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Iterative qubit-excitation based variational quantum eigensolver

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Molecular simulations with the variational quantum eigensolver (VQE) are a promising application for emerging noisy intermediate-scale quantum computers. Constructing accurate molecular ansätze that are easy to optimize and implemented by shallow quantum circuits is crucial for the successful implementation of such simulations. Ansätze are, generally, constructed as series of fermionic-excitation evolutions. Instead, we demonstrate the usefulness of constructing ansätze with “qubit-excitation evolutions”, which, contrary to fermionic excitation evolutions, obey “qubit commutation relations”. We show that qubit excitation evolutions, despite the lack of some of the physical features of fermionic excitation evolutions, accurately construct ansätze, while requiring asymptotically fewer gates. Utilizing qubit excitation evolutions, we introduce the iterative qubit excitation based VQE (IQEB-VQE) algorithm. The IQEB-VQE performs molecular simulations using a problem-tailored ansatz, grown iteratively by appending evolutions of single and double qubit excitation operators. By performing numerical simulations for small molecules, we benchmark the IQEB-VQE, and compare it against other competitive VQE algorithms. In terms of circuit efficiency and time complexity, we find that the IQEB-VQE systematically outperforms the previously most circuit-efficient, practically scalable VQE algorithms.

I. INTRODUCTION

Quantum computers are anticipated to enable simulations of quantum systems more efficiently and accurately than classical computers [1, 2]. A promising algorithm to perform this task on emerging noisy intermediate-scale quantum (NISQ) [3–5] computers is the variational quantum eigensolver (VQE) [6–12]. The VQE is a hybrid quantum-classical algorithm that estimates the lowest eigenvalue of a Hamiltonian H by minimizing the energy expectation value $E(\boldsymbol{\theta}) = \langle \psi(\boldsymbol{\theta}) | H | \psi(\boldsymbol{\theta}) \rangle$ with respect to a parametrized state $|\psi(\boldsymbol{\theta})\rangle = U(\boldsymbol{\theta})|\psi_0\rangle$. Here, $\boldsymbol{\theta}$ is a set of variational parameters, and the unitary $U(\boldsymbol{\theta})$ is an ansatz. Compared to other purely quantum algorithms for eigenvalue estimation, like the quantum-phase-estimation algorithm [13, 14], the VQE requires shallower quantum circuits. This makes the VQE more noise resistant, at the expense of requiring a higher number of quantum measurements and additional classical post-processing.

The VQE can solve the electronic structure problem [6, 15] by estimating the lowest eigenvalue of an electronic Hamiltonian. A major challenge for the practical realization of a molecular VQE simulation on NISQ computers is to construct a variationally flexible ansatz $U(\boldsymbol{\theta})$ that: (1) accurately approximates the ground state of H ; (2) is easy to optimize; and (3) can be implemented by a shallow circuit.

These desired qualities are satisfied, to various levels, by several types of ansätze. The unitary coupled cluster (UCC) type, was the first to be used for molecular VQE simulations [16]. The UCC is motivated by the classical coupled cluster theory [15], and corresponds to a series of unitary evolutions of fermionic excitation operators, which we refer to as “fermionic excitation evolutions” (see Sec. II B). A prominent example of a UCC ansatz is the UCC Singles and Doubles (UCCSD) [17–22], which corresponds to a series of single and double fermionic-excitation evolutions. The UCCSD has been used successfully to implement the VQE for small molecules [16, 17, 23]. Due to their physically-motivated fermionic structure, UCC ansätze respect the symmetries of electronic wavefunctions, which makes these ansätze easy to optimize. Furthermore even a relatively simple UCC ansatz, like the UCCSD, is highly accurate for weakly correlated systems, such as molecules near their equilibrium configuration [16, 17, 24, 25]. However, UCC ansätze are general-purpose built and do not take into account details of the system of interest. They contain redundant excitation terms, resulting in unnecessarily high numbers of variational parameters as well as long ansatz circuits. Moreover, to simulate strongly correlated systems, UCC ansätze require higher-order excitations and multiple-step Trotterization [24], which creates additional overhead for the quantum hardware.

Another type of “hardware-efficient” ansätze [26–30] correspond to universal unitary transformations implemented as periodic sequences of parametrized one- and two-qubit gates. These ansätze are implemented by shallow circuits, and can be highly variationally flexible. However, as they lack physically-motivated structure, these ansätze require a large number of variational parameters and may suffer by vanishing energy gradients along their variational parameters, making classical optimization intractable for large molecules. In some scenarios, this is known as the barren-plateau problem [31–34].

