MITRE: Dibenzothiophene (DBT) Analysis using VQE

Team OATH

May 27, 2025

1. Introduction and Problem Context

Dibenzothiophene (**DBT**, $C_{12}H_8S$), a sulfur-containing PAH, is crucial in fossil fuels, contributing to SOx emissions and catalyst poisoning. Understanding its electronic structure, specifically ground state energy, is vital for hydrodesulfurization (HDS) catalyst design and asphalt degradation insights. The Variational Quantum Eigensolver (VQE) [2, 3] is a promising method for accurate molecular energy calculations on near-term quantum computers. This report details VQE calculations on DBT, establishing a baseline for quantum simulations of such systems.

1.1 Molecular System and Observable Justification

Molecular System Selection: We selected **DBT** over other PAHs due to its high relevance in asphalt chemistry and environmental science. Its heterocyclic sulfur introduces unique electronic properties and reactivity crucial to desulfurization processes and oxidative degradation, central to asphalt aging. DBT's size offers sufficient complexity for initial quantum simulations.

Relevant Chemical Behaviors to Simulate: Using quantum computing, we aim to simulate:

- Ground State Energy and Stability: Fundamental for understanding DBT's intrinsic stability and role in reactions, particularly oxidation.
- Oxidation Energies and Reactivity: Calculating energies of DBT and its oxidized forms helps infer oxidation energies, crucial for asphalt degradation.
- Electronic Structure Analysis: Revealing charge distribution and orbital energies, vital for predicting catalytic activity and molecular interactions.

Observable: Our primary observable is the ground state energy.

2. Hamiltonian Modeling and Qubit Encoding Plan

2.1 Initial Hamiltonian Modeling and Pre-processing Steps

We modeled the molecular Hamiltonian using classical quantum chemistry tools. Molecular coordinates for DBT were extracted from PubChem. PySCF [7] performed Restricted Hartree-Fock (RHF) calculations with STO-3G (77 MOs) and 6-31G (137 MOs) basis sets. Simplifications included:

- An **8-electron, 8-orbital (8e, 8o) active space** chosen around the HOMO-LUMO gap (MO indices [44-51]).
- Frozen core approximations: 88 core electrons in the lowest 44 MOs (indices [0-43]) were fixed.

Nuclear repulsion energy was 795.24154567 Ha. One- and two-electron integrals for the active space were computed.

2.2 Qubit Encoding and Fidelity Trade-offs

We used the Jordan-Wigner mapping [10] to translate the fermionic Hamiltonian into qubit space.

- Basis Set Selection Trade-offs: STO-3G (minimal, lower accuracy, fewer resources) vs. 6-31G (larger, higher accuracy, more resources).

- Active Space Selection/Qubit Count Minimization: The 8e, 8o active space (mapping to **16 physical qubits** for the UCCSD ansatz) was a deliberate choice to minimize qubit count for **NISQ device feasibility**. Larger active spaces offer higher fidelity but significantly increase qubits and variational parameters. Our 16-physical-qubit UCCSD ansatz involves **360 variational parameters**, challenging classical optimization and quantum circuit depth. This selection balances correlation effects with practical resource constraints.

Fermionic Hamiltonians (STO-3G: 4161 terms; 6-31G: 4153 terms) converted to qubit Hamiltonians (STO-3G: 849 terms; 6-31G: 841 terms). The constant term ($C_{\text{Qubit Const}}$) was 710.5547 Ha (STO-3G) and 715.2549 Ha (6-31G).

3. Choice of Quantum Algorithm and Early Results

3.1 Quantum Algorithm Justification

To determine DBT's ground state energy, gain insights into asphalt aging, and establish a foundational quantum computational approach, we chose the Variational Quantum Eigensolver (VQE) algorithm [2, 3] with the Unitary Coupled Cluster Singles and Doubles (UCCSD) ansatz.

- VQE Rationale: It is a **NISQ-compatible** hybrid quantum-classical algorithm, offloading intensive optimization to classical hardware, suitable for current devices.
- UCCSD Rationale: A physically inspired ansatz, it achieves high chemical accuracy by systematically incorporating single and double excitations crucial for electron correlation, balancing expressibility with feasible circuit depth.
- Why not others? We excluded **Quantum Phase Estimation (QPE)** due to its requirement for deep, fault-tolerant circuits. Krylov subspace methods or subspace diagonalization (SQD) are primarily for excited state access; our initial focus is ground state energy.

3.2 Early Results and Computational Structure

VQE calculations for DBT (8e, 8o) are summarized in Table 1. 6-31G RHF energy (-856.4020 Ha) is lower than STO-3G (-846.7064 Ha).

Table 1: Summary of RHF and VQE energies for Dibenzothiophene (8e, 8o). Energies in Hartrees (Ha).

