Approximate quantum circuit compilation for proton-transfer kinetics on quantum processors

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Quantum effects of proton transfer

- Accurate description of proton transfer processes requires a quantum description of kinetic nuclei that captures quantum tunnelling and zero-point energy.
- Several theoretical approaches, such as ring polymer molecular dynamics [1] and multi-configuration time-dependent Hartree [2] have been developed to accurately model proton transfer.
- However, these methods exhibit prohibitive scaling with system size.

Nuclear-Electronic Orbital (NEO) Theory

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

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

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

- NEO approach solves the mixed nuclear-electronic TDSE by constructing a mixed nuclear-electronic wavefunction [3] with nuclear and electronic components $|\Phi_\nu^n\rangle$ and $|\Phi_\mu^e\rangle$ respectively as,

$$\left|\Psi[\vec{C}(t)]\right\rangle = \sum_{\mu\nu} C_{\mu\nu}(t)\left|\Phi_\mu^e\right\rangle\left|\Phi_\nu^n\right\rangle. \quad (2)$$

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

$$\vec{H}(t)\vec{C}(t) = i\frac{\partial}{\partial t}\vec{C}(t), \quad (3)$$

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

$$H_{\kappa\lambda,\mu\nu}(t) = \langle\Phi_\kappa^e|\langle\Phi_\lambda^n|\hat{T}_p + \hat{V}(t)|\Phi_\mu^e\rangle|\Phi_\nu^n\rangle. \quad (4)$$

- We approximate the time-dependent energy and wavefunction in the adiabatic regime variationally along points on reaction pathway by minimising

$$E(t) = \min_{\vec{C}(t)} \frac{\left\langle\Psi[\vec{C}(t)]\left|\hat{T}_p + \hat{V}(t)\right|\Psi[\vec{C}(t)]\right\rangle}{\left\langle\Psi[\vec{C}(t)]\middle|\Psi[\vec{C}(t)]\right\rangle}. \quad (5)$$

Proton-transfer in malonaldehyde

- Kovyrshin *et al.* explored the dynamics of proton transfer in malonaldehyde using NEO Complete Active Space Configuration Interaction (NEOCASCI)[4] via Suzuki-Trotter decomposition. However, this method yields circuits too deep for current quantum computers.
- In this work, we extend the NEO framework for modelling proton transfer to be compatible with current near-term and early fault tolerant quantum hardware.
- First, we enhance the chemical model by employing larger basis sets, Frozen Natural orbital (FNO) approximation, and scaffold relaxation.
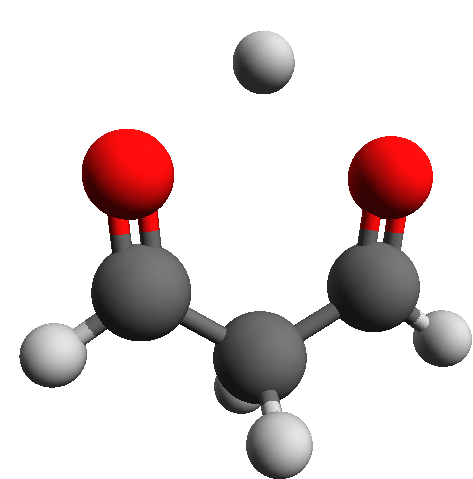

Figure 1: Chemical structure of malonaldehyde. *Left* and *Middle* refer to starting and middle stationary points along the trajectory of the mobile proton. $\Delta E = E_{Middle} - E_{Left}$

Method	ΔE (mHa)	Entanglement entropy *Left/Right*	*Middle*
NEO-CASCI*	5.1	0.00200	0.0038
FNO-NEO-CASCI	11.9	0.00240	0.0066
Semi-empirical model[5]	11.2		
Experimental[6]	13.5		

Table 1: NEO reference energies and their comparison with semi-empirical and experimental values. FNO is able to capture more electronic-nuclear correlations compared to vanilla NEO method.

