Asphalt Quantum: Dibenzothiophene (DBT) Analysis using VQE

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Abstract

Dibenzothiophene (DBT) is a key sulfur-containing polycyclic aromatic hydrocarbon (PAH) relevant to crude oil processing and environmental science. This study employs the Variational Quantum Eigensolver (VQE) to calculate DBT's ground state energy, focusing on an 8-electron, 8-orbital (8e, 8o) active space with STO-3G and 6-31G basis sets. Results demonstrate VQE's applicability to complex PAHs. While VQE energies obtained are higher than RHF energies, indicating areas for methodological refinement (ansatz, optimizer, active space), this work establishes a foundational quantum computational approach for DBT analysis, aiming to provide insights into molecular mechanisms of asphalt aging.

1. Introduction

Sulfur-containing Polycyclic Aromatic Hydrocarbons (PAHs) like dibenzothiophene (DBT, $C_{12}H_8S$) are significant in fossil fuels, contributing to SOx emissions and catalyst poisoning in refining. Understanding DBT's electronic structure, particularly its ground state energy, is crucial for designing effective hydrodesulfurization (HDS) catalysts and for comprehending its role in asphalt degradation. The Variational Quantum Eigensolver (VQE) offers a promising path for accurate molecular energy calculations on near-term quantum computers. This report details VQE calculations on DBT, selected as a representative molecule for asphalt components, using an 8-electron, 8-orbital (8e, 8o) active space. We compare results from two common basis sets, STO-3G and 6-31G, to establish a baseline for quantum simulations of such systems. The primary observable of interest is the ground state energy, which can inform oxidation energies and reactivity.

2. Methodology

The computational methodology involved classical pre-computation steps using PySCF, followed by quantum computations using PennyLane.

2.1. Classical Pre-computation

Restricted Hartree-Fock (RHF) calculations were performed using PySCF to obtain initial molecular orbitals (MOs) and reference energies for DBT. Two basis sets were employed: STO-3G and 6-31G. For STO-3G, this resulted in 77 MOs, while 6-31G yielded 137 MOs. An active space of 8 electrons in 8 spatial orbitals (8e, 8o) was selected around the HOMO-LUMO gap (MO indices [44-51] for both basis sets). With 8 active electrons from 96 total (48 RHF occupied MOs), 88 core electrons in the lowest 44 MOs (indices [0-43]) were frozen. The nuclear repulsion energy for the DBT molecule was calculated to be 795.24154567 Ha. One- and two-electron integrals for the selected active space were then computed for subsequent Hamiltonian construction.

2.2. Quantum Computation (VQE)

The VQE algorithm, implemented using PennyLane v0.41.1, was employed to determine the ground state energy of the active space.

- **Ansatz:** The Unitary Coupled Cluster Singles and Doubles (UCCSD) ansatz was used. For the 8e, 8o active space, this translates to a 16-qubit system (2 spin-orbitals per spatial orbital). The UCCSD ansatz for this system involved 360 variational parameters.

- **Optimizer & Iterations:** The Adam optimizer, with a step size of 0.1, was used for 300 iterations to minimize the energy.

- **Simulation Backend:** Calculations utilized PennyLane's high-performance simulator, 'lightning.qubit'.

The total VQE energy is calculated by combining the VQE result for the active space with the classical energies of the core electrons and nuclear repulsion: $E_{\text{Total VQE}} = E_{\text{Nuc Rep}} + E_{\text{Core HF Elec}} + (E_{\text{VQE raw}} - C_{\text{Qubit Const}})$. Here, $E_{\text{VQE raw}}$ is the eigenvalue obtained from the VQE optimization, and $C_{\text{Qubit Const}}$ is the constant term in the qubit Hamiltonian.

2.3. Hamiltonian Encoding and Qubit Mapping

The fermionic Hamiltonian, representing the electronic structure of the active space, was constructed from the one- and two-electron integrals. This Hamiltonian (STO-3G: 4161 terms; 6-31G: 4153 terms) was transformed into a qubit Hamiltonian (STO-3G: 849 terms; 6-31G: 841 terms) using Jordan-Wigner mapping. For the STO-3G basis set, the active space fermionic Hamiltonian contained 4161 terms. After the Jordan-Wigner transformation, this resulted in an OpenFermion qubit Hamiltonian with 849 terms. For the 6-31G basis set, the fermionic Hamiltonian had 4153 terms, leading to a qubit Hamiltonian with 841 terms. The constant term ($C_{\text{Qubit Const}}$) in the qubit Hamiltonian, including nuclear repulsion, frozen core energy, and active space integral constants, was 710.5547 Ha (STO-3G) and 715.2549 Ha (6-31G).