Recently, a number of works [35–43] suggested new “iterative” VQE algorithms, which instead of using general-purpose, fixed ansätze, construct problem-tailored ansätze on the go. These algorithms can construct arbitrarily accurate ansätze that are optimized in the number of variational parameters and the ansatz circuit depth, at the expense of requiring a larger number of quantum measurements. One of the first iterative VQE algorithms, the adaptive derivative-assembled pseudo-trotter ansatz (ADAPT)-VQE [35], constructs its ansatz by iteratively adding parameterized unitary operators, which we refer to as “ansatz elements”. The ansatz element at each iteration is sampled from a pool of spin-complement single and double fermionic excitation evolutions, based on an energy gradient hierarchy. The ADAPT-VQE is demonstrated to achieve chemical accuracy (10^{-3} Hartree), using an ansatz with several times fewer variational parameters and a shallower circuit than the UCCSD. In the follow-up work [36], the qubit-ADAPT-VQE utilizes an ansatz element pool of more variationally flexible and rudimentary Pauli string exponentials. Due to this, the qubit-ADAPT-VQE constructs even shallower ansatz circuits than the ADAPT-VQE, thus being, to the best of our knowledge, the currently most circuit-efficient, physically-motivated VQE algorithm. Unfortunately, the use of more rudimentary unitary operations comes at the expense of requiring additional variational parameters and iterations to construct an ansatz for a given accuracy.

In this work, we utilize unitary operations that, despite the lack of some of the physical features captured by fermionic excitation evolutions, achieve the accuracy of fermionic excitations evolutions as well as the hardware efficiency of Pauli string exponentials. These operations can be used to construct circuit-efficient molecular ansätze without incurring as many additional variational parameters and iterations, as the qubit-ADAPT-VQE. We call these unitary operations “qubit excitation evolutions”. Qubit excitation evolutions [23, 44–46] are unitary evolutions of “qubit excitation operators”, which satisfy “qubit commutation relations” [45, 46]. Qubit excitation evolutions can

be implemented by circuits that act on fixed numbers of qubits, as opposed to fermionic excitation evolutions, which act on a number of qubits that scales at least as $O(\log_2 N_{\text{MO}})$ with the number of molecular spin-orbitals N_{MO} (see Sec. II B). We show numerically, that qubit excitation evolutions can approximate an electronic wavefunction almost as accurately as fermionic excitation evolutions can (Sec. II E). On the other hand, qubit excitation evolutions enjoy higher complexity than Pauli string exponentials, thus allowing for a more rapid construction of the ansatz.

We utilize qubit excitation evolutions to introduce the iterative qubit-excitation based variational quantum eigensolver (IQEB-VQE) (Sec. II C). As the name suggests, the IQEB-VQE is an iterative VQE algorithm for molecular simulations that grows a problem-tailored ansatz from an ansatz-element pool of single and double qubit excitations. The IQEB-VQE deploys a composite ansatz-growing strategy, based on an energy gradient hierarchy in combination with explicit energy-reduction evaluation for individual qubit excitation evolutions. We benchmark the performance of the IQEB-VQE (Sec. II D) with classical numerical simulations for small molecules: LiH and BeH₂. We show that the IQEB-VQE constructs more circuit efficient ansätze than the ADAPT-VQE and the qubit-ADAPT-VQE. We also show that the IQEB-VQE requires significantly fewer variational parameters and iterations to converge compared to the qubit-ADAPT-VQE. However, if spin conservation must be respected, the IQEB-VQE requires up to twice as many variational parameters as the ADAPT-VQE, but converges after approximately the same number of iterations.

