The Best of Both Worlds: Optimizing Quantum Hardware Resources with Classical Stochastic Methods

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Unitary Coupled Cluster (UCC) approaches are an appealing route to utilising quantum hardware to perform quantum chemistry calculations, as quantum computers can in principle perform UCC calculations in a polynomially scaling fashion, as compared to the exponential scaling required on classical computers. Current noisy intermediate scale quantum (NISQ) computers are limited by both hardware capacity in number of logical qubits and the noise introduced by the deep circuits required for UCC calculations using the Variational Quantum Eigensolver (VQE) approach. We present a combined classical–quantum approach where a stochastic classical UCC pre-processing step is used to determine the important excitations in the UCC ansatz. The reduced number of selected excitations are then used in a UCC-based VQE calculation. This approach gives a systematically improvable approximation, and we show that significant reductions in quantum resources can be achieved, with sub-milliHartree errors in the CH2, N2 and N2H2 molecules.

I. INTRODUCTION

Quantum chemistry, which often concerns itself with solutions to problems with exponentially scaling Hilbert spaces, has long been identified as a good target for quantum computation, which would allow the encoding of such problems in a linear number of qubits. For example, algorithms such as Quantum Phase Estimation[1, 2] (QPE) have been suggested as means of efficiently computing the ground state energies of molecular systems.[3] However, this approach would require fault-tolerant quantum computers. In the current noisy intermediate-scale quantum (NISQ) regime, the field of quantum chemistry calculations on quantum computers is dominated by hybrid quantum-classical approaches and in particular the Variational Quantum Eigensolver[4] (VQE), which requires a parameterised wavefunction. Various parameterised ansatz schemes have been proposed, such as the hardware efficient ansatz[5], the hardware variational ansatz[6], the symmetry preserving ansatz[7] and the unitary coupled cluster (UCC) ansatz[8–11].

UCC has seen a resurgence as a convenient parameterisation for VQE,[4, 12] due to its ability to be easily encoded into a quantum circuit. While its physical origin leads to a series of appealing features, including a relatively well-behaved energy landscape, the qubit encoding of the fermionic operators in the UCC ansatz produces very deep circuits, which are challenging for currently available quantum architectures. Work has been done to decrease the depth of these circuits while maintaining the physicality of the ansatz, for example by using Moller-Plesset[13] (MP2) theory results to screen amplitudes[14, 15] or using adaptive ansätze such as ADAPT-VQE[16] while the latter does generate shorter, highly accurate ansätze, it does so at the cost of an increased number of measurements relative to the standard UCC approach.

In this paper, we propose using the newly developed unitary coupled cluster Monte Carlo[17] (UCCMC) approach to screen amplitudes for a UCC-based VQE calculation. Quantum Monte Carlo (QMC) methods[18, 19] take advantage of the sparsity of most chemical Hamiltonians to generate compact wavefunctions, thereby lowering memory requirements relative to the corresponding classical algorithms. Additionally, the Monte Carlo approach naturally samples “important” contributions to the wavefunction — determinants with large Hamiltonian coupling terms to the reference determinant — first and therefore, while fully converging a QMC calculation may be time-consuming, short runs may be used to quickly identify the most important contributions to a given wavefunction.[20] We use this property of the UCCMC method and in particular its trotterized approximation to provide an initial set of amplitudes for a VQE calculation. We screen amplitudes based on these initial values and assess the effect of using the screened parameter sets on the accuracy of the obtained energy, comparing with the equivalent result from MP2 screening.

In Section 2, we review the underlying theory of both UCC-based VQE and the UCCMC method. Section 3 comprises results and discussion for a range of small molecules in a variety of scenarios and Section 4 presents our conclusions.
II. THEORY

Coupled cluster theory [21, 22] has become well established as the “gold-standard” of \textit{ab initio} chemistry methods. The exponential ansatz

$$|Ψ_{\text{CC}}⟩ = e^{\hat{T}} |Ψ_0⟩, \quad (1)$$

where $\hat{T} = \sum_i \hat{T}_i$ and $\hat{T}_i$ is composed of all valid excitation operators of order $i$, naturally maintains size-consistency when the operator $\hat{T}$ is truncated at some excitation level, with the most commonly employed truncations being coupled cluster singles and doubles (CCSD) and coupled cluster singles, doubles and triples (CCSDT). Such methods are polynomially scaling with the number of parameters to optimize and a more favourable energy-search landscape compared with hardware-tailored ansätze [5]. It also naturally conserves the number of electrons and the Greek indices represent virtual spin orbitals. The Latin indices represent occupied spin orbitals and the Greek indices represent virtual spin orbitals. This can be easily implemented on a quantum computer via an appropriate transformation of the fermionic operators to the unitary bosonic qubit operators using schemes like Jordan-Wigner [26] or Bravyi-Kitaev [27], where algebraic compilation strategies based on the ZX calculus have been proposed [28].

