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Title

Generalized Unitary Coupled Cluster Wave functions for Quantum Computation.

Permalink

<https://escholarship.org/uc/item/7nr994jp>

Journal

Journal of chemical theory and computation, 15(1)

ISSN

1549-9618

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Publication Date

2019

DOI

10.1021/acs.jctc.8b01004

Peer reviewed

Generalized Unitary Coupled Cluster Wavefunctions for Quantum Computation

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Abstract

We introduce a unitary coupled-cluster (UCC) ansatz termed k -UpCCGSD that is based on a family of sparse generalized doubles operators which provides an affordable and systematically improvable unitary coupled-cluster wavefunction suitable for implementation on a near-term quantum computer. k -UpCCGSD employs k products of the exponential of pair coupled-cluster double excitation operators (pCCD), together with generalized single excitation operators. We compare its performance in both efficiency of implementation and accuracy with that of the generalized UCC ansatz employing the full generalized single and double excitation operators (UCCGSD), as well as with the standard ansatz employing only single and double excitations (UCCSD). k -UpCCGSD is found to show the best scaling for quantum computing applications, requiring a circuit depth of $\mathcal{O}(kN)$, compared with $\mathcal{O}(N^3)$ for UCCGSD and $\mathcal{O}((N - \eta)^2\eta)$ for UCCSD where N is the number of spin orbitals and η is the number of electrons. We analyzed the accuracy of these three ansätze by making classical benchmark calculations on the ground state and the first excited state of H_4 (STO-3G, 6-31G), H_2O (STO-3G), and N_2 (STO-3G), making additional comparisons to conventional coupled cluster methods. The results for ground states show that k -UpCCGSD offers a good tradeoff between accuracy and cost, achieving chemical accuracy for lower cost of implementation on quantum computers than both UCCGSD and UCCSD. UCCGSD is also found to be more accurate than UCCSD, but at a greater cost for implementation. Excited states are calculated with an orthogonally constrained variational quantum eigensolver approach. This is seen to generally yield less accurate energies than for the corresponding ground states. We demonstrate that using a specialized multi-determinantal reference state constructed from classical linear response calculations allows these excited state energetics to be improved.

Introduction

Quantum computing promises to provide access to a new set of computational primitives that possess profoundly different limitations from those available classically. It was shown early on that quantum phase estimation (QPE) provides an exponential speed-up over the best “currently” known classical algorithms for determining the ground state of the molecular Hamiltonian.¹ However, the use of this approach is believed to require large, error-corrected, quantum computers to surpass what is possible classically^{2,3}. A more promising path to pursuing such “quantum supremacy”^{4,5} in the context of quantum chemistry on near-term quantum devices is a quantum-classical hybrid algorithm that is referred to as the variational quantum eigensolver (VQE)⁶. Interested readers are referred to a more extensive review in Ref. 7.

Unlike phase estimation, VQE requires only a short coherence time. This hybrid approach uses a quantum computer to prepare and manipulate a parameterized wavefunction, and embeds this in a classical optimization algorithm to minimize the energy of the state as measured on the quantum computer, i.e.,

$$E = \min_{\theta} \langle \psi(\theta) | \hat{H} | \psi(\theta) \rangle, \tag{1}$$

where θ denotes the set of parameters specifying the quantum circuit required to prepare the state $|\psi\rangle$. From a quantum chemistry perspective, there are two key attractive aspects of the VQE framework:

1. The evaluation of the energy of a wide class of wavefunction ansätze which are exponentially costly classically (with currently known algorithms) requires only state preparation and measurement of Pauli operators, both of which can be carried out on a quantum processor in polynomial time. These wavefunction ansätze include unitary coupled-cluster (UCC) wavefunctions,^{6,8} the deep multi-scale entanglement renormalization ansatz (DMERA),⁹ a Trotterized version of adiabatic state prepa-

ration (TASP),¹⁰ the qubit coupled cluster approach (QCC),¹¹ and various low-depth quantum circuits inspired by the specific constraints of physical devices currently available.¹²

2. On a quantum processor, efficient evaluation of the magnitude of the overlap between two states is possible even when two states involve exponentially many determinants. Classically, this is a distinct feature only of tensor network¹³ and variational Monte Carlo¹⁴ approaches. However on a quantum computer, any states that can be efficiently prepared will also possess this advantage.

Given the recent progress and near-term prospects in quantum computing hardware, and the uniqueness of these capabilities, it is interesting to explore these two aspects from a quantum chemistry perspective and this constitutes the major motivation of this work.

The remainder of this paper is organized as follows. (1) We review existing UCC ansätze in the context of traditional coupled cluster theory, focusing in particular on unitary extensions of the generalized coupled-cluster ansatz of Nooijen.¹⁵ We then present a new ansatz, referred to as k -UpCCGSD, that uses k products of the exponential of distinct pair coupled-cluster double excitation operators, together with generalized single excitation operators. We show that this ansatz is more powerful than previous unitary extensions of coupled-cluster, achieving a significant reduction in scaling of circuit depth relative to both straightforward unitary extensions of generalized UCC (UCCGSD) and conventional UCC with single and double excitations (UCCSD). (2) We analyze options for variational optimization of excited states that are subject to orthogonalization constraints with a previously variationally optimized ground state.¹⁶ We explore several distinct options and make an analysis of the possible errors encountered when using such a variational approach. We show that these excited state energies can be significantly improved by using a different reference state for the excited state variational calculation, specifically, by using single excitation reference states. (3) We undertake a systematic analysis of the resource requirements for realization of these UCC ansätze on a quantum computer, relevant to preparation of initial states of molecules

for both QPE and VQE computations. Our resource analysis focuses on the scaling of gate count, circuit depth, and spatial resources with size of the quantum chemistry calculation. We find that the k -UpCCGSD ansatz exhibits a linear dependence of circuit depth (a measure of the computational time that we define explicitly below) on the number of spin-orbitals N , with higher order polynomial dependence obtained for both UCCGSD and UCCSD. (4) To assess the accuracy of the new ansatz, we undertake benchmarking calculations on a classical computer for ground and first excited states of three small molecular systems, namely H_4 (STO-3G, 6-31G), H_2O (STO-3G), and N_2 (STO-3G), making additional comparisons to conventional coupled cluster methods as relevant. Detailed analysis of potential energy curves for ground and excited states of all three species shows that k -UpCCGSD ansatz offers the best trade-off between low cost and accuracy. (5) We conclude with a summary and outlook for further development of unitary coupled cluster ansätze for efficient implementation of molecular electronic states in quantum computations.

Theory

We shall use i, j, k, l, \dots to index occupied orbitals, a, b, c, d, \dots to index unoccupied (or virtual) orbitals, and p, q, r, s, \dots to index either of these two types of orbitals. The indices will denote spin-orbitals unless mentioned otherwise. We use N to denote the number of spin-orbitals and η to denote the number of electrons.

Coupled-Cluster Theory

In this section, we first briefly review traditional coupled cluster (CC) theory and unitary CC (UCC). We shall then draw connections between an existing body of work on variants of coupled cluster theory and a recently described wavefunction ansatz for VQE,¹⁰ before proposing a novel ansatz also motivated by previous work in quantum chemistry. We note that in the quantum information literature it is customary to use UCC to denote the uni-

tary version of restricted CC, in contrast to the quantum chemistry literature where UCC generally refers to unrestricted CC. We follow the quantum information convention in this paper.

Traditional Coupled Cluster

Traditional CC is a successful wave function method used for treating correlated systems in quantum chemistry.¹⁷⁻¹⁹ Coupled-cluster with singles and doubles (CCSD), i.e., where the excitations in the cluster operator \hat{T} are restricted to singles and doubles, is suitable for treating most “weakly-correlated” chemical systems.