II. RESULTS

A. Theoretical background and notation

We begin with a theoretical introduction (required for the self-completeness of the paper) and by defining our notation. Finding the ground-state electron wavefunction $|E_0\rangle$ and corresponding energy E_0 of a molecule (or an atom) is known as the “electronic structure problem” [15]. This problem can be solved by solving the time-independent Schrödinger equation $H|\Phi_0\rangle = E_0|\Phi_0\rangle$, where H is the electronic Hamiltonian of the molecule. Within the Born-Oppenheimer approximation, where the nuclei of the molecule are treated as motionless, H can be second quantized as

$$H = \sum_{i,k}^{N_{\text{MO}}} h_{i,k} a_i^\dagger a_k + \sum_{i,j,k,l}^{N_{\text{MO}}} h_{i,j,k,l} a_i^\dagger a_j^\dagger a_k a_l. \quad (1)$$

As already mentioned N_{MO} is the number of molecular spin-orbitals, $a_i^\dagger$ and a_i are fermionic creation and annihilation operators, corresponding to the i^{th} molecular spin-orbital, and the factors h_{ij} and h_{ijkl} are one- and two-electron integrals, written in a spin-orbital basis [15]. The Hamiltonian expression in equation (1) can be mapped to quantum gate operators using an encoding method, e.g. the Jordan-Wigner (JW) [47] or the Bravyi-Kitaev [48] methods. Throughout this work we assume the more straightforward JW encoding, where the occupancy of the i^{th} molecular spin-orbital is represented by the state of the i^{th} qubit.

The fermionic operators $a_i^\dagger$ and a_i satisfy anti-commutation relations

$$\{a_i, a_j^\dagger\} = \delta_{i,j}, \quad \{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0. \quad (2)$$

106 Within the JW encoding, $a_i^\dagger$ and a_i can be written in terms of quantum gate operators as

$$a_i^\dagger = Q_i^\dagger \prod_{r=0}^{i-1} Z_r = \frac{1}{2}(X_i - iY_i) \prod_{r=0}^{i-1} Z_r \text{ and} \quad (3)$$

$$a_i = Q_i \prod_{r=0}^{i-1} Z_r = \frac{1}{2}(X_i + iY_i) \prod_{r=0}^{i-1} Z_r, \quad (4)$$

108 where

$$Q_i^\dagger \equiv \frac{1}{2}(X_i - iY_i) \text{ and} \quad (5)$$

$$Q_i \equiv \frac{1}{2}(X_i + iY_i). \quad (6)$$

110 We refer to $Q_i^\dagger$ and Q_i as qubit creation and annihilation operators, respectively. They act to change the occupancy
 111 of spin-orbital i . The Pauli- z strings, in equations (3) and (4), compute the parity of the state and act as exchange
 112 phase factors that account for the fermionic anticommutation of $a^\dagger$ and a . Substituting equations (3) and (4) into
 113 equation (1), H can be written as

$$H = \sum_r h_r \prod_s \sigma_s^r, \quad (7)$$

114 where σ_s is a Pauli operator (X_s , Y_s , Z_s or I_s) acting on qubit s , and h_r (not to be confused with h_{ik} and h_{ijkl}) is a
 115 real scalar coefficient. The number of terms in equation (7) scales as $O(N_{\text{MO}}^4)$.

116 Once H is mapped to a Pauli operator representation, the VQE can be used to minimize the expectation value
 117 $E(\boldsymbol{\theta}) = \langle \psi(\boldsymbol{\theta}) | H | \psi(\boldsymbol{\theta}) \rangle$. The VQE relies upon the Rayleigh-Ritz variational principle

$$\langle \psi(\boldsymbol{\theta}) | H | \psi(\boldsymbol{\theta}) \rangle \geq E_0, \quad (8)$$

118 to find an estimate for E_0 . The VQE is a hybrid-quantum-classical algorithm that uses a quantum computer to
 119 prepare the trial state $|\psi(\boldsymbol{\theta})\rangle$ and evaluate $E(\boldsymbol{\theta})$, and a classical computer to process the measurement data and
 120 update $\boldsymbol{\theta}$ at each iteration. The trial state $|\psi(\boldsymbol{\theta})\rangle = U(\boldsymbol{\theta})|\psi_0\rangle$ is generated by an *ansatz*, $U(\boldsymbol{\theta})$, applied to an initial
 121 reference state $|\psi_0\rangle$.