A. The UCC ansatz

We can construct the anti-Hermitian operator $\hat{T} - \hat{T}^\dagger$, the exponential of which gives a unitary operator. The UCC wavefunction is therefore

$$|Ψ_{\text{UCC}}⟩ = e^{\hat{T} - \hat{T}^\dagger} |Ψ_0⟩ \quad (2)$$

and its energy can be found variationally as

$$E_0 = \min \langle Ψ_0 | e^{-(\hat{T} - \hat{T}^\dagger)} \hat{H} e^{\hat{T} - \hat{T}^\dagger} |Ψ_0⟩. \quad (3)$$

Although $e^{-(\hat{T} - \hat{T}^\dagger)} \hat{H} e^{\hat{T} - \hat{T}^\dagger}$ has a non terminating Baker–Campbell–Hausdorff (BCH) expansion, which makes the implementation of UCC costly on a classical computer, the unitary operator $e^{\hat{T} - \hat{T}^\dagger}$ can be decomposed as a series of universal quantum gates on a quantum computer. We start by writing the cluster operator in terms of individual excitations.

$$U(t) = e^{\sum_n t_n (\tau_n - \tau_n^\dagger)} \quad (4)$$

where $\tau_n$ represents a fermionic excitation operator and $t_n$ its corresponding cluster amplitude. We can take a Trotter-Suzuki expansion [23, 24] of $U(t)$ such that

$$|Ψ_{\text{UCC}}⟩ \approx |Ψ_{\text{UCC}}⟩ = \left( \prod_n e^{i\frac{t_n}{\rho} (\tau_n - \tau_n^\dagger)} \right)^\rho |Ψ_0⟩. \quad (5)$$

with equality achieved as $\rho \to \infty$. We can take $\rho = 1$ which has been shown [12] to be a good approximation, leading to negligible errors in the resulting energy, to obtain

$$|Ψ_{\text{UCC}}⟩ \approx U(t) |Ψ_0⟩ = \prod_n e^{t_n (\tau_n - \tau_n^\dagger)} |Ψ_0⟩, \quad (6)$$

also known as the disentangled UCC ansatz. [25] For the case of UCCSD the singles are represented by

$$\hat{T}_1 = \sum_{i,α} t_{iα}^α (\hat{a}_{iα}^\dagger \hat{a}_{α} - \hat{a}_{iα} \hat{a}_{α}^\dagger), \quad (7)$$

and doubles are represented by

$$\hat{T}_2 = \sum_{i>j,α>β} t_{ij}^{αβ} (\hat{a}_{iα}^\dagger \hat{a}_{jβ}^\dagger \hat{a}_{α} \hat{a}_{β} - \hat{a}_{jβ}^\dagger \hat{a}_{iα} \hat{a}_{α}^\dagger \hat{a}_{β}), \quad (8)$$

where the Latin indices represent occupied spin orbitals and the Greek indices represent virtual spin orbitals.

B. Quantum computing and the UCC ansatz

NISQ hardware is characterized by small qubit counts and high noise levels, due mainly to short qubit coherence times, quantum gate errors, faulty readout operations and cross-talk between qubits during operation. These limitations prevent the use of error-correction protocols that would enable large quantum computations. Thus, it is advantageous to reduce the amount of quantum computation to a minimum. As a result, there is a strong research effort dedicated to the development of hybrid quantum-classical algorithms. One of the main algorithmic workhorses of this field is the Variational Quantum Eigensolver [4], where a minimizer run on a classical machine optimizes a cost function evaluated by the quantum computer. In chemistry problems, this corresponds to finding the expected value of the energy with respect to a parametrized ansatz wavefunction. Alternative approaches have appeared in recent years; we highlight methods based on imaginary time propagation of a trial wavefunction, either via a variational principle [29] or approximating the nonunitary evolution with an appropriate quantum circuit [30], and techniques to variationally optimise the reduced density matrix of the system [31].