Quantum resource reduction

- Nykänen *et al.* extended Adaptive Derivative-Assembled Pseudo-Trotter Ansatz Variational Quantum Eigensolver (ADAPT-VQE) method for FNO framework [7, 8].
- We utilise this method, called FNO-NEO-ADAPT-VQE, to construct two sets of high fidelity quantum circuits while adhering to current hardware restrictions.
  - * ADAPT-VQE (deep), retaining $> 99.8\%$ fidelity with FNO-NEO-CASCI reference
  - * ADAPT-VQE (shallow), retaining $> 97\%$ fidelity with FNO-NEO-CASCI reference
- Further, we employ Adaptive Approximate Circuit Compilation (ADAPT-AQC), an adaptive algorithm based on approximate circuit compiling [9] to further compress ADAPT-VQE (shallow) circuits quantum circuits. We construct two sets of circuits:
  - * ADAPT-AQC (high), maintaining $> 99\%$ fidelity with ADAPT-VQE (shallow)
  - * ADAPT-AQC (low), within 97% fidelity with ADAPT-VQE (shallow) and within ~ 50 two-qubit entangling gate depth

Summary of compressed circuits

Method	State	2Q-count	2Q-depth	Fidelity	E [mHa]	ΔE [mHa]
FNO-NEO-CASCI	*Left*	–	–	–	-600.666	
	Middle	–	–	–	-588.809	11.857
HF-product	*Left*	0	0	0.888	-552.090	
	Middle	0	0	0.936	-549.241	2.850
ADAPT-VQE (deep)	*Left*	1844	1362	0.998	-599.268	
	Middle	940	662	0.999	-587.497	11.771
ADAPT-VQE (shallow)	*Left*	551	411	0.971	-591.237	
	Middle	271	211	0.976	-579.609	11.628
ADAPT-AQC (high)	*Left*	81	51	0.961	-578.785	
	Middle	405	90	0.967	-565.358	13.427
ADAPT-AQC (low)	*Left*	81	51	0.961	-578.785	
	Middle	85	12	0.953	-551.645	27.140
ADAPT-AQC (low+ZNE)	*Left*	–	–	–	-548 ± 7	
	Middle	–	–	–	-524 ± 10	24 ± 12
ADAPT-AQC (low+ZNE)	*diff*	–	–	–	–	18 ± 3

Table 2: Summary of ADAPT-VQE and ADAPT-AQC circuits, along with energies and proton transfer barriers computed via statevector simulations. ADAPT-AQC (low+ZNE) incorporates noise models. Two-qubit gate depths and counts refer to circuits transpiled for IBM Heron r2 processors. Circuit fidelities are given with respect to the FNO-NEO-CASCI wavefunction. A constant offset of 265 Ha is added to reported absolute energies.