The CCSD wave function is usually written with an exponential generator acting on a reference state,

$$|\psi\rangle = e^{\hat{T}}|\phi_0\rangle, \tag{2}$$

where for CCSD we have a cluster operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2, \tag{3}$$

with

$$\hat{T}_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i \tag{4}$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i. \tag{5}$$

In traditional CCSD, we evaluate the energy by projection of the Schrödinger equation, $\hat{H}|\psi\rangle = E|\psi\rangle$ first with $\langle\phi_0|$:

$$E \equiv \langle\phi_0|\hat{H}|\psi\rangle. \tag{6}$$

We then project with $\langle\phi_\mu|$ where μ is any single ($\langle\phi_i^a|$) or double ($\langle\phi_{ij}^{ab}|$) substitution. The

t -amplitudes are then obtained by solving a set of non-linear equations:

$$0 = \langle \phi_\mu | \hat{H} | \psi \rangle - Et_\mu, \quad (7)$$

with $|\phi_\mu\rangle = \hat{t}_\mu |\phi_0\rangle$. The cost of solving Eq. (7) scales as $\mathcal{O}(\eta^2(N - \eta)^4)$, where η is the number of electrons and N is the total number of spin-orbitals possessed by the system.

It is evident from Eq. (6) that the projective way of evaluating energy is not in general variational, except in some obvious limits where CCSD is exact (e.g., for non-interacting two-electron systems¹⁷⁻¹⁹). With spin-restricted orbitals, it is quite common to observe catastrophic non-variational failure of CCSD when breaking bonds or, more broadly, in the presence of strong correlation. This non-variational catastrophe is often attributed to the way in which traditional CCSD parametrizes quadruples (i.e., $\hat{T}_2^2/2!$)²⁰⁻²⁵ and searching for solutions to this problem without increasing the computational cost is an active area of research.²²⁻²⁵ Unfortunately, attempting to avoid this breakdown by variationally evaluating the energy of a CC wave function leads to a cost that scales exponentially with system size.

Unitary CC

A simple approach to avoid the non-variational catastrophe on a quantum computer is to employ a unitary CC (UCC) wavefunction,²⁶⁻³⁰

$$|\psi\rangle = e^{\hat{T} - \hat{T}^\dagger} |\phi_0\rangle, \quad (8)$$

where for the case of UCCSD, \hat{T} is defined as in Eqs. (3) - (5). We can then evaluate the energy in a variational manner,

$$E(\{t_i^a\}, \{t_{ij}^{ab}\}) \equiv \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (9)$$

using the standard VQE approach^{6,7,32} that is summarized later in this work. UCC has a long history in electronic structure for quantum chemistry, with a number of theoretical works dedicated to the approximate evaluation of Eq. (9) within a polynomial amount of time,²⁶⁻³⁰ since the approach appears to scale exponentially if implemented exactly using a classical computer. UCC is more robust than traditional CC, due to the fact that the unitary cluster operator involves not only excitation operators (\hat{T}) but also de-excitation operators (\hat{T}^\dagger). Nevertheless, the single reference nature of Eq. (8) can still lead to difficulties when treating strongly correlated systems on classical computers. This was investigated in Ref. 31 for the Lipkin Hamiltonian.

Unlike a classical computer, a quantum computer can efficiently employ a UCC wavefunction, even with a complicated multi-determinantal reference state, since both preparation of the state and evaluation of its expectation values can be carried out using resources that scale polynomially with system size and number of electrons.^{6,32} For UCC with singles and doubles (UCCSD), one must implement a Trotterized version of the exponentiated cluster operator, with $\mathcal{O}((N - \eta)^2 \eta^2)$ terms, where each term acts on a constant number of spin-orbitals.

Generalized CC

In the early 2000's, there was an active debate on the question of whether the exact ground state wavefunction of an electronic Hamiltonian can always be represented by a general two-body cluster expansion. Motivated by earlier work of Nakatsuji,³³ Nooijen conjectured¹⁵ that it is possible to express an exact ground state of a two-body Hamiltonian as

$$|\psi\rangle = e^{\hat{T}}|\phi_0\rangle, \quad (10)$$

where

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \tag{11}$$

$$= \frac{1}{2} \sum_{pq} t_p^q \hat{a}_q^\dagger \hat{a}_p + \frac{1}{4} \sum_{pqrs} t_{pq}^{rs} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p. \tag{12}$$

This yields an exponential ansatz with a number of free parameters, the t_p^q and t_{pq}^{rs} values, that is equal to the number of parameters in the Hamiltonian. Here the single and double “excitation” terms do not distinguish between occupied and unoccupied orbitals and they are therefore called “generalized” singles and doubles (GSD). Although early work showed that the numerical performance of the resulting wavefunction was promising, the conjecture of Ref. 15 has been the subject of an active debate and was later disproved.³⁴⁻⁴¹

Generalized Unitary CC

We explore here a generalized form of the UCC wavefunction introduced in the VQE literature.⁶ Our approach uses the generalized excitations of Nakatsuji and Nooijen described above in the ansatz

$$|\psi\rangle = e^{\hat{T} - \hat{T}^\dagger} |\phi_0\rangle, \tag{13}$$

with \hat{T} the cluster operator from Eq. (11). We shall term this ansatz UCCGSD. A unitary version of coupled cluster with generalized singles and doubles was first mentioned in Nooijen’s paper,¹⁵ but has never been thoroughly studied classically without making an approximation to the energy evaluation.

We note that a similar approach to defining a UCC ansatz by relating the terms in the Hamiltonian to generalized singles and doubles operators has appeared recently in the quantum computing literature,¹⁰ where the performance of a Trotterized version of such a UCCGSD on small hydrogen chains and equilibrium geometry molecular systems has been characterized. As we shall show explicitly later in this work, the UCCGSD wavefunction is far more robust and accurate than the simpler UCCSD wavefunctions for the chemical

applications considered here.

Unitary Pair CC with Generalized Singles and Doubles Product Wavefunctions

The method of pair coupled-cluster double excitations (pCCD),⁴² also known as AP1roG,⁴³ extends a widely used quantum chemistry method known as generalized valence-bond perfect-pairing (GVB-PP)⁴⁴. pCCD is less prone than spin-restricted CCSD (RCCSD) to a non-variational failure when breaking bonds, despite the fact that it is computationally much simpler than RCCSD. pCCD is a coupled cluster wavefunction with a very limited number of doubles amplitudes (containing only the two body excitations that move a pair of electrons from one spatial orbital to another),

$$\hat{T}_2 = \sum_{ia} t_{i_\alpha i_\beta}^{a_\alpha a_\beta} \hat{a}_{a_\alpha}^\dagger \hat{a}_{a_\beta}^\dagger \hat{a}_{i_\beta} \hat{a}_{i_\alpha}, \tag{14}$$

where the summation runs over occupied and unoccupied spatial orbitals. pCCD is capable of breaking a single-bond qualitatively correctly, but fails to break multiple bonds. Orbital optimization of pCCD wavefunctions includes the important effects of the single excitations in a UCC wavefunction. In exchange for its high computational efficiency and reduced incidence of non-variationality, pCCD has other disadvantages: it loses invariance to unitary transformation within the occupied-occupied and virtual-virtual subspaces present in CCD, and it does not recover the dynamic correlation that CCD has.

We define the unitary pCCSD (UpCCSD) wavefunction to have the full singles operator as in Eq. (4) together with the unitary doubles operator of Eq. (14). We show below in the analysis of the quantum resource requirements that the circuit depth (time complexity) of preparing a UpCCSD state on a quantum computer scales linearly with the system size as quantified by the number of spin-orbitals. However, our initial exploration of UpCCSD yielded errors in the absolute energies that were generally larger than the threshold for chemical accuracy. We therefore improve this wavefunction by the following two modifications:

(i) we use the generalized singles and doubles operators employed in Refs. 33, 15, and (ii) we take a product of a total of k unitary operators to increase the flexibility of the wavefunction. We shall refer to this model as k -UpCCGSD.

Formally, k -UpCCGSD is defined in the following manner. For a chosen integer k ,

$$|\psi\rangle = \prod_{\alpha=1}^k \left(e^{\hat{T}^{(\alpha)} - \hat{T}^{(\alpha)\dagger}} \right) |\phi_0\rangle, \quad (15)$$

where each $\hat{T}^{(k)}$ contains an independent set of variational parameters (i.e., the singles and paired doubles amplitudes, the t_p^q 's and the $t_{p_\alpha p_\beta}^{q_\alpha q_\beta}$'s respectively). Since the doubles operator in UpCCGSD is very sparse, the circuit depth required to prepare a k -UpCCGSD state still scales linearly with the system size, with a prefactor that is increased by a factor of k . This is similar in spirit to other recently proposed low depth ansätze⁴⁵ and also to the repeated independent variational steps of the Trotterized adiabatic state preparation approach¹⁰ but, to our knowledge, this form of wavefunction has never been explored in either classical or quantum computational electronic structure calculations for quantum chemistry.