The UCC ansatz is attractive for this kind of quantum algorithm as it has a reduced number of parameters to optimize and a more favourable energy-search landscape compared with hardware-tailored ansätze. [5]. It also naturally conserves the number of electrons and the $M_z$ spin projection quantum number during the calculation, thus helping to prevent convergence to unwanted
states, or avoiding the barren plateau problem observed for hardware-efficient ansätze. However, these advantages are obtained at the cost of large circuit depths. For example, in the Jordan-Wigner mapping, fermionic creation and annihilation operators may be expressed as

\[ a_j^\dagger = \bigotimes_i Z_i \bigotimes \frac{1}{2} (X_j - iY_j), \]  

\[ a_j = \bigotimes_i Z_i \bigotimes \frac{1}{2} (X_j + iY_j). \]  

Therefore a single fermionic excitation operator becomes

\[ t_{ij}^{\alpha\beta} (a_j^\dagger a_i a_j^\dagger a_i) = \frac{t_{ij}^{\alpha\beta}}{8} \bigotimes_{k=1}^{j-1} Z_k \bigotimes_{l=\alpha+1}^{\beta-1} Z_l (X_i X_j Y_\alpha X_\beta + Y_i X_j Y_\alpha X_\beta + X_i Y_j Y_\alpha Y_\beta + X_i Y_j X_\alpha Y_\beta) \]  

\[ - Y_i X_j X_\alpha X_\beta - X_i Y_j X_\alpha X_\beta - Y_i Y_j X_\alpha Y_\beta - Y_i Y_j X_\alpha Y_\beta). \]  

Therefore each excitation included in the ansatz contributes with a series of Pauli gadgets (see Fig. 1), requiring a large number of two-qubit gates. These gates are responsible for most of the noise produced during a quantum computation on NISQ devices, so it is very important to reduce their number. Being able to identify which excitations have a negligible contribution to the total energy would enable their elimination in the ansatz and reduce the overall circuit depth of the state preparation step in variational quantum algorithms. Successful screening of excitations aims to bring the circuit execution time within the coherence time of near term hardware with maximal fidelity with the unscreened ansatz, incurring a minimum energy penalty.

C. QMC algorithms

Monte Carlo algorithms have become popular approaches to more effectively use classical computational resources for quantum chemistry. Real-space approaches such as Diffusion Monte Carlo (DMC) [33, 34] suffer from the so-called “sign problem”, which causes them to naturally converge to bosonic solutions. This can be somewhat mitigated by using arbitrary nodal sur-

\[ C_1(\tau) - \delta \tau \langle D_1 | \hat{H} - E | D_1 \rangle C_1(\tau) - \sum_j \delta \tau \langle D_1 | \hat{H} | D_j \rangle C_j(\tau) = C_1(\tau + \delta \tau) \]

This equation can be solved stochastically by sampling the population dynamics of a set of walkers (‘psips’) in the Hilbert space of the system, which undergo the following processes:[18]
FIG. 1: Pauli gadget for $e^{-i\frac{\theta}{2}(Z_0 \otimes X_1 \otimes X_2 \otimes Y_3)}$

- spawning from $|D_1\rangle$ to $|D_j\rangle$ with probability 
  \[ p_{\text{spawn}}(j|i) \propto \delta \tau |H_{ij}|; \]  
  (17)

- death with probability 
  \[ p_{\text{death}}(i) \propto \delta \tau |H_{ii} - S|; \]  
  (18)

- annihilation of particles of opposite sign on the same determinant.

In the death step, the shift $S$ replaces the unknown exact energy $E$. This acts as a population control parameter and, once the system has reached a steady state, converges to the true energy. Another estimator for $E$ and, once the system has reached a steady state, converges to the true energy.

In the death step, the shift $S$ replaces the unknown exact energy $E$. This acts as a population control parameter and, once the system has reached a steady state, converges to the true energy. Another estimator for $E$ is the projected energy

\[ E_{\text{proj}} = \langle D_0 | \hat{H} | \Psi \rangle / \langle D_0 | \Psi \rangle = \sum_{i \neq 0} N_i N_0 \] 

A set of equations similar to Eq. 14 holds for the CC wavefunction given in Eq. 1. Since \( \langle D_1 | \Psi_{\text{CC}} \rangle = t_1 + \mathcal{O}(t^2) \), we can write

\[ t_1(\tau) - \delta \tau \langle D_1 | \hat{H} - E | \Psi_{\text{CC}} \rangle \approx t_1(\tau + \delta \tau). \]  

(20)

This can be described stochastically by the same three processes considered for FCIQMC, leading to an algorithm known as Coupled Cluster Monte Carlo (CCMC).\[19\] However, one must also take into consideration contributions from composite clusters. For example,

\[ \langle D_{ij}^{\alpha \beta} | \Psi_{\text{CC}} \rangle = t_{ij}^{\alpha \beta} + t_i^{\alpha} t_j^{\beta} - t_{ij}^{\alpha \beta}, \]  

(21)

and therefore any of these three terms may contribute to death on $t_{ij}^{\alpha \beta}$ or to spawning onto some exciton coupled to it by the Hamiltonian. The selection process is therefore somewhat more complicated than for FCIQMC, originally consisting of the steps below:\[19\]