Energy Component	STO-3G	6-31G
Total RHF Energy	-846.7064	-856.4020
Nuclear Repulsion	795.2415	795.2415
Core HF Electronic	-1477.6575	-1493.5535
VQE Eigenvalue (raw)	620.7905	650.8478
Qubit Hamiltonian Const.	710.5547	715.2549
Active Space Electronic (VQE)	-89.7642	-64.4071
Final Total VQE Energy	**-772.1802**	**-762.7191**
VQE "Corr." Energy (vs RHF)	74.5262	93.6829

Despite VQE convergence (300 iterations, Adam optimizer, step size 0.1), total VQE energies significantly exceeded RHF energies. This suggests the current UCCSD ansatz and optimization did not capture sufficient correlation, indicating areas for methodological refinement.

Optimization Strategies: Our Phase 2 VQE optimization used the UCCSD ansatz (16-physical-qubit, 360 parameters) with the Adam optimizer. Phase 3 will explore:
- Advanced Ansätze: ADAPT-VQE or k-UpCCGSD for shallower circuits/fewer parameters.
- Optimizer Tuning: Explore SPSA, COBYLA, warm starts, learning rate schedules.
- Genetic Algorithms: For complex, non-convex loss landscapes.

4. Platform Access Strategy and Feasibility Rationale

The 16-physical-qubit UCCSD system (360 parameters) challenges NISQ hardware. Our strategy balances high-performance simulation with targeted QPU access.

4.1 Platform Access Strategy and Feasibility

- Simulators (for initial results & time savings):
    - NVIDIA GPUs with PennyLane Lightning: For rapid local development and parameter tuning.
    - Amazon Braket SV1: Up to 50 qubits/4TB memory for noise-free benchmarks and larger active space simulations.
- QPUs and Error Mitigation (for testing on real hardware):
    - IBM Quantum (Heron processors): Accessing Heron [5] (133 fixed-frequency transmon qubits, high connectivity, 99.7% 2-qubit gate fidelity) for our 16-physical-qubit model. We'll use Fire Opal software (Q-CTRL) for advanced error mitigation.
    - IonQ (Forte): Accessing Forte [6] (trapped-ion architecture, $\sim$32 physical algorithmic qubits, all-to-all connectivity, $>$99.9% 2-qubit gate fidelity). Its high coherence benefits VQE and accommodates our 16-physical-qubit model.

Feasibility Rationale: Our approach is realistic given NISQ hardware constraints. For our 8e, 8o active space, we require **16 physical qubits**. For scaling to truly complex, fault-tolerant problems, these 16 spin-orbitals would map to **16 logical qubits**, necessitating a significantly larger number of physical qubits (hundreds to thousands per logical qubit for error correction) [1]. Estimated shot counts per energy evaluation on QPUs range from $10^3 - 10^4+$, with 100+ iterations. Simulators are preferred for initial scaling. This design supports future optimization and benchmarking.

5. Resource Needs and Testing Plan for Phase 3

- Resource Needs: Significant quantum computer time ($10^3 - 10^4+$ shots/energy evaluation), high-performance classical computing (CPUs/NVIDIA GPUs), and continued access to software tools (PennyLane [8], PySCF [7]) and cloud platforms (Amazon Braket, IBM Quantum Experience [5]).
- Testing Plan:
    - *Simulator Validation:* Rigorous testing of refined methodologies and ansätze on `lightning.qubit` and Amazon Braket SV1 for ideal performance.
    - *Real Hardware Benchmarking:* Execute VQE on IBM Quantum [5] and IonQ [6]. Compare QPU results to simulator and classical benchmarks (e.g., CCSD(T), CASSCF/CASPT2), analyzing convergence, accuracy, and error mitigation impact.
    - *Scalability Testing:* Gradually increase active space or explore larger, similar PAHs to assess scalability and resource needs.

This work is a stepping stone for complex quantum simulations in catalyst design, materials science, and environmental chemistry, aiming to understand asphalt aging for durable road materials.

References

[1] Z. Cao, Y. Cao, et al. (2024). *Quantum Computation for Quantum Chemistry*. Springer.

[2] A. Peruzzo, J. McClean, et al. (2014). A variational eigenvalue solver on a photonic quantum processor. *Nature Communications*, 5(1), 4213.

[3] J. R. McClean, J. Romero, et al. (2016). The theory of variational hybrid quantum-classical algorithms. *New Journal of Physics*, 18(2), 023023.

[4] P. J. O'Malley, et al. (2016). Scalable Quantum Simulation of Molecular Energies. *Physical Review X*, 6(3), 031007.

[5] IBM Quantum Experience. (n.d.). *Learn about our quantum systems*. Retrieved from https://quantum.ibm.com/.

[6] IonQ. (n.d.). *IonQ Forte*. Retrieved from https://ionq.com/products/ionq-forte.

[7] PySCF. (n.d.). *Python-based Simulations of Chemistry Framework*. Retrieved from https://pyscf.org/.

[8] PennyLane. (n.d.). *Quantum machine learning with PennyLane*. Retrieved from https://pennylane.ai/.

[9] S. Bravyi, et al. (2017). Tapering the Number of Qubits in Quantum Simulations of Fermionic Systems. *Physical Review Letters*, 118(22), 220504.

[10] J. D. Whitfield, et al. (2011). Simulation of molecular energies on a quantum computer. *Molecular Physics*, 109(5), 735-742.