Excited State Algorithms

Previous Work

Obtaining excited states under the variational quantum eigensolver (VQE) framework has attracted considerable interest recently due to the substantial progress made in experimental realization of ground state VQE simulations^{6,12,46-49}. Algorithms proposed to extend this hybrid approach to excited states include the quantum subspace expansion (QSE) algorithm⁵⁰, the folded spectrum (FS) method⁶, the witnessing eigenstates (WAVES) strategy⁴⁶, and a method based on penalizing overlap with an approximate ground state^{16,51}. We shall refer to the last of these as orthogonally constrained VQE (OC-VQE).

The QSE method is motivated by a linear-response approach: it samples the Hamiltonian matrix elements in the linear response space of a ground state wave function and diagonalizes

it to obtain an excitation spectrum. A major drawback of this method is an obvious steep increase in the number of measurements after the ground state VQE calculation, since every matrix element needs to be sampled. Furthermore, QSE suffers from the well-known problem of linear-response methods, that is, it can only describe excited states that are within a small perturbation of a given ground state. However, the proper description of chemically relevant excited states sometimes requires inclusion of a higher order of excitations. A classic example of this is the dark low-lying excited state of butadiene, which requires that the linear response space include quadruple excitations in order to obtain a converged result.⁵²

The FS method is closely related to the variance minimization algorithm widely used in the quantum Monte Carlo community:⁵³

$$E(\omega) = \min_{\theta} \langle \psi(\theta) | (\hat{H} - \omega)^2 | \psi(\theta) \rangle. \quad (16)$$

One advantage of this algorithm over the WAVES and OC-VQE algorithms is its ability to target a state whose energy is the closest to a preset ω , as in Eq. (16). Although this ability to variationally target specific excited states is very desirable, the algorithm inherently involves the evaluation of a quadratic term in \hat{H} , which greatly increases the number of Hamiltonian terms. Due to its steep scaling, $\mathcal{O}(N^8)$ in a standard gaussian basis set, application of the FS method (if possible) is likely to be limited to very small systems.

The WAVES algorithm relies on the ability of a quantum computer to efficiently perform time evolution conditioned on the state of a control qubit.⁴⁶ The protocol applies single qubit tomography to the first qubit of the state $\frac{1}{\sqrt{2}} |0\rangle \otimes |\psi\rangle + \frac{1}{\sqrt{2}} |1\rangle \otimes e^{-i\hat{H}t} |\psi\rangle$, for a given input state $|\psi\rangle$ and time t . The reduced density matrix of the control qubit describes a pure state if and only if $|\psi\rangle$ is an eigenstate of the Hamiltonian, or a superposition of degenerate eigenstates. Using this idea, it is possible to variationally target excited states (although not specific energies as is possible with the FS method), by varying the parameters of the trial state to maximize the purity of the measured single qubit state. This advantage is offset by

the requirement that the quantum computer must implement a controlled version of the time evolution operator, which imposes steep demands on the relatively noisy quantum computing devices currently available.

Orthogonally Constrained VQE

In this work we explore an alternative to the aforementioned three methods which has the advantage that it requires roughly the same number of measurements as the ground state VQE calculation and only a doubling of the necessary circuit depth.¹⁶ This algorithm can be naturally used with the two generalized coupled cluster wavefunction ansätze described above, or with any other circuit suitable for ground state VQE. Furthermore, OC-VQE can describe excited states that lie beyond the linear-response regime of the ground state. The approach assumes that a circuit for the ground state wavefunction is already available from a standard VQE calculation. One then defines an effective Hamiltonian whose lowest eigenstate is the first excited state and whose lowest eigenvalue is the energy of said state.

One such choice is given by

$$\hat{H}_{\text{OC-VQE}} = \hat{H} + \mu |\psi_0\rangle \langle \psi_0|, \tag{17}$$

where $|\psi_0\rangle$ is the ground state wavefunction and the second term constitutes a level shift operator. For the molecular systems studied here, both the ground and first excited states are bound states (i.e., the electronic energies of these states are negative). Under these assumptions, we can choose $\mu = -E_0 = -\langle \psi_0 | \hat{H} | \psi_0 \rangle$.¹⁶ This level shift imposes an energy penalty of $\mu |\langle \psi_0 | \psi_1 \rangle|^2$ on any trial state $|\psi_1\rangle$ that overlaps with $|\psi_0\rangle$. Such an energy level shift technique is commonly used in quantum chemistry to enforce constraints within a variational framework^{54–57}. Similar techniques have also been used in density matrix renormalization group calculations.¹³ Minimizing the expectation value of $\hat{H}_{\text{OC-VQE}}$ with respect to the parameters in $|\psi_1\rangle$ defines this first OC-VQE procedure.

The choice of effective Hamiltonian in Eq. (17) is not unique. We have also explored the form

$$\hat{H}'_{\text{OC-VQE}} = (1 - |\psi_0\rangle\langle\psi_0|) \hat{H} (1 - |\psi_0\rangle\langle\psi_0|). \quad (18)$$

Eq. (17) and Eq. (18) are identical if and only if $|\psi_0\rangle$ is an eigenstate of \hat{H} with an eigenvalue E_0 . If we choose $\mu = \infty$, the two approaches yield the same first excited state for a given approximate ground state $|\psi_0\rangle$. Both Eqs. (17) and (18) minimize the trial energy in the orthogonal complement space of $|\psi_0\rangle$, and these two different effective Hamiltonians have been interchangeably utilized in various contexts in quantum chemistry.^{55,57} We choose to work with Eq. (17) here, since it has a clear implementation suitable for a near term quantum device without requiring costly controlled unitary implementations of the state preparation circuits.

Specifically, it is clear that OC-VQE can be effectively implemented using the Hamiltonian of Eq. (17) so long as an efficient algorithm for measuring the magnitude of the overlap between the ground state and a trial excited state is available. On a classical computer, measuring the overlap between, for instance, two UCC states scales exponentially while on a quantum device this task is only polynomial scaling.¹⁶ We describe one implementation of the necessary overlap calculation between two parameterized quantum states in the Quantum Resource Requirements section below, and refer the reader to recent work by Higgott et al.¹⁶ for additional discussion on minimizing the effect of errors on this measurement.

Energy Error Analysis of OC-VQE

When an exact ground state $|\psi_0\rangle$ of \hat{H} is used to construct the effective Hamiltonian $\hat{H}_{\text{OC-VQE}}$ in Eq. (17), the exact ground state of $\hat{H}_{\text{OC-VQE}}$ yields the exact excited state of the original Hamiltonian \hat{H} . We now show that use of an approximate ground state, $|\tilde{\psi}_0\rangle$, in the construction of $\hat{H}_{\text{OC-VQE}}$ will cause the excited state energy to incur an error that is similar in size to the error in the ground state energy, i.e. $E_0 - \langle\tilde{\psi}_0|\hat{H}|\tilde{\psi}_0\rangle$. We define the relevant

excited state Hamiltonian,

$$\hat{H}_{\text{exc}} = \hat{H} - \tilde{E}_0 |\tilde{\psi}_0\rangle \langle \tilde{\psi}_0|, \quad (19)$$

and consider the difference in energy between the ground states of \hat{H}_{exc} and of \hat{H}_{exc} in Eq. (17).

Writing the approximate ground state as $|\tilde{\psi}_0\rangle = \sqrt{1 - \epsilon^2} |\psi_0\rangle + \epsilon |\psi_\perp\rangle$, where $\langle \psi_0 | \psi_\perp \rangle = 0$, we can rewrite Eq. 19 as

$$\hat{H}_{\text{exc}} = \hat{H}_{\text{exc}} + \hat{V}, \quad \hat{V} = -\epsilon E_0 |\psi_\perp\rangle \langle \psi_0| - \epsilon E_0 |\psi_0\rangle \langle \psi_\perp| + \mathcal{O}(\epsilon^2). \quad (20)$$

The first excited state of \hat{H} , which we denote $|\psi_1\rangle$, is by definition an approximation to the ground state of \hat{H}_{exc} . Assuming that ϵ is small, we compute the first order correction to the energy using Eq. (20). Because $|\psi_0\rangle$ and $|\psi_1\rangle$ are orthogonal, it is immediately clear that $\langle \psi_1 | V | \psi_1 \rangle$ is zero to first order in ϵ . Therefore, the difference between the true excited state energy, E_1 , and the energy given by finding the ground state of the approximate excited state Hamiltonian, \hat{H}_{exc} , is $\mathcal{O}(\epsilon^2)$, which is on the same scale as the error in the ground state energy, $\epsilon^2 (\langle \psi_\perp | \hat{H} | \psi_\perp \rangle - E_0)$.