1. a cluster size $s$ is selected with probability 
  \[ p(s) = \frac{1}{2^{s+1}} \]  
  (22)

2. a particular cluster of $s$ distinct excitors is selected with probability 
  \[ p(e|s) = s! \prod_{i=1}^{s} \frac{|N_i|}{N_{\text{ex}}}. \]  

(23)

where $N_{\text{ex}}$ is the total population on excitors. The total selection probability is therefore

\[ p_{\text{sel}}(e) = p(e|s)p(s) \]

(24)

Improvements have since been made to this selection algorithm to better importance-sample the wavefunction.[35]

Recently, some of us have implemented a stochastic version of unitary coupled cluster and its trotterized approximation,[17] the details of which are expanded upon in the following section.

1. (p)UCCMC

While the UCC wavefunction is generally found by variationally optimising the parameters, it is also possible[36, 37] to solve a set of projected UCC (pUCC) equations,

\[ \langle D_1 | \hat{H} - E | \Psi_{\text{UCC}} \rangle = 0. \]  

(25)

This projective method is naturally more amenable to the QMC algorithms described above, as it leads to similar population dynamics to those in Eq. 20. However, the presence of de-excitation operators $\hat{T}^\dagger$ in the full UCC ansatz substantially changes the structure of the allowed clusters, removing the constraint that cluster sizes must be at most equal to the maximum excitation level considered in the calculation. However, the expansion can be truncated to a finite cluster size, which, if large enough, does not significantly affect the accuracy of the obtained answer. The selection scheme for UCCMC is then as follows:

1. select a cluster size $s$ with probability $p(s) = \frac{1}{2^{s+1}}$. 

\[ p_{\text{sel}}(e) = p(e|s)p(s) \]
2. for all but the first excitor in the cluster, decide with probability $\frac{1}{2}$ whether it will be an excitation or de-excitation operator

3. a particular cluster is selected as before, with probability given by Eq. (23)

Having selected the cluster, it undergoes stochastic spawning and death as before. Overall this constitutes the projected Unitary Coupled Cluster Monte Carlo (pUCCMC) algorithm. The final aspect one must be careful of is the projection of the wavefunction onto the HF reference, as this includes contributions beyond the reference population. This projection may be sampled stochastically during the course of the calculation, concurrently with the reference population and the $\frac{N^C}{N}$ terms.

2. Trotterized pUCCMC

Consider once again the trotterized UCC ansatz with $\rho = 1$.

$$\Psi_{tUCC} = \prod_n e^{t_n(\tau_n - p_n)} |\Psi_0\rangle$$ (26)

This ansatz now depends on the order of excitors in the product, with different orders leading to different cluster amplitudes and potentially different energy values. Recent work by Evangelista et al.[25] has defined an optimal ordering that guarantees complete wavefunction expressibility in this framework. Applying $e^{t_n(\tau_n - I_n)}$ to an arbitrary single determinant wavefunction $|\Psi\rangle$ leads to three possibilities:

1. $\hat{\tau}_1^\dagger |\Psi\rangle = 0$ and $\hat{\tau}_1 |\Psi\rangle \neq 0$

$$e^{t_n(\tau_n - I_n)} |\Psi\rangle = \cos(t_n) |\Psi\rangle + \sin(t_n) |\Psi_1\rangle$$ (27)

where $|\Psi_1\rangle$ is the result of applying the excitation to $|\Psi\rangle$.

2. $\hat{\tau}_1^\dagger |\Psi\rangle \neq 0$ and $\hat{\tau}_1 |\Psi\rangle = 0$

$$e^{t_n(\tau_n - I_n)} |\Psi\rangle = \cos(t_n) |\Psi\rangle - \sin(t_n) |\Psi^\dagger\rangle$$ (28)

where $|\Psi^\dagger\rangle$ is the result of applying the deexcitation to $|\Psi\rangle$.

3. $\hat{\tau}_1^\dagger |\Psi\rangle = 0$ and $\hat{\tau}_1 |\Psi\rangle = 0$

$$e^{t_n(\tau_n - I_n)} |\Psi\rangle = |\Psi\rangle$$ (29)

To translate this into a stochastic algorithm, for each excitor present in the wavefunction, the algorithm assesses which of the cases listed above is appropriate. If the excitor cannot be applied, the next excitor is considered. If the excitor can be applied, this is done with probability

$$p_{\text{excit}} = \frac{|\sin(t)|}{|\sin(t)| + |\cos(t)|}$$ (30)

and the cluster amplitude is multiplied by $\pm \sin(t)$. With probability $1 - p_{\text{excit}}$, the operator is not applied and the cluster amplitude is multiplied by $\cos(t)$. The cluster then undergoes the same spawning, death and annihilation steps as in traditional CCMC, leading to a trotterized pUCCMC approach (tpUCCMC). As in the case of full pUCCMC, this ansatz modifies the projection of the wavefunction onto the reference, making it different from the reference population. Depending on the ordering of the excitors, a closed form for this projection may be found, but in general it can easily be sampled during the stochastic propagation.