3. Results and Discussion

VQE calculations for DBT with both STO-3G and 6-31G basis sets within an 8-electron, 8-orbital active space are summarized in Table 1. As expected, the RHF energy for the 6-31G basis set (-856.4020 Ha) is lower (more negative) than that for STO-3G (-846.7064 Ha), indicating a better classical description with the larger basis set.

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

VQE optimization (300 iterations): 6-31G converged from approx. 726.49 Ha to 650.8478 Ha (Fig. 1); STO-3G from approx. 726.77 Ha to 620.7905 Ha.

Despite VQE convergence, total VQE energies significantly exceeded RHF energies, reflected in positive "VQE Correlation Energies" ($E_{\text{Total VQE}} - E_{\text{Total RHF}}$) of +74.53 Ha (STO-3G) and +93.68 Ha (6-31G). Ideally, VQE should capture correlation and yield energies $\leq$ RHF. The positive values indicate that the VQE calculations, with the current UCCSD ansatz and optimization parameters, did not capture sufficient correlation energy to improve upon the RHF reference within the chosen active space. This discrepancy highlights challenges in the expressiveness of the ansatz, the choice of active space, or the optimization landscape for this particular system size and complexity. Potential improvements include ADAPT-VQE, optimizer tuning, and active space re-evaluation to better capture correlation effects. Despite these challenges, the successful execution of the VQE pipeline for DBT establishes a framework for further quantum chemical investigations of asphalt-related molecules.
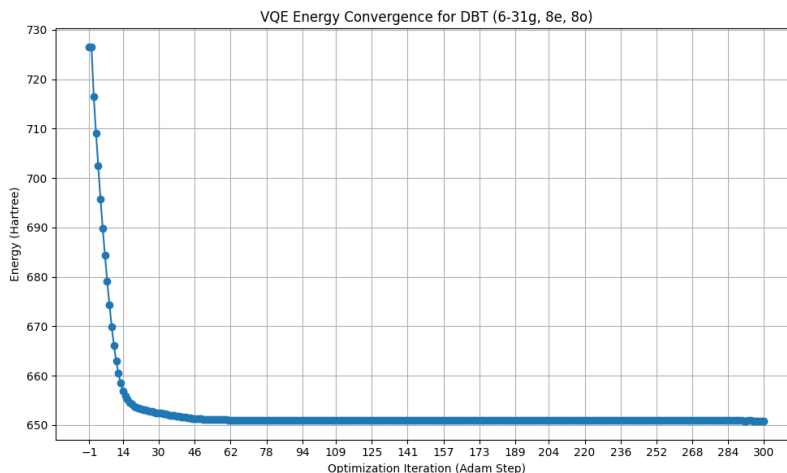
Figure 1: VQE Energy Convergence for DBT (6-31G, 8e, 8o). Final raw VQE energy: 650.8478 Ha.

4. Conclusion and Roadmap to Phase 3

VQE was successfully applied to calculate dibenzothiophene's (DBT) ground state energy (STO-3G/6-31G, 8e8o, 16 qubits). Although VQE energies exceeded RHF values, indicating refinement needs, the quantum chemistry pipeline is functional and foundational for future studies.

Phase 3 Roadmap:

- **Computational Strategy:** The 16-qubit (8e, 8o) UCCSD system (360 parameters) challenges current NISQ hardware due to circuit depth. Our strategy involves:
  - *High-Performance Simulation:* Continued use of **NVIDIA GPUs with PennyLane Lightning** for rapid local development and parameter tuning. For larger noise-free benchmarks, **Amazon Braket SV1** state-vector simulator will be employed to assess ideal algorithm performance.
  - *QPU Execution & Error Mitigation:* We plan to explore execution on leading QPUs. Specifically, **IBM Quantum hardware (e.g., Heron processors) coupled with Fire Opal software** will be targeted for its advanced error mitigation capabilities, crucial for deep UCCSD circuits. Additionally, **IonQ hardware (e.g., Forte)** will be considered to leverage its high qubit connectivity and coherence, offering a comparison across different QPU architectures. Access will be primarily via cloud platforms. Estimated shot counts per energy evaluation on QPUs range from $10^3 - 10^4+$.

- **Methodological Refinements:** Efforts include developing efficient ansätze (e.g., ADAPT-VQE, k-UpCCGSD), optimizing VQE parameters, and thorough active space re-evaluation (e.g., via CASSCF). Results will be benchmarked against classical methods (e.g., CCSD(T), CASSCF/CASPT2).

- **Scaling and Impact:** The pipeline will be tested on larger systems/DBT derivatives, aiming to apply these techniques to understand asphalt aging (e.g., oxidation, modifier interactions) for durable road materials.

This work serves as a stepping stone for complex quantum simulations in catalyst design, materials science, and environmental chemistry.

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5. References

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