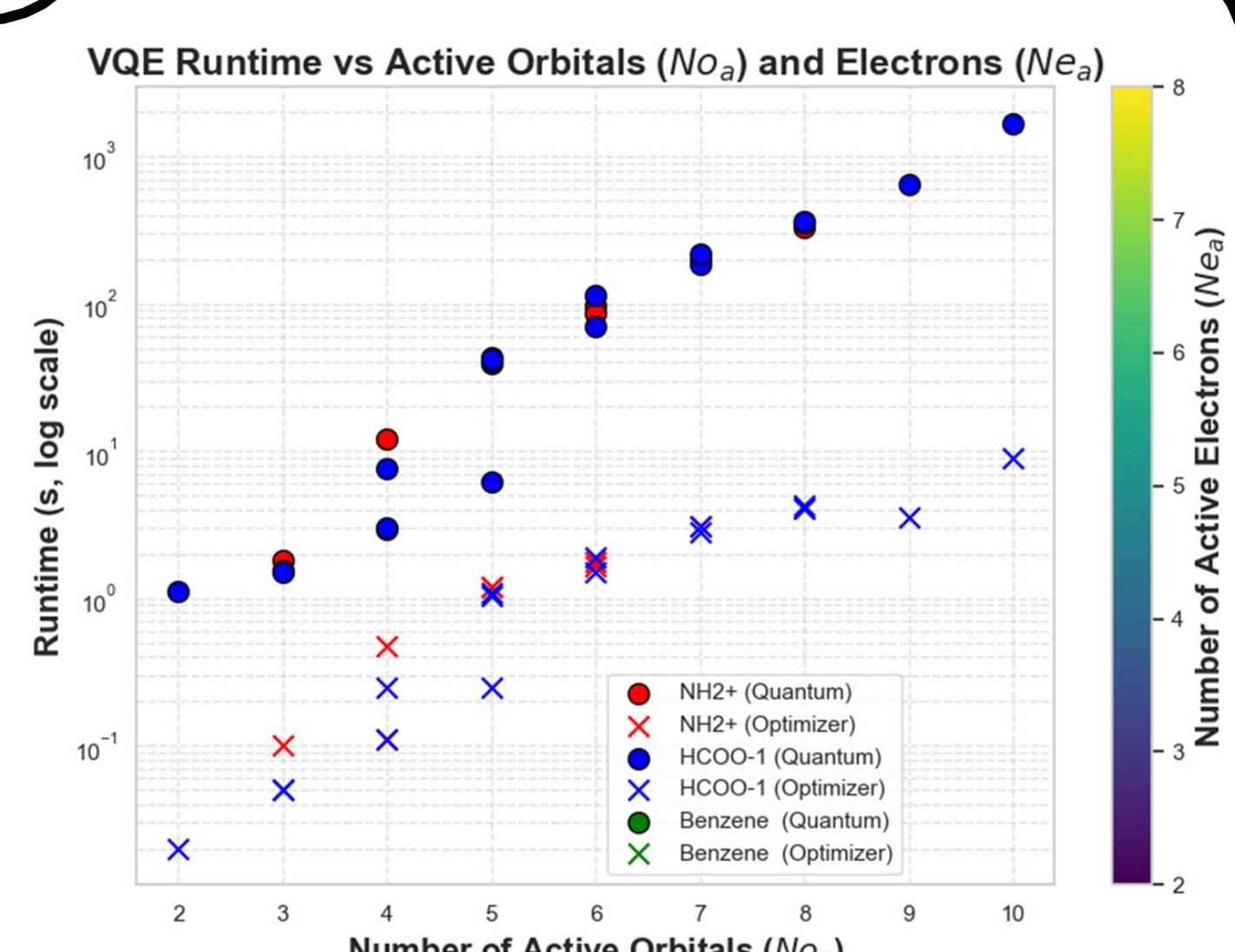