D. Technical details

The VQE calculations have been performed using a minimal (STO-3G) basis set for all molecular species considered. Molecular integrals and molecular orbital coefficients have been obtained using the PySCF package.[39] The wavefunction ansatz has been encoded into quantum circuits on a qubit register using the Jordan-Wigner scheme in the EUMEN program. For the optimization loop in the VQE procedure, the L-BFGS method has been applied. The state vector simulator Qulacs[40] has been used to evaluate the quantum circuits.

All QMC calculations have been carried out in a development version of HANDE-QMC.[41] Where directly compared, VQE and tpUCCMC calculations use the same ordering of excitors, applying all single (de)excitation operators ahead of the doubles. All screened VQE UCCSD calculations used the relevant tpUCCMCSD amplitudes as starting values for the parameters.

III. RESULTS

In this section, we assess the viability of the tpUCCSD method as a screening technique for UCCSD-based VQE. Given one method is based on a projective approach, while the other is variational, we first ascertain whether the wavefunctions obtained by the two approaches are sufficiently similar for tpUCCSD amplitudes to be a good predictor of VQE UCCSD amplitudes. To assess this, we turn our attention to the LiH molecule. In the STO-3G basis, this system consists of 4 electrons in 12 spin-orbitals, which can easily be treated by both VQE and tpUCCMCSD. The system can be further simplified by freezing the core Li 1s electrons. As seen in Fig. 2, in both cases the energies obtained by the two methods agree within 50 $\mu$Eh, for both the expectation value and the projected energy for tpUCCMCSD.

However, for tpUCCMCSD predictions to be useful as a starting guess or screening for VQE UCCSD amplitudes, the methods must agree not only in energy, but also in individual cluster amplitudes. In order for this agreement to be achieved, care must be taken that the
same ordering is used in both ansätze. While for such small systems any arrangement of the excitors in the trotterized UCC wavefunction will be able to describe the ground state wavefunction, the individual amplitudes may vary extensively, particularly in the more highly correlated regime. For frozen core LiH, the tpUCCMCSD amplitudes agree with their deterministic counterparts within the $1\sigma$-error bars.

Having convinced ourselves that the VQE UCCSD and tpUCCMCSD results are compatible, we investigate the latter’s potential as a screening technique for the former. Table I gives the number of amplitudes in the LiH wavefunction of different orders of magnitude in a stochastic snapshot of the tpUCCMCSD expansion. We find that the lowest threshold ($t > 0.001$), recovers more than 99.9% of the correlation energy at all geometries, while decreasing the size of the considered Hilbert space by 14 - 43%.

![Figure 2: Frozen core (left) and all-electron (right) LiH STO-3G energies, computed with pUCCMCSD (orange circles - projected energy, green squares - variational energy) and tpUCCMCSD (blue circles - projected energy, red crosses - variational energy). In the left panel, the black line corresponds to UCCSD VQE. In the right figure, the black dashed line corresponds to the deterministic UCCSD benchmark of Cooper and Knowles[43] and the black solid line line to UCCSD VQE. In both cases, the stochastic energies agree with the VQE results to within 50 $\mu E_h$.](image)

**TABLE I:** Size of the totally symmetric $\Sigma^+$ UCCSD Hilbert space and number of amplitudes above different thresholds for LiH in the STO-3G basis at a range of bond lengths, together with the percentage of the correlation energy recovered using each of the thresholds as a cutoff for amplitudes included in the VQE UCCSD ansatz, relative to the complete VQE UCCSD calculation.

| Bond length /Å | $\Sigma^+$ UCCSD Hilbert Space | $t > 0.1$ % $E_{corr}$ | $t > 0.01$ % $E_{corr}$ | $t > 0.001$ % $E_{corr}$ |
|----------------|-------------------------------|------------------------|------------------------|------------------------|
| 0.995          | 35                            | 0                      | 0                      | 87.43                  | 29                      | 99.93 |
| 1.395          | 35                            | 1                      | 71.20                  | 8                      | 98.75                  | 19                      | 99.94 |
| 1.795          | 35                            | 1                      | 70.54                  | 8                      | 98.94                  | 22                      | 99.95 |
| 2.195          | 35                            | 3                      | 88.90                  | 8                      | 99.13                  | 25                      | 99.99 |

Even $t > 0.01$ generally recovers more than 97% of the correlation energy in all cases, despite only using 8 parameters.

