Quantum Benchmarking Of Molecular Ground-State Energy Estimation

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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 methylene (CH_2) and Benzene (C_6H_6) using quantum software and running on CPU and GPU devices. While we cannot draw conclusions on energy accuracy, we prove the GPU acceleration of VQE.

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

$$\Psi_{\mathrm{HF}} = \frac{1}{\sqrt{N!}}\det[\psi_1(\mathbf{x}_1)\,\psi_2(\mathbf{x}_2)\,\cdots\psi_N(\mathbf{x}_N)]$$

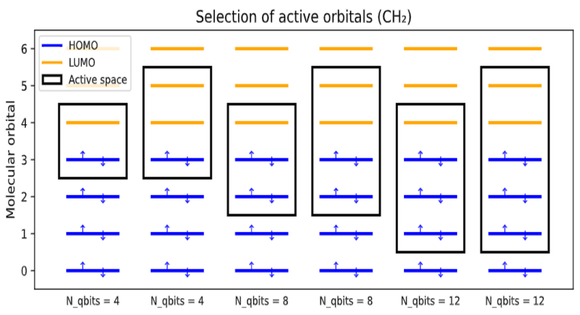
2. Hartree-Fock Approximation

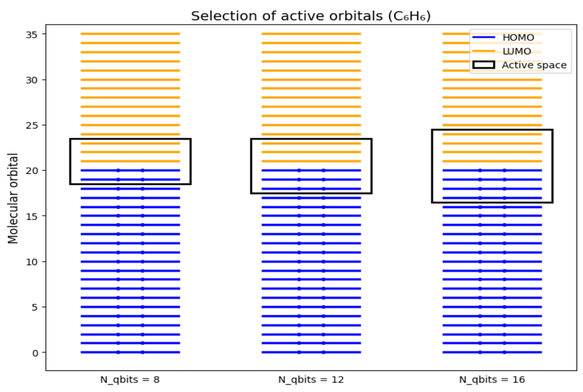
$$H^{AS} = \sum_{pq}^{\text{active}} \tilde{h}_{pq}\hat{a}_p^\dagger\hat{a}_q + \frac{1}{2}\sum_{pqrs}^{\text{active}} g_{pqrs}\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s + E_{\text{core}}$$

5. Active Space Hamiltonian

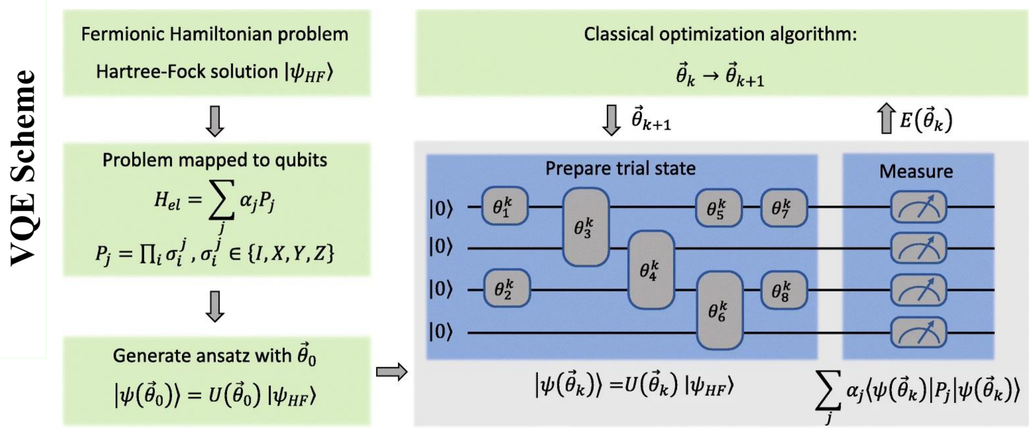
Methodology

- We use the CUDA Quantum (CUDA-Q) framework, enabling simulations on both CPU and GPU backends.
- Within the `sto-3g` 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.



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.

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.

Methylene (CH_2) :

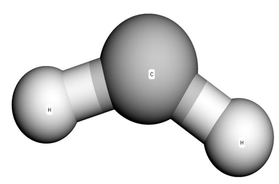
✓ For large active space (e.g. nele_cas=6, norb_cas=5), GPU can be ~30× faster than CPU.
✓ For small active space , the speedup is marginal or negligible.
✓ In one case, CPU was even slightly faster (likely due to overhead/delay in GPU scheduling or under-utilization).

Benzene (C_6H_6):

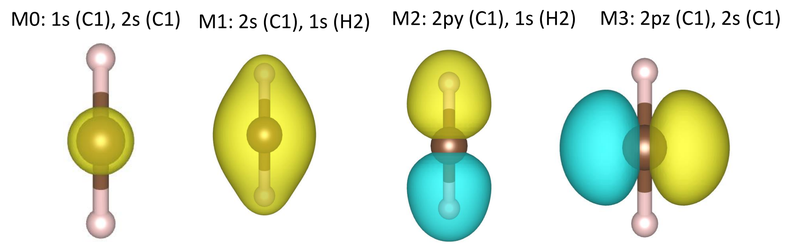
✓ The large active space (e.g. ncore=14 , nele_cas=14, norb_cas=8) shows over 260× speedup, highlighting GPU superiority for large-scale quantum simulations.
✓ For the smallest case, GPU is still about 2.3× faster than CPU.