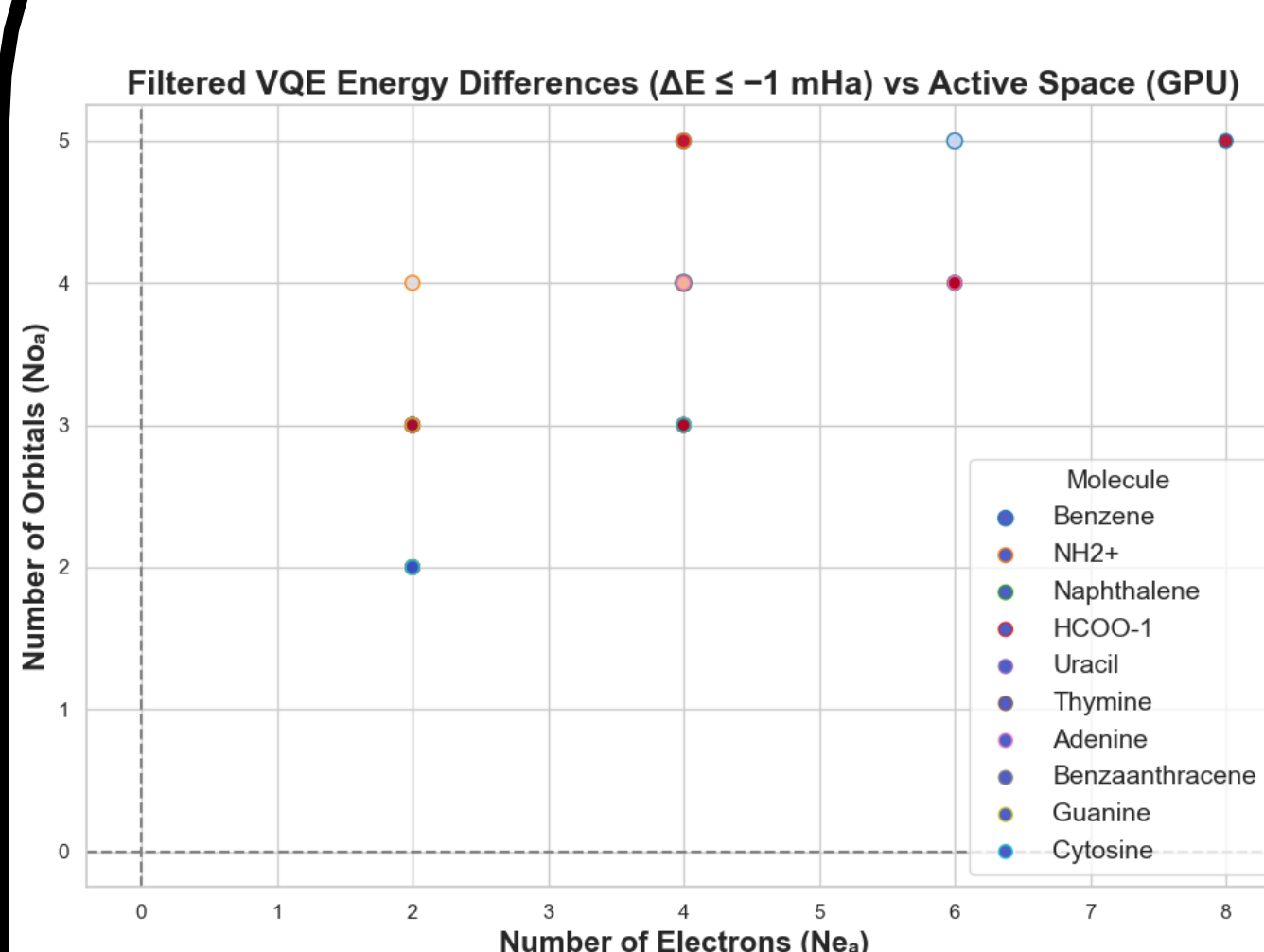1. Electronic Hamiltonian