Following on from these results, we investigate the applicability of tpUCCMC screened VQE to a series of small molecules in different scenarios: CH$_2$, which has a triplet ground state, N$_2$ which becomes increasingly strongly correlated as the bond between the nitrogen atoms is broken and N$_2$H$_2$, where there is a crossing of diabatic states as it rotates from a trans to a cis geometry. In all cases, we use a snapshot of the amplitudes at the end of a short tpUCCMCSD run for screening.

For CH$_2$, considered with frozen 1s electrons on the C atom, we once again observe good agreement between tpUCCMCSD and VQE energies and wavefunctions, provided the same excitor ordering is used throughout. In this case, the tpUCCMCSD amplitudes are less spread out in magnitude and therefore the screening is less ef-
sufficient at decreasing the number of VQE parameters to be considered (see Table II for an example). As expected from this distribution of amplitudes, screening at either \( t > 0.01 \) or \( t > 0.001 \) gives errors of less than 1 milliHartree relative to the full UCCSD VQE calculation, for both singlet and triplet \( \text{CH}_2 \). Using MP2 as a screening method is competitive for the singlet state (see Figs. 3 and 4). For the triplet, the MP2 screened results exhibit a systematic error of more than 10 milliHartree which persists across all screening thresholds, as seen in Figs. 5 and 6. Therefore, tpUCCMCSD screening is clearly dominant.

The \( \text{N}_2 \) molecule as it approaches dissociation is one of the archetypal examples of static correlation and poses significant challenges to methods such as coupled cluster, which are based around the assumption that a single determinant dominates the wavefunction. For example, for \( r_{NN} > 3.6a_0 \) CCSD(T)[44] overestimates the correlation energy and diverges as the bond length is increased.[45] As can be seen in Fig. 7, the unitary, variationally optimised ansatz avoids the failure of the traditional CCSD ansatz, with the energy consistently above the FCI value and generally lower errors. In this case, both MP2 and tpUCCMCSD screening provide similar quality results, but the system highlights a few interesting differences between the two methods. First, in the left panel of Fig. 7 we observe that, while in MP2 there are consistently some amplitudes allowed by the screening, tpUCCMCSD does not have any amplitudes above 0.1 for half of the geometries considered. As such, the screened method cannot provide any improvement over Hartree–Fock. Obviously, this threshold is too high and the results obtained with ei-

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**FIG. 3:** \( \text{CH}_2 \) singlet energy computed with UCCSD VQE across the bending mode with different coefficient thresholds, using MP2 (blue circles) and tpUCCMCSD (orange crosses) as screening methods. From left to right, we consider coefficients greater than 0.1, 0.01 and 0.001 respectively. For all methods, the error (bottom panel) decreases as more amplitudes are included, with tpUCCMCSD providing better final converged energies than MP2.

**FIG. 4:** \( \text{CH}_2 \) singlet energy computed with UCCSD VQE across the stretching mode with different coefficient thresholds, using MP2 (blue circles) and tpUCCMCSD (orange crosses) as screening methods. From left to right, we consider coefficients greater than 0.1, 0.01 and 0.001 respectively. Once again, convergence is better for tpUCCMCSD than MP2.
Table II: Size of the totally symmetric UCCSD Hilbert space and number of amplitudes above different thresholds for triplet CH$_3$ in STO-3G at a range of CH bond lengths, with $\angle$HCH = 135°.

| Bond length /Å | UCCSD Hilbert Space | $t > 0.1$ | $t > 0.01$ | $t > 0.001$ |
|----------------|----------------------|----------|----------|-----------|
| 1.06           | 31                   | 0        | 24       | 30        |
| 1.08           | 31                   | 0        | 25       | 30        |
| 1.10           | 31                   | 0        | 26       | 29        |
| 1.12           | 31                   | 0        | 26       | 29        |
| 1.14           | 31                   | 0        | 25       | 29        |
| 1.16           | 31                   | 0        | 26       | 30        |
| 1.18           | 31                   | 0        | 26       | 29        |

These features emphasize the fact that a constant amplitude threshold does not necessarily generate a consistent number of parameters across all geometries of a given system. Where such consistency is desirable, which will often be the case when constructing a description of a physical system, a threshold based directly on the number of parameters included may be preferable.

