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Variational Quantum Nuclear-Electronic Dynamics: Proton Transfer on Quantum Computers

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Quantum effects of proton transfer

- Proton transfer reactions are ubiquitous in many chemical and biological processes.
- Accurate description of proton transfer requires a quantum description of the kinetic nuclei that captures quantum tunnelling and zero-point energy.
- Several theoretical approaches to accurately model proton transfer like Ring Polymer Molecular Dynamics [1] and Multi-configuration time-dependent Hartree [2] have been developed, however they exhibit prohibitive scaling with the system size.

Nuclear-Electronic Orbital (NEO) Theory

- NEO approach solves the mixed nuclear-electronic time-independent Schrödinger equation by constructing a mixed nuclear-electronic wavefunction [3].
- NEO framework has be complemented with existing electronic structure methods at different levels of theory like NEO Hartree-Fock (NEOHF) and NEO Complete Active Space Configuration Interaction (NEOCASCI) [4].
- These, however, still suffer from the scalability limitations of the underlying electronic structure methods.

NEO approach for modelling proton transfer

- NEO framework has been extended for implementation on quantum hardware [5].
- Kovyrshin *et al.* utilised NEO framework with the Unitary Coupled Cluster (UCC) ansatz to calculate the energy barrier of proton transfer in malonaldehyde [6].
- This work demonstrated that NEO with UCC singlets and doublets could reach energy barrier predicted by NEOCASCI to within 10^{-4} Hartree.
- Electronic-only CASCI calculation overestimates the barrier of proton transfer, which emphasises the importance of electron-nuclear correlation

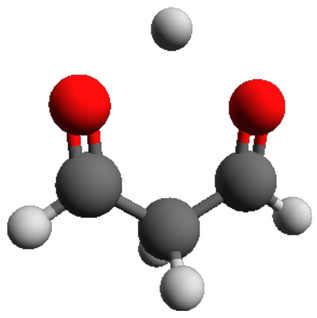

Figure 1: Malonaldehyde

Method	$\Delta E/\mathrm{Ha}$
CASCI	0.011962
NEOCASCI	0.005011
NEOUCCSD	0.004924
NEOUCCSDT	0.005007
NEOUCCSDTQ	0.005009

Table 1: Barrier for proton transfer in malonaldehyde calculated using different flavours of NEO. Values reproduced from Ref. [6].

Quantum resource reduction using ADAPT-VQE

- NEO framework with UCC ansatze offers a way of modelling proton transfer in polynomial time using the Quantum Phase Estimation (QPE) [7] algorithm.
- However, these circuits are too deep to be meaningfully realised on current hardware for chemically interesting systems.
- Nykänen *et al.* extended the hardware efficient Adaptive Derivative-Assembled Pseudo-Trotter Ansatz Variational Quantum Eigensolver (ADAPT-VQE) for NEO framework. This method, titled Frozen Natural orbital (FNO)-NEO-ADAPT-VQE enables high fidelity circuit construction tailored for currently available quantum hardware [8].
- By using a FNO basis, they were able to reduce the qubit requirement, while the adaptive ansatze building led to shallower circuits.

Adaptive approximate matrix product state preparation

- Adaptive Approximate Circuit Compilation (ADAPT-AQC), an adaptive algorithm based on approximate circuit compiling to construct high fidelity shallow circuits that approximates a given quantum circuits was recently proposed by Jadenberg *et al.* [9].
- In conjunction with ADAPT-VQE, this provides a toolbox of implementing quantum circuits to caprute proton dynamics of small molecules on currently available quantum hardware.

Approximate quantum compilation of proton-transfer dynamic for quantum processors

- In this work, we demonstrate a quantum computing pipeline based on NEO framework to model proton transfer of malonaldehyde.
- We suggest strategies to construct quantum circuits to tailor for current and future quantum hardware.
- We perform proton transfer barrier estimation simulations using realistic hardware noise models.

Theory

- The dynamics of the system is described by the Time-Dependent Schrödinger Equation (TDSE)

$$i\hbar \frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \left[\hat{T}_p + \hat{V}(t)\right] \left|\Psi(t)\right\rangle, \tag{1}$$

where $\hat{T}_p$ is the kinetic energy operator for the proton, and $\hat{V}(t)$ is a time-dependent potential given by

$$\hat{V}(t) = \hat{V}_p(t) + \hat{V}_{ep}(t) + \hat{H}_e(t) \tag{2}$$

where $\hat{V}_p(t)$ describes the interaction of the proton with the classical nuclear scaffold, $\hat{V}_{ep}(t)$ is the proton-electron interaction and $\hat{H}_e(t)$ is the electronic Hamiltonian contribution.