Of course, in practice, we also do not find the exact ground state energy of \hat{H}_{exc} , instead incurring an additional error in our determination of the excited state energy from the second round of approximate minimization. However, if we make the assumption that the VQE procedure on \hat{H}_{exc} is carried out well enough (and the ansatz is flexible enough) to yield an approximate ground state which is ϵ_1 away from the true ground state of \hat{H}_{exc} , then our overall error in the energy will be $\mathcal{O}(\epsilon^2 + \epsilon_1^2)$.

Quantum Resource Requirements

To assess the benefits of unitary coupled cluster theory for quantum computation it is important to quantify the cost of both state preparation and measurement needed to use these

states on quantum processors. Our presentation here addresses the resources required for state preparation for a general quantum computation - we refer the reader to prior work for additional details specific to measurement in the VQE hybrid implementation³². This resource analysis requires an accounting of the number of quantum gates (“gate count” or “circuit size”), the time required to implement them, and the number of qubits on which they act. We shall take the total gate count to be determined by the number of two-qubit gates. In general, the relationship between the gate count and the number of sequential time steps required to implement them when parallelization is taken into account, the “circuit depth,” will depend on the architectural details of the quantum processor. For many applications in quantum chemistry optimal results can nevertheless be obtained with minimal assumptions.^{58,59}

We now present the implementation details necessary for evaluating the scaling of our proposed ansätze with respect to the numbers of spin-orbitals and electrons represented by the state. Our presentation here addresses the resources required for a general quantum computation - we refer the reader to prior work for additional details specific to the VQE hybrid implementation.³²

In order to treat the UCC ansatz on a quantum computer, it is necessary to map⁶⁰⁻⁶² the reference state and the exponentiated cluster operator from a Hilbert space of N fermionic spin-orbitals to a collection of quantum gates acting on N qubits. Therefore, the qubit resource requirement is linear in the number of spin-orbitals. For a UCC ansatz, the total gate count would be naïvely expected to be lower bounded by the number of cluster amplitudes t_p^q and t_{ps}^{rs} , possibly with additional overhead deriving from the mapping to fermionic modes and the limited connectivity of a real device. Regarding the former, while the Jordan-Wigner transformation allows the representation of fermionic creation and annihilation operators in terms of products of single qubit Pauli operators in a way that properly encodes the canonical commutation relations,⁶⁰ direct application of this transformation maps the fermionic operators acting on individual spin-orbitals to qubit operators that act non-locally on $\mathcal{O}(N)$

qubits, leading to a corresponding overhead for the circuit depth. However, recent work in Refs. 59 and 63 describes procedures for implementing a Trotter step of unitary coupled cluster in a manner that not only entirely eliminates this Jordan-Wigner overhead, but also allows for the parallel implementation of individual exponentiated terms from the cluster operator on a linearly connected array of qubits. We note that a practical implementation of UCC relies on approximating $e^{\hat{T}-\hat{T}^\dagger}$ by a small number of Trotter steps, which leads to ansätze that are not exactly equivalent to the ones considered in our numerical calculations. Nevertheless, it has been demonstrated that the variational optimization of as few as one Trotter steps of UCC can yield highly accurate quantum chemical calculations.⁶⁴

Energy measurement and wavefunction optimization in the VQE framework both require repeated state preparation to overcome the statistical nature of the measurement process.^{6,32,32} Therefore, in analyzing the asymptotic time complexity for quantum computation of the approaches considered here, we focus on the cost of state preparation as quantified by the gate count and the circuit depth required for a fixed number of Trotter steps. Generally, we expect a practical benefit from minimizing both the number of free parameters that must be optimized (i.e., the cluster amplitudes) and the circuit depth.

The scaling of the circuit depth was derived here by assuming the maximum possible parallelization of terms in the cluster operator that act on distinct spin-orbitals and neglecting the Jordan-Wigner overhead.⁶³ Within this approach it is then clear that the k -UpCCGSD ansatz allows reduction of the circuit depth from the gate count by a factor of N , since the doubles pairs may be grouped into $\mathcal{O}(N)$ sets of $\mathcal{O}(N)$ terms, each of which acts on distinct spin-orbitals and can the $\mathcal{O}(N)$ sets can therefore be executed in parallel. We note that the results can also be obtained by using the procedure in Ref. 59 without additional numerical truncation. The resulting asymptotic scaling of gate count and circuit depth with respect to both the number of spin-orbitals N and electrons η is shown in Table 1 for all three unitary ansätze. Specific values for the numbers of cluster amplitudes used for the individual molecules for which benchmarking studies are performed will be shown in Table

9 in the results section.

Table 1: Resources required for preparing the three classes of UCC wavefunctions UCCSD, UCCGSD, and k -UpCCGSD, on a quantum device using a fixed number of Trotter steps. The gate count refers to the total number of quantum gates. The circuit depth is the number of sequential steps allowing for quantum gates acting on neighboring qubits to be executed in parallel (see text for details). η denotes the number of electrons and N the number of spin-orbitals in the active space for a given molecule. k denotes the number of products in the k -UpCCGSD wavefunction.

Method	Gate Count	Circuit Depth
UCCSD	$\mathcal{O}((N - \eta)^2 \eta^2)$	$\mathcal{O}((N - \eta)^2 \eta)$
UCCGSD	$\mathcal{O}(N^4)$	$\mathcal{O}(N^3)$
k -UpCCGSD	$\mathcal{O}(kN^2)$	$\mathcal{O}(kN)$

Quantum implementation of Overlap Measurements

In order to implement the excited state algorithm used this work, Eq. (17), it is necessary to estimate not only the expectation value of the energy, but also $|\langle \psi_0 | \psi_1(\theta) \rangle|^2$, where $|\psi_0\rangle$ is a parameterized guess for the ground state wavefunction and $|\psi_1(\theta)\rangle$ is the excited state ansatz. Allow \hat{U}_1 to be the quantum circuit that generates $|\psi_1(\theta)\rangle$ from the $|0\rangle$ state of the qubit register, i.e., $|\psi_1(\theta)\rangle = \hat{U}_1|0\rangle$. Let \hat{U}_0 be the unitary which prepares $|\psi_0\rangle$. The circuit that applies \hat{U}_0^\dagger can be constructed simply by inverting each of the gates that compose \hat{U}_0 . The quantity $|\langle \psi_0 | \psi_1(\theta) \rangle|^2$ can therefore be rewritten as $|\langle 0 | \hat{U}_0^\dagger \hat{U}_1 | 0 \rangle|^2$. This is exactly equal to the probability that the zero state will be observed when the state $\hat{U}_0^\dagger \hat{U}_1 | 0 \rangle$ is measured in the computational basis. Consequently, the magnitude of the overlap may be estimated by repeated state preparation and measurement. Because of the necessity to apply both \hat{U}_1 and \hat{U}_0^\dagger , these measurements require a doubling of the circuit depth compared to the other observables. However, the overall cost of the measurements required for the OC-VQE approach for quantum chemistry in a molecular orbital basis will still be dominated by the measurement of the $\mathcal{O}(N^4)$ terms in the original Hamiltonian.

Benchmark implementations on a Classical Computer

Computational Details

All the full configuration interaction (FCI) calculations needed to benchmark the demonstration examples in this work are performed through `Psi4`⁶⁵ along with its `OpenFermion`⁶⁶ interface. All UCCSD calculations are performed with an in-house code that uses `OpenFermion`⁶⁶ together with `TensorFlow`⁶⁷ for efficient gradient evaluations. The energy as a function of the cluster amplitudes is computed variationally as in Eq. 9 and the gradient of this function is used in conjunction with `SciPy`'s implementation of the BFGS algorithm,⁶⁸ a quasi-Newton method for optimization which does not require explicit calculation of the Hessian. The limit of our code is about 16 spin-orbitals, which allowed us to examine various model systems presented below. A production level code may follow the implementation of `Evangelista`⁸, which may facilitate prototyping VQE ansätze. All other calculations required for the demonstrations presented in this work are done with the development version of `Q-Chem`.⁶⁹ All calculations were performed with the frozen core approximation applied to oxygen and nitrogen.