Finally, the energy landscape of the cis–trans interconversion of N$_2$H$_2$ allows us to investigate another highly-correlated regime around the transition state of this transformation. For simplicity, we investigate the rotation about the carbon–carbon bond starting from the equilibrium geometry of trans N$_2$H$_2$[46], without allowing any relaxation of other geometrical parameters. At the Hartree–Fock level, the singlet state of this system would be characterised by two diabatic states which cross at 86.8(1)°[42]. This introduces an unphysical discontinuity in the energy surface, which often remains even after the application of further correlated methods.[47] In order to be able to treat this system using VQE, we freeze the 8 lowest-energy electrons. The resulting system exhibits an additional interesting feature as two FCI states of different spatial symmetry cross, as can be seen in Figure 8. The conservation of various symmetries — spin, particle number, point group — in quantum circuits is an interesting problem and in this system it turns out to be crucial for the correct description of the energy surface. Indeed, not enforcing point group symmetry leads to a very compelling yet unphysical state which transitions smoothly from the A to the B state as the system approaches a 90° rotation.

Once point group symmetry constraints are considered, VQE based on the UCCSD ansatz with the excitations symmetry filtered correctly reproduces the behaviour observed in the exact surface, however starting from an $m_s = 0$ open-shell Hartree–Fock reference or an $m_s = 1$ reference leads to different energies for the B state. For the rest of our analysis we focus on the $m_s = 0$ A state and the $m_s = 1$ B state, which correspond to the two lowest-energy states in the system. The order of magnitude of amplitudes in a short tpUCCMCSD run for this system at various rotation angles are given in Table IV. This system exhibits many of the behaviors we noted in smaller examples. For the singlet state, both MP2 and tpUCCMCSD screened UCCSD VQE converge to the correct UCCSD energy with increasing number of
amplitudes, but for the triplet state MP2 fails to converge, retaining an error of at least 30 milliHartree even for the lowest threshold - see Fig. 8. This leads MP2 screening to predict the wrong ordering of the singlet and triplet states for rotation angles around 90°.

Fig. 9 shows the convergence of VQE UCCSD energy as a function of amplitude threshold and circuit depth for the A state at 0° and the B state at 90°. This highlights the same trend as before, with tpUCCMCSD screening only slightly more efficient than MP2 as a function of screening threshold for the singlet state, but clearly superior for the triplet. In both cases, using tpUCCMCSD it is possible to recover more than 90% of the correlation energy with a circuit that is only half as deep as the full VQE UCCSD implementation. Similar figures for some of the other systems studied in this paper are available in the Supplemental Material.\[42\]

IV. CONCLUSION

We have shown that UCCMC can be used successfully as a screening method for UCCSD-based VQE, with short, potentially unconverged stochastic runs providing a set of amplitudes that may be truncated at a given coefficient threshold before being further optimised by VQE. We expect the method would also be compatible with the newly developed Projected Quantum Eigen solver.\[48\] Importantly, the classical screening approach is entirely a pre-processing step, so requires no additional quantum resources. In the case of singlet states, the results using UCCMC for screening are seen to converge slightly faster with screening threshold than the corresponding MP2-screened values. For triplets, we have found that the MP2-screened calculations fail to converge to the true ground state at all, making UCCMC all the more useful in this case. For all molecules we have considered, the
| Bond length /Å | UCCSD Hilbert space | tpUCCMCSD t > 0.1 | tpUCCMCSD t > 0.01 | tpUCCMCSD t > 0.001 | MP2 t > 0.1 | MP2 t > 0.01 | MP2 t > 0.001 |
|----------------|----------------------|-------------------|-------------------|-------------------|------------|------------|------------|
| 0.9            | 54                   | 0                 | 36                | 52                | 2          | 24         | 53         |
| 1.1            | 54                   | 2                 | 44                | 52                | 2          | 26         | 49         |
| 1.3            | 54                   | 0                 | 42                | 53                | 2          | 30         | 49         |
| 1.5            | 54                   | 3                 | 47                | 53                | 4          | 35         | 53         |
| 1.7            | 54                   | 0                 | 42                | 53                | 8          | 39         | 53         |
| 1.9            | 54                   | 2                 | 34                | 52                | 12         | 41         | 53         |

TABLE III: Size of the totally symmetric UCCSD Hilbert space and number of amplitudes above different thresholds for frozen core N₂ in STO-3G at a range of bond lengths, screened with both MP2 and tpUCCMCSD.

FIG. 8: N₆H₂ energy computed with UCCSD VQE with different coefficient thresholds, using MP2 (blue and green circles) and tpUCCMCSD (orange and red crosses) for screening. We consider two states, a closed-shell singlet state of A symmetry in the C₂ point group and a triplet state of B symmetry. The A state is the ground state around the cis and trans geometries of N₆H₂, but the triplet becomes favoured around a rotation angle of 90°. From left to right, we consider coefficients greater than 0.1, 0.01 and 0.001 respectively. For the A state, as with all singlet molecules so far, both MP2 and tpUCCMCSD converge towards the true UCCSD energy, although in this case at 0.001 MP2 is noticeably worse than tpUCCMCSD. For the B state however, MP2 is unable to capture the correlation, and does not improve with added amplitudes. This gives unphysical results, with the B state higher in energy than the A state for all geometries.

accuracy of the results increases monotonically with the number of amplitudes included in the ansatz, allowing one to balance result quality with resource limitations as necessary.