122 Iterative VQE algorithms construct their ansätze on the go, taking into account details of the system of interest.
 123 At the m^{th} iteration in algorithms like our IQEB-VQE and the ADAPT-VQE, one or several unitary operators,
 124 $\{U_r^{(m)}(\theta_r^{(m)})\}$, which we refer to as ansatz elements, are appended to the left of the already existing ansatz, $U(\boldsymbol{\theta}^{(m-1)})$:

$$U(\boldsymbol{\theta}^{(m)}) = \prod_r U_r^{(m)}(\theta_r^{(m)}) U(\boldsymbol{\theta}^{(m-1)}) = \prod_{p=m}^1 \prod_r U_r^{(p)}(\theta_r^{(p)}). \quad (9)$$

125 The ansatz elements, $U_r^{(m)}(\theta_r^{(m)})$, at each iteration, are chosen from a finite ansatz element pool $\mathbb{P}$, based on a growth
 126 strategy that aims to achieve the lowest estimate of $E(\boldsymbol{\theta}^{(m)})$. After a new ansatz $U(\boldsymbol{\theta}^{(m)})$ is constructed, the new set
 127 of variational parameters $\boldsymbol{\theta}^{(m)} = \boldsymbol{\theta}^{(m-1)} \cup \{\theta_r^{(m)}\}$ is optimized by the VQE, and a new estimate $E(\boldsymbol{\theta}^{(m)})$ is obtained.
 128 This, iteratively greedy, strategy results in an ansatz that is tuned specifically to the system being simulated, and
 129 can approximate the ground eigenstate of the system with considerably fewer variational parameters and a shallower
 130 ansatz circuit, compared to general-purpose fixed ansätze, like the UCCSD.

In the ADAPT-VQE, the ansatz element pool $\mathbb{P}$ is the set of all spin-complement pairs of single and double fermionic excitation evolutions. In the qubit-ADAPT-VQE, $\mathbb{P}$ is a set of parametrized exponentials of XY -Pauli strings of lengths 2 or 4 that have an odd number of Y s. The growth strategy of the ADAPT-VQE and the qubit-ADAPT-VQE is to add, at each iteration, the ansatz element with the largest energy gradient magnitude

$$\left| \frac{\partial}{\partial \theta^{(m)}} \langle \psi^{(m-1)} | U^{(m)\dagger}(\theta^{(m)}) H U^{(m)}(\theta^{(m)}) | \psi^{(m-1)} \rangle \right|_{\theta=0},$$

where $|\psi^{(m-1)}\rangle$ is the trial state at the $(m-1)^{\text{th}}$ iteration. For detailed descriptions of the ADAPT-VQE and the qubit-ADAPT-VQE, we refer the reader to the original Refs. [35] and [36], respectively.

B. Ansatz elements

Single and double fermionic excitation operators, are defined, respectively, by the skew-Hermitian operators

$$T_{ik} \equiv a_i^\dagger a_k - a_k^\dagger a_i \quad \text{and} \quad (10)$$

$$T_{ijkl} \equiv a_i^\dagger a_j^\dagger a_k a_l - a_k^\dagger a_l^\dagger a_i a_j. \quad (11)$$

Single and double fermionic-excitation evolutions are thus given, respectively, by the unitaries

$$A_{ik}(\theta) = e^{\theta T_{ik}} = \exp \left[\theta (a_i^\dagger a_k - a_k^\dagger a_i) \right] \quad \text{and} \quad (12)$$

$$A_{ijkl}(\theta) = e^{\theta T_{ijkl}} = \exp \left[\theta (a_i^\dagger a_j^\dagger a_k a_l - a_k^\dagger a_l^\dagger a_i a_j) \right]. \quad (13)$$

Using equations (3) and (4), for $i < j < k < l$, A_{ik} and A_{ijkl} can be expressed in terms of quantum gate operators as

$$A_{ij}(\theta) = \exp \left[-i \frac{\theta}{2} (X_i Y_k - Y_i X_k) \prod_{r=i+1}^{k-1} Z_r \right] \quad \text{and} \quad (14)$$

$$A_{ijkl}(\theta) = \exp \left[i \frac{\theta}{8} (X_i Y_j X_k X_l + Y_i X_j X_k X_l + Y_i Y_j Y_k X_l + Y_i Y_j X_k Y_l - X_i X_j Y_k X_l - X_i X_j X_k Y_l - Y_i X_j Y_k Y_l - X_i Y_j Y_k Y_l) \prod_{r=i+1}^{j-1} Z_r \prod_{r'=k+1}^{l-1} Z_{r'} \right]. \quad (15)$$

As seen from equations (14) and (15), fermionic excitation evolutions act on a number of qubits that scales as $O(N_{\text{MO}})$. Therefore, they are implemented by circuits whose size (in terms of number of $CNOT$ s) also scales as $O(N_{\text{MO}})$. We provided a $CNOT$ -efficient method to construct circuits for fermionic excitations evolutions in Ref. [46]. The circuits for a single and a double fermionic excitation evolutions have $CNOT$ counts of $2(k-i) + 1$ and $2(l+j-i-k) + 9$, respectively.