There are several possible strategies for optimizing the amplitudes of a k -UpCCGSD wavefunction. One attractive approach is to optimize only one set of amplitudes in $\hat{T}^{(k)}$, while fixing all the amplitudes associated with a $(k - 1)$ -UpCCGSD wavefunction. This has the potential benefit of reducing the extra computational cost for optimization of more amplitudes as the index k is increased. However, we found that in practice, this optimization generally requires a larger k value to achieve chemical accuracy than simultaneous optimization of all k sets of amplitudes in k -UpCCGSD. Therefore, for the results presented below, we optimized all k sets of amplitudes simultaneously.

In general, with UCC methods it is not clear whether one obtains global minima of the energy for a given class of wavefunctions. Efficiently obtaining a global minimum in a non-linear optimization problem is an open problem in applied mathematics.⁷⁰ In order

to approximate the true minimum, each gradient-based optimization was therefore carried out between thirty and two hundred times (depending on the cost) starting from randomly chosen initial points.

We note that the BFGS optimization as we have performed it here on a classical computer is unsuitable for use on a quantum device due to the stochastic error associated with the measurement of observables in the VQE framework. Given this, it will be necessary to find better ways to handle optimization for large scale VQE experiments.

Applications to Chemical Systems

We now describe application of the three UCC ansätze UCCSD, UCCGSD, and k -UpCCGSD, to three molecular systems possessing different geometries, namely H_4 , H_2O , and N_2 .

H_4 (in D_{4h} and D_{2h} symmetry)

H_4 is an interesting model system for testing CC methods with singles and doubles. We study here the potential energy curve of H_4 for deviations from the square geometry with fixed bond distance, $R_{\text{H-H}} = 1.23 \text{ \AA}$. Then we vary R in the following coordinate system (values are given in \AA),

$$\text{H1} : (0, 0, 0)$$

$$\text{H2} : (0, 0, 1.23)$$

$$\text{H3} : (R, 0, 0)$$

$$\text{H4} : (R, 0, 1.23).$$

This particular geometry setup has been used by others in Refs. 22, 71–75. At $R = 1.23 \text{ \AA}$ (the D_{4h} geometry), we have two quasidegenerate RHF determinants, which poses a great challenge to single-reference CC methods with only singles and doubles.

We assess the ground state UCC methods including those developed in this work and

compare them against RCCSD and coupled-cluster valence bond with singles and doubles (CCVB-SD) within the minimal basis, STO-3G.^{76,77} CCVB-SD corrects for ill-behaving quadruples in RCCSD and is able to break any number of bonds exactly within the valence active space. In this sense, it is one of the most powerful classical CC methods with singles and doubles within the valence active space. There are two solutions for RCCSD and CCVB-SD, each one being obtained with one of the two low-lying RHF determinants. The two RHF solutions cross at $R = 1.23 \text{ \AA}$. We present the results obtained with the lowest RHF reference for a given R .

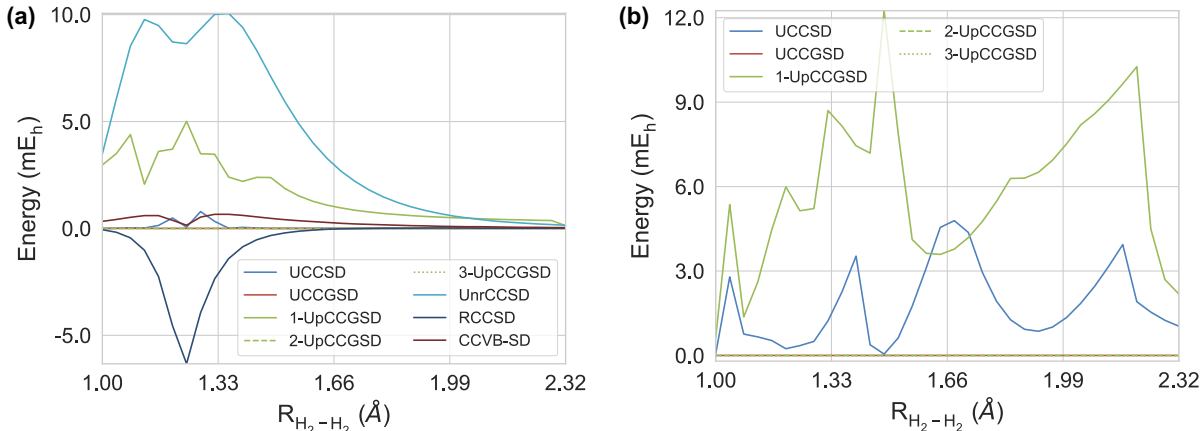


Figure 1: The error in the absolute energy of the various CC methods examined in this work for (a) the ground state and (b) the first excited state of H_4 as a function of the distance between two H_2 's. The basis set used here is STO-3G ($N = 8$, $\eta = 4$). For both plots, UCCGSD, 2-UpCCGSD, and 3-UpCCGSD are overlapping near zero error in the absolute energy.

In Figure 1 (a), we present the absolute energy error in ground state of the aforementioned CC methods as a function of R . We first point out that unrestricted CCSD (UnrCCSD) performs worst in an absolute sense among the methods examined here. This is because the H-H distance in each H_2 is stretched enough to get spin-contamination on each H_2 . This makes the entire potential energy curve of H_4 heavily spin-contaminated within the range of R examined. RCCSD has clearly gone non-variational while CCVB-SD remains above the exact ground state energy at all distances. Except 1-UpCCGSD and UCCSD, all the UCC variants are numerically exact. 1-UpCCGSD is much worse than all the rest of UCC

methods and adding one more product (i.e. 2-UpCCGSD) makes the energy numerically exact.

Unlike full doubles CC models, the energy of k -UpCCGSD is generally not invariant under unitary rotations among orbitals. This is likely a primary cause of the multiple unphysical local minima observed for 1-UpCCGSD. This problem can be ameliorated by increasing the value of k , as shown in Figure 1 (a). The difficulty of optimizing pair wavefunctions has been discussed in some earlier works. Interested readers are referred to Ref. 78.

In Figure 1 (b), the performance of UCC methods on the first excited state of H_4 was assessed within the OC-VQE framework. It is clear that UCCSD and 1-UpCCGSD exhibit larger errors than those of the ground state. This illustrates a potential drawback of OC-VQE in terms of accuracy when we do not have a high quality ground state. However, with better ansätze this drawback can be made insignificant. The excited states from UCCGSD, 2-UpCCGSD, and 3-UpCCGSD are numerically exact, illustrating the power of these novel wavefunction ansätze which go beyond the capability of UCCSD while also offering a lower asymptotic scaling.

Table 2: The non-parallelity error (NPE) (mE_h) in (a) the ground state and (b) the first excited state of H_4 within the STO-3G basis set ($N = 8$, $\eta = 4$).

(a)

	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD	UnrCCSD	RCCSD	CCVB-SD
NPE	0.79	0.00	4.88	0.00	0.00	9.90	6.35	0.62

(b)

	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD
NPE	4.75	0.00	11.62	0.00	0.00

In Table 2, we present the non-parallelity error (NPE) in the ground state and the first excited state for each CC method. NPE is defined as the difference between the maximum and minimum error and is a useful measure of performance, since we are interested in relative energetics in most chemical applications. In the ground state, UnrCCSD is the worst in terms of NPE. CCVB-SD is comparable to UCCSD and RCCSD and 1-UpCCGSD are comparable. UCCGSD, 2-UpCCGSD, and 3-UpCCGSD all have zero NPEs as they are numerically exact

everywhere. In the case of the first excited state, UCCSD and 1-UpCCGSD performs worse than their ground state performance as observed before. All the other UCC methods are numerically exact.

We repeat the same calculations within the 6-31G basis. There are a total of 16 spin-orbitals in this case: in terms of resource on a quantum device this corresponds to the most expensive calculation reported in this work. This test is interesting because some dynamic correlation effects can be captured in 6-31G, in contrast to STO-3G, and these pose a greater challenge to pair CC methods.