- We can write the NEOCI wavefunction with nuclear and electronic components $|\Phi^n_\nu\rangle$ and $\left|\Phi^e_\mu\right\rangle$ respectively as

$$\left|\Psi[\vec{C}(t)]\right\rangle = \sum_{\mu\nu} C_{\mu\nu}(t) \left|\Phi^e_\mu\right\rangle |\Phi^n_\nu\rangle \ . \tag{3}$$

- This leads to an equation of motion for the CI coefficients $\vec{C}(t)$

$$\vec{H}(t)\vec{C}(t) = i\frac{\partial}{\partial t}\vec{C}(t)\,, \tag{4}$$

where the matrix elements of $\vec{H}(t)$ are defined by

$$H_{\kappa\lambda,\mu\nu}(t) = \langle\Phi^e_\kappa| \langle\Phi^n_\lambda| \hat{T}_p + \hat{V}(t) \left|\Phi^e_\mu\right\rangle |\Phi^n_\nu\rangle \ . \tag{5}$$

- Previously, Kovyrshin *et al.* explored the dynamics of this model through Suzuki-Trotter decomposition [10]. This approach is too computationally demanding for current hardware.
- To make our approach viable with current and near-future hardware, we explore the adiabatic regime of proton transfer by slowly varying the Hamiltonian. At each time step, the energy of the instantaneous proton-electron Hamiltonian is obtained by variationally minimising

$$E(t) = \min_{\vec{C}(t)} \frac{\left\langle\Psi[\vec{C}(t)]\right| \hat{T}_p + \hat{V}(t) \left|\Psi[\vec{C}(t)]\right\rangle}{\left\langle\Psi[\vec{C}(t)]\middle|\Psi[\vec{C}(t)]\right\rangle}. \tag{6}$$

Pipeline for proton transfer simulation

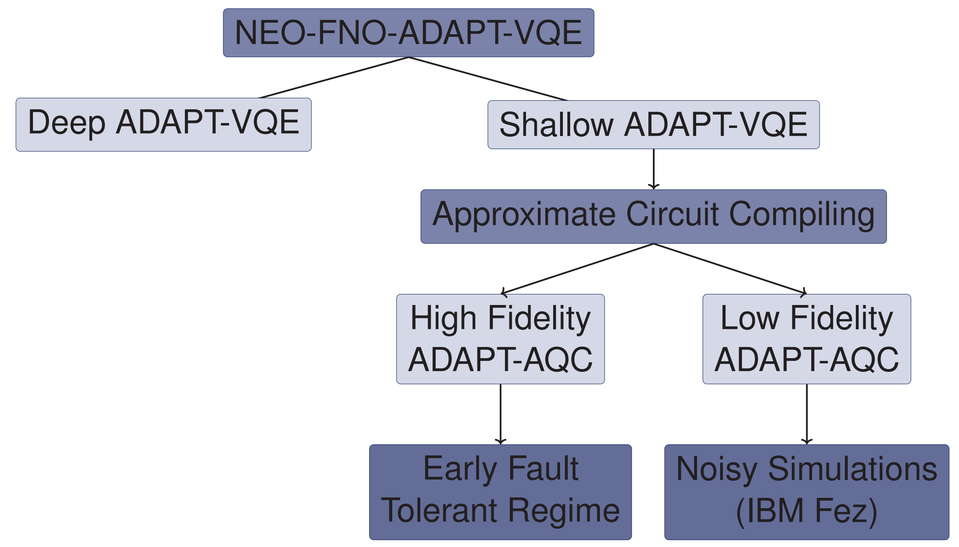

Figure 2: Starting with a variationally optimized FNO-NEO-ADAPT-VQE ansatz, we generate two sets of ADAPT-VQE circuits using different convergence thresholds. These are further truncated via ADAPT-AQC to optimize circuit depth. Deeper circuits are simulated without noise to emulate early fault tolerance, while shallower ones are simulated on the noisy IBM Fez model with ZNE.

Results

Soon to be published!

Acknowledgements

This work was supported by the Hartree National Centre for Digital Innovation, a UK Government-funded collaboration between STFC and IBM.

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