- * ADAPT-VQE circuits are within chemical accuracy. However, due to quantum resource requirement they are only compatible with error-corrected devices.
- * AQC-high circuits approximate the proton transfer energy barrier within 2 mHa with less than 100 entangling gate depth, compatible with early fault tolerant devices.
- * AQC-low circuits are compatible with current noisy devices, but they overestimate the energy barrier by $\approx 60\%$.
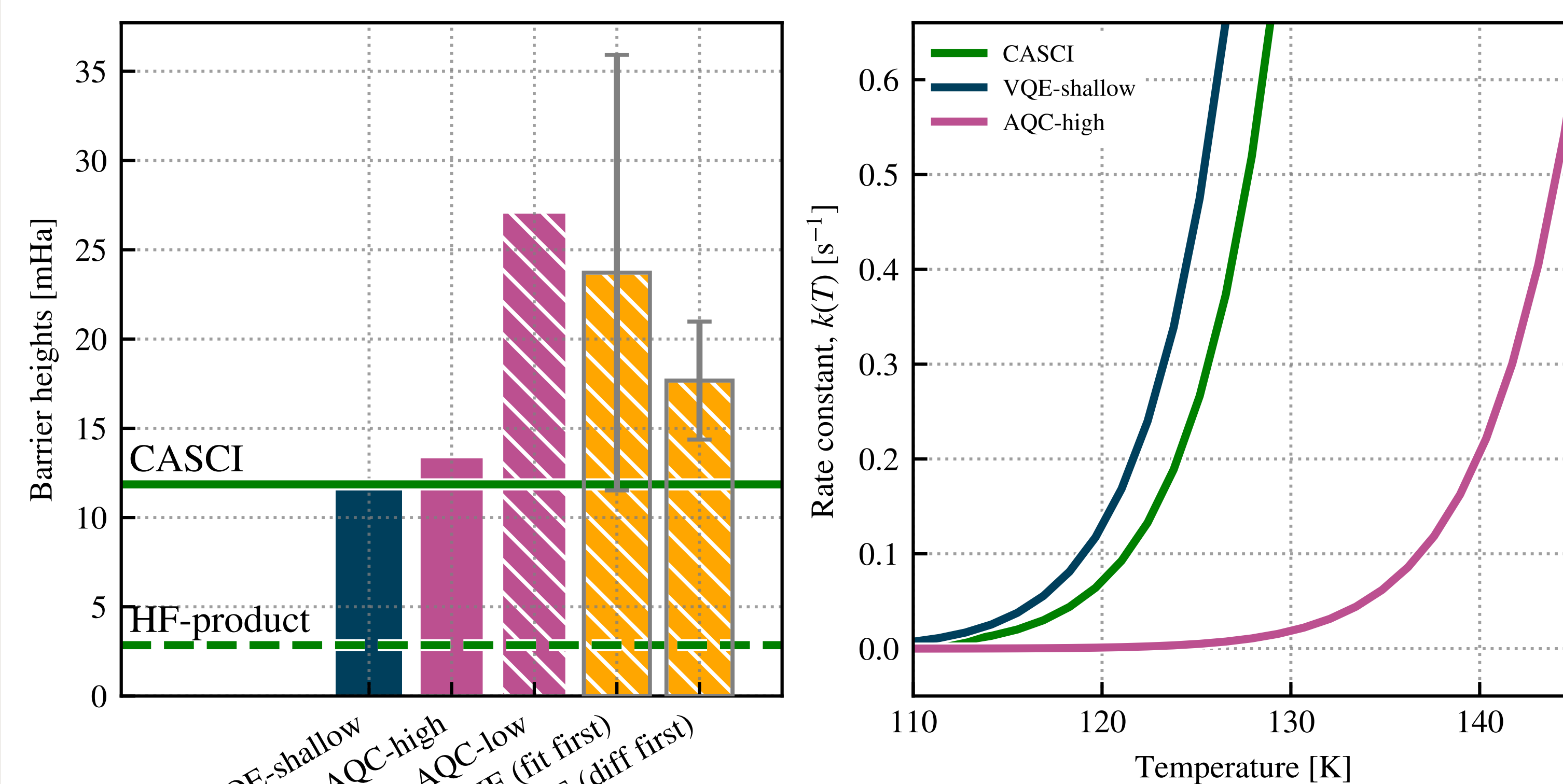
Energy barrier and rate constant of proton transfer

Figure 2: *Left:* energy difference of the potential barrier (in mHa) for the VQE-shallow circuits, AQC-high and -low (noiseless, pink hatched), and the noisy AQC-low circuits with ZNE using two extrapolation methods ('fit first' and 'diff first', yellow hatched). The ZNE-based bars indicate the median value sampled from 100 randomised gate-folded circuits. *Right:* proton transfer rate constants, $k(T)$, as a function of temperature, T, computed using quantum-corrected transition state theory rate expression.

- * Direct Zero Noise Extrapolation (ZNE) on barrier heights recovered 18-24 mHa values, demonstrating that energy differences may be more amenable to error mitigation than absolute state energies.
- * While the AQC-high circuits are within 10% of reference energy, they underestimate the rate constants at 120K by 60%.

Acknowledgements

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