Table 3: The error in absolute energy (mE_h) and non-parallelity error (NPE) (mE_h) in the ground state of H_4 within the 6-31G basis ($N = 16$, $\eta = 4$) as a function of the distance (R) between two H_2 's (\AA).

R	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD	UnrCCSD	RCCSD	CCVB-SD
1.01	0.25	0.00	3.56	0.33	0.05	3.14	0.24	0.55
1.12	0.84	0.00	7.49	0.54	0.05	5.78	0.40	1.34
1.23	3.83	0.00	18.20	0.38	0.05	3.24	-0.79	3.21
1.34	0.86	0.00	14.99	0.46	0.03	6.00	0.01	1.41
1.45	0.27	0.00	6.49	0.24	0.02	5.56	0.10	0.74
1.56	0.13	0.00	2.48	0.17	0.02	3.47	0.12	0.48
1.67	0.08	0.00	1.86	0.11	0.01	1.99	0.11	0.35
1.78	0.06	0.00	1.76	0.10	0.01	1.14	0.10	0.26
1.89	0.04	0.00	1.51	0.04	0.01	0.67	0.09	0.21
2.00	0.03	0.00	1.14	0.03	0.01	0.40	0.08	0.17
2.11	0.03	0.00	2.28	0.04	0.00	0.25	0.07	0.13
2.22	0.02	0.00	2.20	0.03	0.01	0.16	0.06	0.11
NPE	3.81	0.00	17.06	0.51	0.05	5.84	1.19	3.10

In Table 3, the error in the ground state is presented as a function of R . In terms of NPE, UCCGSD is again numerically exact and thus best. 2-UpCCGSD and 3-UpCCGSD are within 1 mE_h of UCCGSD and exhibit larger errors than the corresponding results in the STO-3G basis. RCCSD performs better with the 6-31G basis set and it is better than UCCSD. As it clearly becomes non-variational at $R = 1.23 \text{ \AA}$, we suspect that this is a fortuitous outcome for RCCSD. Moreover, UnrCCSD is the worst amongst the traditional CC methods considered in this work, which emphasizes the importance of spin-purity.

Lastly, we discuss the quality of the first excited state from UCC methods on H_4 within the 6-31G basis set⁷⁹ as presented in Figure 4. It is immediately obvious that the degraded ground state performance of UCCSD is amplified in the excited state calculation and that 1-

Table 4: The error in absolute energy (mE_h) and non-parallelity error (NPE) (mE_h) in the first excited state of H_4 within the 6-31G basis ($N = 16$, $\eta = 4$) as a function of the distance (R) between two H_2 's (\AA).

R	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD
1.01	2.55	0.00	9.49	0.92	0.12
1.12	12.17	0.00	4.66	1.02	0.19
1.23	6.99	0.00	14.27	1.74	0.15
1.34	10.46	0.00	13.30	1.02	0.15
1.45	14.07	0.00	12.16	1.31	0.18
1.56	11.79	0.00	9.87	0.91	0.18
1.67	8.94	0.00	9.17	0.80	0.17
1.78	7.71	0.00	10.76	0.63	0.15
1.89	9.38	0.00	13.44	0.58	0.16
2.00	9.74	0.00	17.26	0.49	0.14
2.11	9.46	0.00	17.53	0.46	0.15
2.22	8.44	0.00	21.14	0.42	0.18
NPE	11.52	0.00	16.47	1.31	0.07

UpCCGSD continue to perform poorly. This is consistent with the STO-3G results. However, it should be emphasized that UCCGSD is still numerically exact and the 3-UpCCGSD error is still less than $0.1 mE_h$. UCCSD's poor performance strongly validates our development of better wavefunction ansätze beyond UCCSD, particularly for obtaining good excited states within the OC-VQE framework.

Double Dissociation of H_2O (C_{2v})

The double dissociation of H_2O is another classic test platform for various wavefunction methods.⁸⁰⁻⁸³ As we stretch two single bonds, we have total 4 electrons that are strongly entangled. The traditional RCCSD method can easily become non-variational, as will be demonstrated below. At a fixed angle $\theta_{HOH} = 104.5^\circ$ and within the C_{2v} symmetry, we varied the bond distance between H and O and obtained potential energy curves for various CC methods within the STO-3G basis set.^{76,77}

In Figure 2, the error in the absolute energy of the ground state and the first excited state of H_2O is presented as a function of the R_{O-H} distance. In Figure 2 (a), RCCSD performs much worse than CCVB-SD and UnrCCSD especially after 1.75 \AA and exhibits a very significant non-variationality upon increasing the O-H distance. There is a kink between 2.02 \AA and 2.04 \AA in both RCCSD and CCVB-SD, that is due to a change in the character

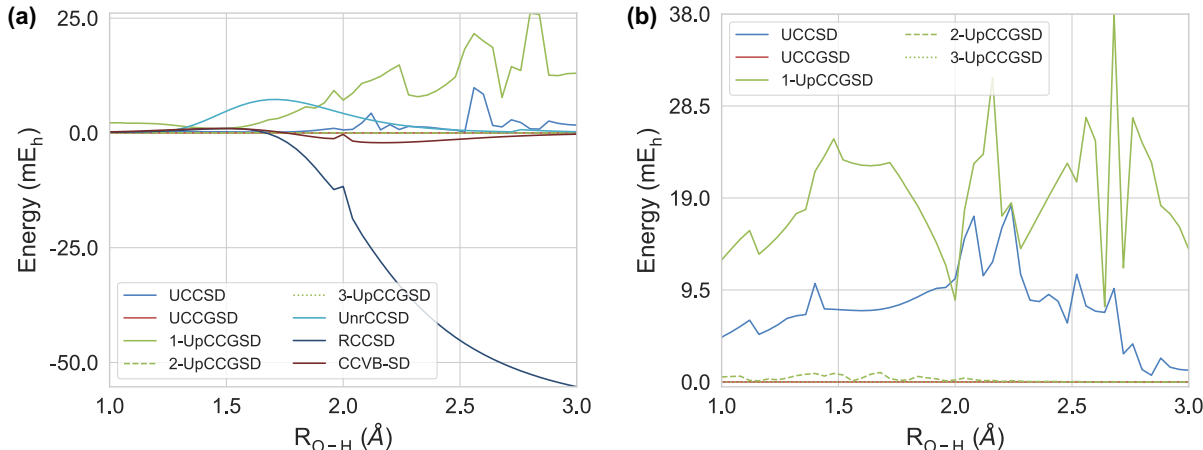


Figure 2: The error in the absolute energy of the various CC methods examined in this work for (a) the ground state and (b) the first excited state of H_2O as a function of the distance between O and H. The basis set used here is STO-3G ($N = 12$, $\eta = 8$). For the ground state (a), UCCGSD, 2-UpCCGSD, and 3-UpCCGSD are overlapping near zero error in the absolute energy. For the excited state (b), UCCGSD and 3-UpCCGSD are overlapping near zero error in the absolute energy.

of the converged amplitudes. The RHF solutions for these CC calculations are delocalized and obey spatial symmetry. We also note that there is another spatially-symmetric RHF solution that is lower in energy than the orbitals we found. This solution starts to appear from 2.02 \AA and is more stable than the other for longer bond distances. This solution has orbitals either localized on O or two H's. This reference yields much higher CCVB-SD and RCCSD energies at 2.04 \AA . These two low-lying RHF solutions might cause multiple amplitudes solutions close in energy. We found that the largest T_1 amplitude of CCVB-SD is 0.28 at 2.02 \AA and 0.07 at 2.04 \AA . This discontinuity does not appear with a larger basis set such as cc-pVDZ so it is likely an artifact of using a minimal basis. With the delocalized RHF solution, CCVB-SD performs best among the classical CC methods examined here.

UCCSD and 1-UpCCGSD perform much worse than the other UCC methods, as also observed above in H_4 . Other UCC methods are more or less numerically exact on the scale of the plot. The performance of the first excited state as presented in Figure 2 (b) is consistent with the ground state performance. UCCGSD and 3-UpCCGSD are numerically exact and 2-UpCCGSD is within $1 mE_h$ for all $R_{\text{O-H}}$ values. UCCSD and 1-UpCCGSD do

not deliver reliable excited state energies.