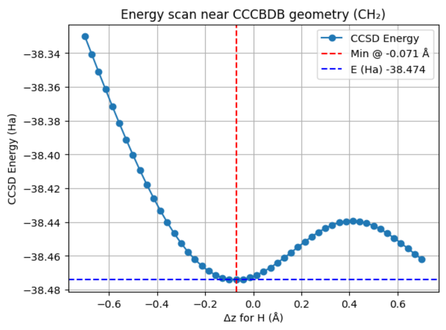
Classical algorithms: structure and molecular orbitals

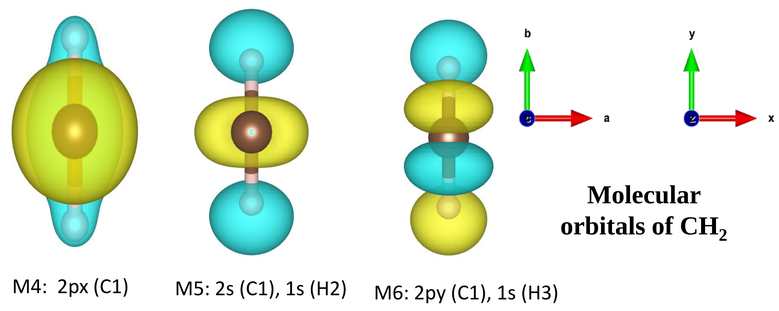
- Starting atomic structure: Computational Chemistry Comparison and Benchmark Database (CCCBDB).
- Configuration optimization: searching for minimum energy, using the `sto-3g` basis set.
- Isosurface plots of Molecular Orbitals form the basis for choosing the active space.



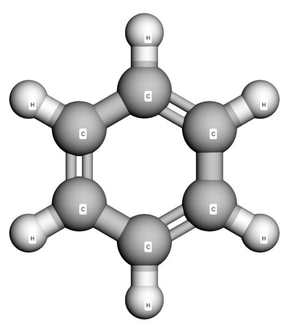
Methylene: CH_2



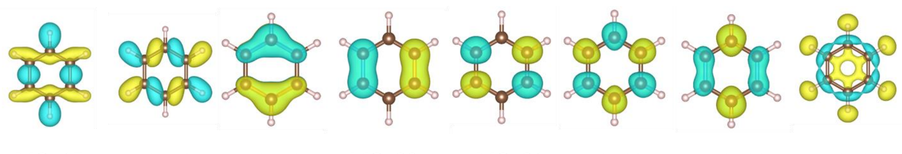




Molecular orbitals of CH_2



Benzene: C_6H_6



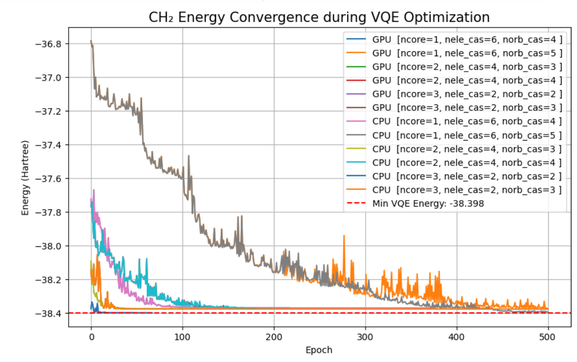
Molecular orbitals used in the active space of C_6H_6

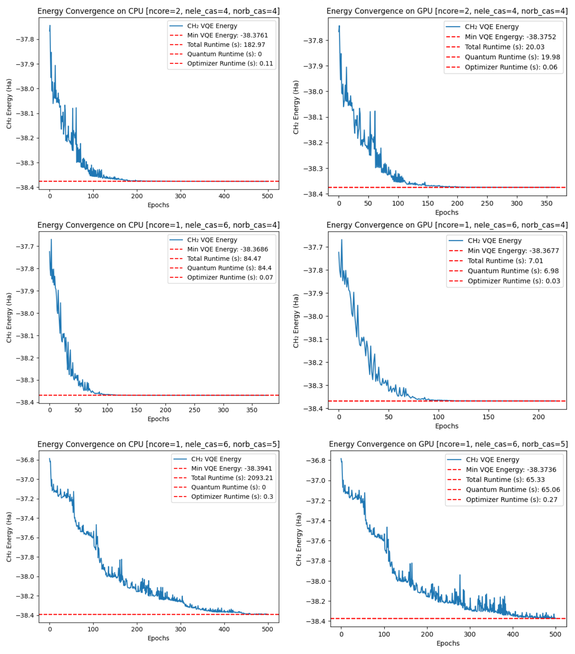
Results

Methylene (CH_2)