Qubit excitation operators are defined by the qubit annihilation and creation operators, Q_i and $Q_i^\dagger$ [equations (5) and (6)], which satisfy the qubit commutation relations

$$\{Q_i, Q_i^\dagger\} = I, [Q_i, Q_j^\dagger] = 0 \text{ if } i \neq j, \text{ and } [Q_i, Q_j] = [Q_i^\dagger, Q_j^\dagger] = 0 \text{ for all } i, j. \quad (16)$$

Some authors have referred to these commutation relations as parafermionic [45]. Single and double qubit excitation operators are given, respectively, by the skew-Hermitian operators

$$\tilde{T}_{ik} \equiv Q_i^\dagger Q_k - Q_k^\dagger Q_i \quad \text{and} \quad (17)$$

$$\tilde{T}_{ijkl} \equiv Q_i^\dagger Q_j^\dagger Q_k Q_l - Q_k^\dagger Q_l^\dagger Q_i Q_j. \quad (18)$$

Thus, single and double qubit-excitation evolutions are given, respectively, by the unitary operators

$$\tilde{A}_{ik}(\theta) = e^{\theta \tilde{T}_{ik}} = \exp [\theta (Q_i^\dagger Q_k - Q_k^\dagger Q_i)] \quad \text{and} \quad (19)$$

$$\tilde{A}_{ijkl}(\theta) = e^{\theta \tilde{T}_{ijkl}} = \exp [\theta (Q_i^\dagger Q_j^\dagger Q_k Q_l - Q_k^\dagger Q_l^\dagger Q_i Q_j)]. \quad (20)$$

Using equations (5) and (6), $\tilde{A}_{ik}$ and $\tilde{A}_{ijkl}$ can be re-expressed in terms of quantum gate operators as

$$\tilde{A}_{ik}(\theta) = \exp \left[-i \frac{\theta}{2} (X_i Y_k - Y_i X_k) \right] \quad \text{and} \quad (21)$$

$$\begin{aligned} \tilde{A}_{ijkl}(\theta) = \exp \left[i \frac{\theta}{8} (X_i Y_j X_k X_l + Y_i X_j X_k X_l + Y_i Y_j Y_k X_l + Y_i Y_j X_k Y_l \right. \\ \left. - X_i X_j Y_k X_l - X_i X_j X_k Y_l - Y_i X_j Y_k Y_l - X_i Y_j Y_k Y_l) \right]. \end{aligned} \quad (22)$$

As seen from equations (21) and (22), unlike fermionic excitation evolutions, qubit excitation evolutions act on a fixed number of qubits, and can be implemented by circuits that have a fixed number of *CNOT*s. Single qubit excitation evolutions can be performed by the circuit in Fig. 1, with a *CNOT* count of 2. Double qubit excitation evolutions can be performed by the circuit in Fig. 2, which we introduced in Ref. [46], with a *CNOT* count of 13.

FIG. 1: Circuit implementing the single qubit excitation evolution of equation (21).

For larger systems, qubit excitation evolutions are increasingly more *CNOT*-efficient compared to fermionic excitation evolutions, whose *CNOT* count scales as $O(N_{\text{MO}})$ in the JW encoding and as $O(\log N_{\text{MO}})$ in the BK encoding. On the other hand, single and double qubit excitation evolutions, as seen from equations (21) and (22), correspond to combinations of 2 and 8, mutually commuting Pauli string exponentials, respectively. Hence, by constructing ansätze with qubit excitation evolutions instead of Pauli string exponentials, we decrease the number of variational parameters. A further advantage of qubit excitation evolutions is that they allow for the local circuit-optimizations of Ref. [46], which Pauli string exponentials do not.

When comparing the IQEB-VQE with the ADAPT-VQE (see Sec. II G), we assume the use of the qubit- and fermionic-excitation evolutions circuits as outlined above. To our knowledge, these are the most *CNOT*-efficient circuits for these two types of unitary operations. For the qubit-ADAPT-VQE, we assume that an exponential of a Pauli string of length l is implemented by standard *CNOT* staircases, with *CNOT* count of $2(l - 1)$ [6, 46, 49]. Global circuit optimization is beyond the scope of this paper.