Table 5: The non-parallelity error (NPE) (mE_h) in (a) the ground state and (b) the first excited state of H_2O within the STO-3G basis set ($N = 12$, $\eta = 8$).

(a)

	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD	UnrCCSD	RCCSD	CCVB-SD
NPE	9.75	0.00	25.16	0.07	0.00	7.15	56.26	3.11

(b)

	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD
NPE	17.57	0.00	30.22	0.98	0.01

In Table 5, we present the NPE of both the ground state in (a) and the first excited state in (b) of H_2O . UCCGSD, 2-UpCCGSD, and 3-UpCCGSD all yield reliable potential energy curves, while curves from the other methods are not as reliable. It should be noted that UCCSD performs worse than the best classical method considered here, UnrCCSD, but improved wavefunctions such as UCCGSD and 3-UpCCGSD are more or less exact for both states.

Dissociation of N_2

The dissociation of N_2 is very challenging for CC methods with only singles and doubles.^{83,84} At a stretched geometry, there are a total of 6 electrons that are strongly entangled. RCCSD exhibits severe non-variationality and UnrCCSD has a non-negligible non-parallelity error due to poor performance in the intermediate bond length (spin-recoupling) regime. To obtain a qualitatively correct answer within the traditional CC framework with a RHF reference, one would need RCCSD with the addition of triples, quadruples, pentuples and hexuples which contains far more excitations than RCCSD. Alternatively, one could employ CCVB-SD as it is able to break N_2 exactly within the STO-3G basis.^{76,77}

In Table 6, we present the NPEs for ground state N_2 for the various CC methods examined in this work. In terms of the number of electrons that are strongly correlated, this system is the most challenging problem investigated in this work. RCCSD is highly non-variational and not acceptably reliable for any distance considered except for 1.0 Å. CCVB-SD exhibits

Table 6: The error in absolute energy (mE_h) and non-parallelity error (NPE) (mE_h) in the ground state of N_2 within the STO-3G basis ($N = 16$, $\eta = 10$) as a function of the distance (R) between two N's (\AA).

R	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD	4-UpCCGSD	5-UpCCGSD	6-UpCCGSD
1.0	1.63	0.44	37.69	9.46	1.55	0.23	0.07	0.03
1.4	4.04	1.50	27.36	10.08	4.00	1.58	0.67	0.27
1.8	3.56	0.77	23.19	10.00	3.05	1.30	0.78	0.38
2.2	11.80	0.42	45.90	15.66	2.70	0.32	0.25	0.19
2.6	12.97	0.16	60.54	15.46	1.86	0.07	0.07	0.02
3.0	14.64	0.43	64.28	18.31	3.73	0.08	0.01	0.03
NPE	13.01	1.33	41.09	8.84	2.45	1.51	0.77	0.37

R	RCCSD	UnrCCSD	CCVB-SD
1.0	2.58	2.58	3.98
1.4	11.53	7.47	14.46
1.8	-19.55	9.08	3.82
2.2	-159.58	2.09	-4.94
2.6	-199.20	0.48	-2.21
3.0	-208.21	0.11	-0.59
NPE	219.74	8.98	19.40

non-variationality but eventually dissociates properly. However, in terms of NPE CCVB-SD is not reliable. UnrCCSD has a NPE of 8.98 mE_h due to poor performance at intermediate bond lengths. UCC methods also struggle to properly dissociate. UCCSD is worse than UnrCCSD in terms of NPE. Furthermore, UCCGSD is now not numerically exact, with a NPE of 1.33 mE_h . In order to achieve a NPE less than 1 mE_h , k needs to be greater than 4. The fact that k -UpCCGSD is systemetically improvable and can achieve very accurate results with a lower cost than UCCSD is very encouraging.

Table 7: The error in absolute energy (mE_h) and non-parallelity error (NPE) (mE_h) in the first excited state of N_2 within the STO-3G basis ($N = 16$, $\eta = 10$) as a function of the distance (R) between two N's (\AA).

R	UCCSD	UCCGSD	1-UpCCGSD	2-UpCCGSD	3-UpCCGSD	4-UpCCGSD	5-UpCCGSD	6-UpCCGSD
1.0	25.77	1.00	45.13	17.56	6.46	2.85	1.33	0.70
1.4	28.35	3.21	62.22	24.20	9.41	4.72	2.62	1.71
1.8	40.46	7.89	42.53	14.68	2.97	1.77	0.78	0.94
2.2	31.57	6.55	8.57	7.32	4.16	2.44	1.78	0.64
2.6	15.09	1.13	-0.32	1.01	0.43	0.37	0.35	0.11
3.0	8.52	0.10	-5.05	-2.83	0.12	0.14	0.05	0.14
NPE	31.94	7.79	67.27	27.02	9.29	4.59	2.57	1.61

Lastly, we discuss the performance of the UCC methods in the first excited state $^1\Pi_g$ which is presented in Table 7. Obtaining an accurate description for the first excited state

of N_2 within the OC-VQE framework is extremely challenging. The best performing UCC method is 6-UpCCGSD with a NPE of $1.61 mE_h$. UCCGSD exhibits a NPE of $7.79 mE_h$, which, while certainly better than that of UCCSD ($31.94 mE_h$), is not close to the threshold for chemical accuracy. These results highlight the challenge of constructing wavefunction ansätze capable of accurately representing the excited states of strongly correlated systems.

Discussion of Excited State Energies

We analyze here the error of UCCGSD for the first excited state of N_2 at 1.8 \AA , which is significant, at $7.89 mE_h$. For the purpose of demonstration, we ran another set of calculations with an exact orthogonality constraint constructed from the exact ground state. The results obtained with this exact constraint are presented in Table 8.

Table 8: The error in absolute energy (mE_h) for the first excited state of N_2 at 1.8 \AA when using the exact ground state for the OC-VQE penalty term together with the UCCGSD ansatz and multiple reference states. Here $\eta = 10$ electrons in $N = 8$ spin-orbitals.

Determinants	Error	Reference
1	10.23	Ground State RHF
2	3.18	Singly Excited Configuration ($\pi_x \rightarrow \pi_x^*$)
4	0.45	Two Singly Excited Configurations ($\pi_x \rightarrow \pi_x^*$ and $\pi_y \rightarrow \pi_y^*$)

The ground state RHF determinant is likely to be a poor reference state for excited states. This is clearly demonstrated in Table 8 with an error of $10.23 mE_h$ in the case of the ground state RHF reference. The first excited state of N_2 is a rather simple electronic state in the sense that it is mainly dominated by single excitations from the ground state wave function. At 1.8 \AA , these single excitations are mainly $\pi \rightarrow \pi^*$ and there are a total of two excitations like this along x and y cartesian components assuming that the molecular axis is the z -axis. Therefore, a more sensible starting point for OC-VQE would be to use these singly excited configurations. This leads to an error of $3.18 mE_h$ with two determinants of the $\pi_x \rightarrow \pi_x^*$ type and to an error of $0.45 mE_h$ with additional two determinants of the $\pi_y \rightarrow \pi_y^*$ type. A total of 4 determinants (or 2 spin-adapted singlet configurations) were

enough to reach the chemical accuracy. In general, a much more sensible reference state for excited states like this can be cheaply obtained via regular linear response methods such as configuration interaction singles.⁸⁵ Furthermore, the natural transition orbital basis⁸⁵ can be used to generate a minimal multi-determinantal reference which will be usually of two determinants.

Summary of Chemical Applications

Table 9: A summary of the results of this work: the number of amplitudes and the non-parallelity error (NPE) (mE_h) for each method applied to each molecule and basis. The excited NPEs are obtained with restricted Hartree-Fock references.