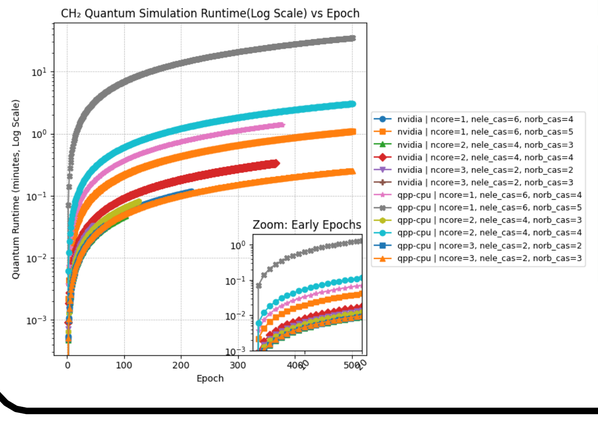
Active Space	VQE Energy (CPU)	VQE Energy (GPU)	Quantum SimulationTime (s, CPU)	Quantum Simulation Time (s, GPU)	Optimizer Time (s, CPU)	Optimizer Time (s, GPU)	Runtime (s, CPU)	Runtime (s, GPU)	Runtime Speedup (CPU/GPU)
ncore=1, nele_cas=6, norb_cas=4	-38.36862	-38.367669	84.4	6.98	0.07	0.03	84.47	7.01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

CH_2 - VQE Computation Runtime Data





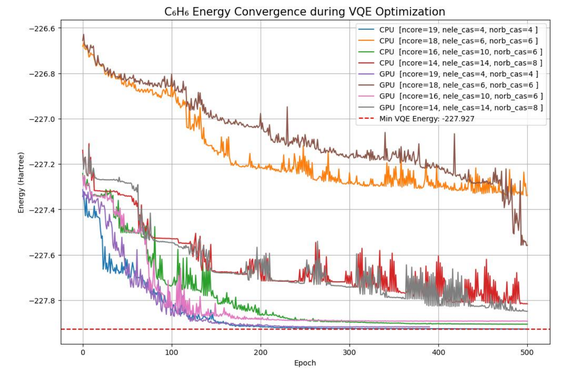
Comparative Analysis of VQE w.r.t Epoch

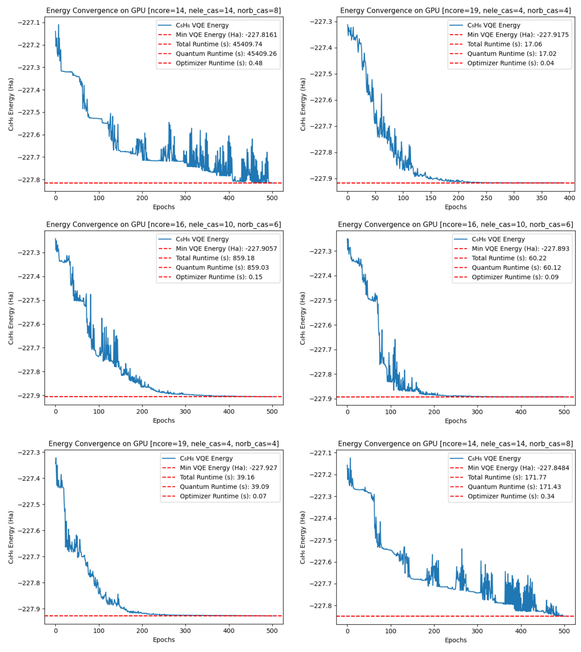


Benzene (C_6H_6)

Active Space	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)
ncore=19, nele_cas=4, norb_cas=4	-227.92704	-227.91746	39.09	17.02	0.07	0.04	39.16	17.06	**2.30×**
ncore=18, nele_cas=6, norb_cas=6	-227.33727	-227.55781	2703.1	192.31	0.72	0.66	2703.81	192.97	**14.01×**
ncore=16, nele_cas=10, norb_cas=6	-227.90568	-227.89304	859.03	60.12	0.15	0.09	859.18	60.22	**14.27×**
ncore=14, nele_cas=14, norb_cas=8	-227.81613	-227.84837	45409.3	171.43	0.48	0.34	45409.7	171.77	**264.41×**

C_6H_6 - VQE Computation Runtime Data





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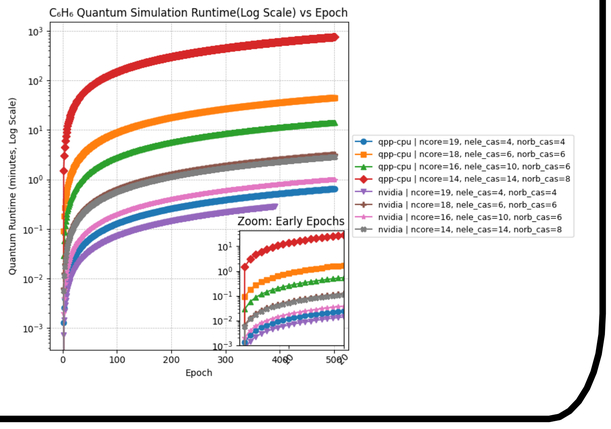

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