$$\hat{H} = \sum_{pq} h_{pq}a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs} h_{pqrs}a_p^\dagger a_q^\dagger a_r a_s$$
3. Second Quantization Hamiltonian

$$\Psi_{HF} = \frac{1}{\sqrt{N!}}\det[\psi_1(\mathbf{x}_1)\,\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N)]$$
2. Hartree-Fock Approximation

$$H^{AS} = \sum_{pq}^{active}\tilde{h}_{pq}\hat{a}_p^\dagger\hat{a}_q + \frac{1}{2}\sum_{pqrs}^{active}g_{pqrs}\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s + E_{core}$$
5. Active Space Hamiltonian

Results

Methylene (CH_2) - VQE Computation Runtime Data

Active Space [1] (N_c, Ne_a, No_a)	VQE Energy (CPU)	VQE Energy (GPU)	Quantum Simulation Time (s, CPU)	Quantum Simulation Time (s, GPU)	Optimizer Time (s, CPU)	Optimizer Time (s, GPU)	Runtime (s, CPU)	Runtime (s, GPU)	Runtime Speedup (CPU/GPU)
(1, 6, 4)	-38.36862	-38.367669	84.4	6.98	0.07	0.03	84.47	7.01	12.05x
(1, 6, 5)	-38.39409	-38.373627	2092.91	65.06	0.3	0.27	2093.2	65.33	32.04x
(2, 4, 3)	-38.37477	-38.374512	4.84	2.88	0.01	0.01	4.85	2.89	1.68x
(2, 4, 4)	-38.37613	-38.375208	182.87	19.98	0.11	0.06	182.97	20.03	9.13x
(3, 2, 2)	-38.39752	-38.397453	1.96	1.97	0.01	0.01	1.97	1.98	0.99x
(3, 2, 3)	-38.37531	-38.374991	15.22	2.77	0.05	0.01	15.27	2.78	5.49x

Benzene (C_6H_6) - VQE Computation Runtime Data

Active Space [1] (N_c, Ne_a, No_a)	VQE Energy (CPU)	VQE Energy (GPU)	Quantum Simulation Time (s, CPU)	Quantum Simulation Time (s, GPU)	Optimizer Time (s, CPU)	Optimizer Time (s, GPU)	Runtime (s, CPU)	Runtime (s, GPU)	Runtime Speedup (CPU/GPU)
(19, 4, 4)	-227.92704	-227.91746	39.09	17.02	0.07	0.04	39.16	17.06	2.30×
(18, 6, 6)	-227.33727	-227.55781	2703.1	192.31	0.72	0.66	2703.8	193	14.01×
(16, 10, 6)	-227.90568	-227.89304	859.03	60.12	0.15	0.09	859.18	60.22	14.27×
(14, 14, 8)	-227.81613	-227.84837	45409.3	171.43	0.48	0.34	45410	171.8	264.41×

[1] (N_c, Ne_a, No_a) = (Number of core orbitals, Number of electrons in active space, Number of orbitals in active space).

Summary

- Our results show a significant acceleration in runtime for GPU based simulations compared to CPU implementations, while maintaining comparable energy accuracy within mHa differences.
- The gain increases monotonically with the size of the active space.
- The approach is generalizable to other molecular species, including open-shell molecules.

✓ The large active space shows over 260× speedup, highlighting GPU superiority for large-scale quantum simulations.
✓ For the smallest case, GPU is still about 2.3× faster than CPU.

References

[1]. Ieva Liepuoniute, Kirstin D Doney, Javier Robledo-Moreno, Joshua A Job, Will S Friend, and Gavin O Jones. Quantum-centric study of methylene singlet and triplet states. arXiv preprint arXiv:2411.04827, 2024.
[2]. Konstantin M Makushin and Aleksey K Fedorov. Simulating methylamine using a symmetry-adapted, qubit excitation-based variational quantum eigensolver. Quantum Reports, 7(2):21, 2025.
[3]. R. D. Johnson, NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 21. Gaithersburg, MD: National Institute of Standards and Technology, 2019.