Molecule	Basis	Electrons	Spin-Orbitals	Ansatz/Method	Amplitudes	NPE (ground)	NPE (excited)
H4	STO-3G	4	8	UCCSD	20	0.79	4.75
				UCCGSD	27	0.00	0.00
				1-UpCCGSD	12	4.88	11.62
				2-UpCCGSD	24	0.00	0.00
				3-UpCCGSD	36	0.00	0.00
H4	6-31G	4	16	UCCSD	156	3.81	11.52
				UCCGSD	434	0.00	0.00
				1-UpCCGSD	56	17.06	16.47
				2-UpCCGSD	112	0.51	1.31
				3-UpCCGSD	168	0.05	0.07
H2O	STO-3G	8	12	UCCSD	72	9.75	17.57
				UCCGSD	135	0.00	0.00
				1-UpCCGSD	30	25.16	30.22
				2-UpCCGSD	60	0.07	0.98
				3-UpCCGSD	90	0.00	0.01
N2	STO-3G	10	16	UCCSD	240	13.01	31.94
				UCCGSD	434	1.33	7.79
				1-UpCCGSD	56	41.09	67.27
				2-UpCCGSD	112	8.84	27.02
				3-UpCCGSD	168	2.45	9.29
				4-UpCCGSD	224	1.51	4.59
				5-UpCCGSD	280	0.77	2.57
6-UpCCGSD	336	0.37	1.61				

In Table 9, we present a summary of the results in this section. In particular, we focus on the tradeoff between the number of amplitudes and the accuracy (i.e. NPE). UCCSD does not perform very well given the number of amplitudes. k -UpCCGSD with a similar number of amplitudes always performs better than UCCSD which demonstrates the compactness of k -UpCCGSD. UCCGSD offers very accurate energies at the expense of requiring a significant

number of amplitudes. In all cases we considered it was possible to achieve chemical accuracy using k -UpCCGSD with less amplitudes than UCCGSD. We also note that excited states are in general more challenging than ground state calculations. Furthermore, there is no fortuitous error cancellation in excitation gaps in this approach. Therefore, it is important to obtain near-exact energies for both ground and excited states in order to achieve chemical accuracy for excitation gaps. As noted above, using multi-determinantal reference wavefunction can improve the accuracy significantly. Considering the tradeoff between the cost and the accuracy, we recommend k -UpCCGSD for general applications. However, it should be noted that for k -UpCCGSD to be effective, it is essential to choose k large enough to obtain sub-chemical accuracy. Otherwise the lack of smoothness associated with this novel ansatz will inhibit application goals such as exploring potential energy surfaces.

Summary and Outlook

In this work, we have presented a new unitary coupled cluster ansatz suitable for preparation, manipulation, and measurement of quantum states describing molecular electronic states, k -UpCCGSD, and compared its performance to that of both a generalized UCC ansatz UCCGSD, and the conventional UCCSD. A resource analysis of implementation of these new wavefunctions on a quantum device showed that k -UpCCGSD offers the best asymptotic scaling with respect to both circuit depth and amplitude count. Specifically, the circuit depth for k -UpCCGSD scales as $\mathcal{O}(kN)$ while that for UCCGSD scales as $\mathcal{O}(N^3)$ and that for UCCSD with $\mathcal{O}((N - \eta)^2\eta)$.

We performed classical benchmark calculations with these ansätze for the ground state and first excited state of three molecules with very different symmetries, H_4 (STO-3G, 6-31G), H_2O (STO-3G), and N_2 (STO-3G), to analyze the relative accuracy obtainable from these ansätze. Comparison was also with results from conventional coupled cluster wavefunctions where relevant. The benchmarking calculations show that the new ansatz of unitary

pair coupled-cluster with generalized singles and doubles (k -UpCCGSD) offers a favorable tradeoff between accuracy and time complexity.

We also made excited state calculations, using a variant of the recently proposed orthogonally constrained variational quantum eigensolver (OC-VQE) framework¹⁶. Our implementation of this takes advantage of the close relation of this approach to some excited state methods in quantum chemistry.^{16,55,86} OC-VQE works as a variational algorithm where there is a constraint imposed on the energy minimization in order to ensure the orthogonality of an excited state to a ground state wavefunction that has been previously obtained from a ground state VQE hybrid quantum-classical calculation. This approach requires only a modest increase in resources to implement on a quantum device compared to the resources required for ground state VQE, and is furthermore capable of targeting states outside of a small linear response subspace defined from the VQE ground state.

Assessing the classically computed potential energy curves of these three molecules, we found that the error associated with excited states obtained by the OC-VQE approach in conjunction with the standard UCCSD reference, is considerably larger than the error of the ground state calculation. The excited states of UCC singles and doubles are never of high quality, except for simple two-electron systems where UCCSD is exact.¹⁶ We found that energies of both ground and excited states can be greatly improved by employing either UCCGSD, i.e., UCC with generalized singles and doubles, or the k -fold products of k -UpCCGSD. Furthermore, we demonstrate that the quality of excited state calculations in the OC-VQE framework can be dramatically improved by choosing a chemically motivated reference wavefunction.

UCCGSD was found to be numerically exact for H₄ (STO-3G, 6-31G) and H₂O (STO-3G) for both ground and excited states. However, its non-parallelity error (NPE) is 1.33 mE_h for the ground state of N₂ and 7.79 mE_h for the first excited state of N₂. k -UpCCGSD was found to be numerically exact for a large enough k , where the required value of k increases with the difficulty of the problem. It would be interesting to study the required value of k

for fixed accuracy on a broader class of problems in the future.

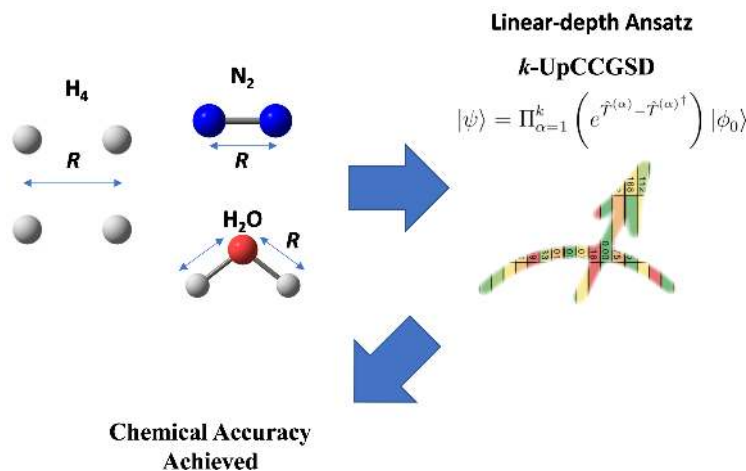
In summary, this work demonstrates the advantages of wavefunction ansätze that go beyond UCCSD and indicates the desirability of further refinement of such ansätze to forms that are accurate for both ground and excited states. The performance of k -UpCCGSD is particularly encouraging, showing a tradeoff between accuracy and resource cost that allows chemical accuracy to be achieved with resources scaling only linearly in the number of spin-orbitals. Our analysis of excited states indicates that these pose significant challenges and there is a need for focus on these. In particular, we anticipate that further development of novel algorithms not within the variational framework may be necessary to obtain high quality excited state energetics, particularly when working with an approximate ground state.

Finally we note that the wavefunctions we have investigated in this work can be fruitfully combined with existing classical approximations to UCC based on the truncation of the Baker-Campbell-Hausdorff expansion of $\langle \phi_0 | e^{T^\dagger - T} H e^{T - T^\dagger} | \phi_0 \rangle$.⁸⁷⁻⁸⁹ This would allow for the efficient initialization of the cluster amplitudes, making it possible to further optimize them using the VQE hybrid approach to quantum computation, and also avoiding the difficulties posed by a random initialization.⁹⁰ In future work, it would be interesting to further explore the balance between the cost and accuracy of unitary coupled cluster ansätze obtained here by building on chemically motivated approximations. Two especially promising directions that we believe could yield a further reduction of the number of amplitudes and the gate depth required for a fixed accuracy, are i) the adaption the recently proposed full coupled-cluster reduction⁹¹ method for use on a quantum computer, and ii) the elimination of singles amplitudes through the use of approximate Brückner orbitals⁹²⁻⁹⁶ obtained by classical pre-processing. Ultimately, the resulting wavefunctions could themselves serve as inputs to a fully quantum computation of more accurate ground and excited state energies, e.g., with the quantum phase estimation algorithm, or to a quantum simulation of quantum dynamics.

Acknowledgement

The work of W. Huggins and K. B. Whaley was supported by the U.S. Department of Energy, Office of Science, Office of Advanced Scientific Computing Research, Quantum Algorithm Teams Program. J. Lee and M. Head-Gordon acknowledge support from the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We thank Dr. Dave Small for stimulating discussions on the performance of CCVB-SD on the H₂O dissociation benchmark.

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