Standard noise models such as amplitude and phase damping[49] predict exponential decay of the quantum signal with time, controlled by the relaxation time T₁ and dephasing time T₂[50]. Significantly reducing the depth, and therefore the computation time, of the VQE circuit, as we have seen is possible for N₆H₂, where more than 90% of the correlation energy could be recovered with half the circuit depth, would therefore lead to a major reduction in the error rates observed on real hardware.

We expect the benefits of such screening methods to get more significant as one considers larger systems. While the Hilbert spaces required for UCC calculations will scale with high-order polynomials of the system size, few of the amplitudes in this space will have large coefficients and therefore contribute significantly to the energy, at least in the largely single-reference, dynamically correlated areas of the landscape where coupled cluster methods perform well. Furthermore, it has been shown that linear scaling coupled cluster can be achieved by careful screening of amplitudes by distance[51–55]. We fully expect that the trotterized UCC approach and its stochastic counterpart will be able to take advantage of this,
especially on systems of multiple molecules and propagate these gains forward into screened VQE calculations.

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| State | Dihedral angle / ° | UCCSD Hilbert Space | $t > 0.1$ | $t > 0.01$ | $t > 0.001$ |
|-------|------------------|---------------------|--------|----------|----------|
| A     |                  |                     |        |          |          |
|       | 0                | 100                 | 1      | 40       | 90       |
|       | 30               | 185                 | 1      | 71       | 166      |
|       | 60               | 185                 | 1      | 65       | 175      |
|       | 90               | 185                 | 1      | 65       | 161      |
|       | 120              | 185                 | 1      | 56       | 172      |
|       | 150              | 185                 | 1      | 42       | 97       |
|       | 180              | 100                 | 1      | 40       | 77       |
|       |                  | 83                  | 1      | 44       | 140      |
|       |                  | 160                 | 0      | 51       | 147      |
|       |                  | 160                 | 0      | 49       | 150      |
|       |                  | 160                 | 0      | 51       | 149      |
|       |                  | 160                 | 0      | 45       | 147      |
|       |                  | 83                  | 1      | 36       | 76       |
| B     |                  |                     |        |          |          |

TABLE IV: Size of the UCCSD Hilbert space and number of \textit{tpUCCMCAS} amplitudes above different thresholds for the lowest singlet and triplet $\textrm{N}_2\textrm{H}_2$ states in STO-3G at a range of dihedral $\angle\textrm{HHNNH}$. 

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Supplemental Material for “The Best of Both Worlds: Optimizing Quantum Hardware Resources with Classical Stochastic Methods”

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I. LIH AMPLITUDES

FIG. 1. Frozen core LiH amplitudes for full pUCCMCSD and trotterized pUCCMCSD with 3 different orderings. The energies obtained agree in all cases, but the amplitudes themselves are significantly order-dependent. The Monte Carlo amplitudes are compared to deterministic pUCCSD and tpUCCSD (same as order 1) amplitudes.
II. CH$_2$ AMPLITUDES

FIG. 2. Triplet CH$_2$ amplitudes. The black line is VQE tUCCSD value and the green line corresponds to same ordering of excitors in tpUCCMCSD. The blue and orange lines are pUCCMCSD and tpUCCMCSD using the default ordering[1] respectively.
III. $\text{N}_2\text{H}_2$ DIABATIC STATES

FIG. 3. Hartree-Fock and FCI energies for the A ($m_s = 0$) and B ($m_s = 1$) states of $\text{N}_2\text{H}_2$ in STO-3G as it rotates from a trans to a cis geometry.
IV. MP2 VS. TPUCCMC SCREENING PERFORMANCE

FIG. 4. Percentage of UCCSD correlation energy recovered for triplet CH$_2$ with MP2 (blue circles) and tpUCCMCSD (orange crosses) screening at a series of geometries. MP2 fails to converge for the triplet state, while tpUCCMCSD allows recovery of significant fractions of the correlation energy while reducing the circuit depth by up to half for all geometries.
FIG. 5. Percentage of UCCSD correlation energy recovered for N\textsubscript{2} with MP2 (blue circles) and tpUCCMCSD (orange crosses) screening near equilibrium (left) and for a stretched bond (right). Performance is comparable between the two methods, with tpUCCMC slightly more efficient in terms of both threshold and depth.

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