If $\Delta E^{(m)} < \epsilon$, where $\epsilon > 0$ is an energy threshold:

(a) Exit

Else:

(a) Append $\tilde{A}^{(m)}(\theta^{(m)})$ to the ansatz: $U(\theta^{(m)}) = \tilde{A}^{(m)}(\theta^{(m)})U(\theta^{(m-1)})$

(b) Set $E^{(m)} = E^{(m-1)} - \Delta E^{(m)} p$

(c) Set the values of the new set of variational parameters, $\theta^{(m)} = \theta^{(m-1)} \cup \{\theta_{p'}\}$, to $\theta_{p'}^{(m)}$

5. (Optional) If the ground state of the system of interest is known, *a priori*, to have the same spin as $|\psi_0\rangle$, append to the ansatz the spin-complementary of $\tilde{A}^{(m)}(\theta^{(m)})$, $\tilde{A}'^{(m)}(\theta'^{(m)})$, unless $\tilde{A}^{(m)}(\theta^{(m)}) \equiv \tilde{A}'^{(m)}(\theta'^{(m)})$:

$$U(\theta^{(m)}) = \tilde{A}'^{(m)}(\theta'^{(m)})\tilde{A}^{(m)}(\theta^{(m)})U(\theta^{(m-1)}). \quad (24)$$

6. Enter the $m + 1$ iteration by returning to step 1

We now provide some more information and observations about the steps of our algorithm. The IQEB-VQE loop starts by preparing the trial state $|\psi^{(m-1)}\rangle$ obtained in the $(m-1)^{\text{th}}$ iteration. To identify a suitable qubit excitation evolution to append to the ansatz, first we calculate (step 2) the gradient of the energy expectation value, with respect to the variational parameter of each qubit excitation evolution in $\mathbb{P}(\tilde{A}, N_{\text{MO}})$. The gradients are evaluated at $\theta_p = 0$ because of the presumption that $|\psi_0\rangle$ is close to the ground state, which suggests that the optimized value of θ_p is close to 0. The gradients [equation (23)] are calculated by measuring, on a quantum computer, the expectation value of the commutator of H and the corresponding qubit excitation operator $\tilde{T}_p$, with respect to $|\psi^{(m-1)}\rangle$. The expression for the gradient in equation (23) is derived explicitly in Sec. I of the supplementary information. Given that H is represented by up to $O(N_{\text{MO}}^4)$ Pauli strings [equation (7)], each gradient will require up to $O(N_{\text{MO}}^4)$ expectation-value measurements. Since $\|\mathbb{P}(\tilde{A}, N_{\text{MO}})\| \propto N_{\text{MO}}^4$, step 2 will require up to $O(N_{\text{MO}}^8)$ quantum measurements. If multiple quantum devices are available, step 2 can be parallelized.

The gradients calculated in step 2, indicate how much each qubit excitation can decrease $E^{(m-1)}$. However, the largest gradient does not necessarily correspond to the largest energy reduction, optimized over all variational parameters. In step 3, we identify the set of n qubit excitation evolutions with the largest energy gradient magnitudes: $\tilde{\mathbb{A}}^{(m)}(n) \in \mathbb{P}(\tilde{A}, N_{\text{MO}})$. We assume that $\tilde{\mathbb{A}}^{(m)}(n)$ likely contains the qubit excitation that reduces $E^{(m-1)}$ the most. For each of the n qubit excitation evolutions in $\tilde{\mathbb{A}}^{(m)}(n)$, we run the VQE with the ansatz from the previous iteration to calculate how much it contributes to the energy reduction. For the molecular simulations presented in this work, we set $n = 10$, since increasing n any further does not change significantly the size of the ansatz. If multiple quantum devices are available, step 3 can also be parallelized.

In step 4, we pick the qubit excitation, $\tilde{A}^{(m)}(\theta^{(m)})$, with the largest contribution to the energy reduction, $\Delta E^{(m)}$. If $\Delta E^{(m)}$ is below some threshold $\epsilon > 0$, we exit the iterative loop. If instead the $|\Delta E^{(m)}| > \epsilon$, we add $\tilde{A}^{(m)}(\theta^{(m)})$ to the ansatz.

If it is known, *a priori*, that the ground state of the simulated system has spin zero, as the Hartree-Fock state does, we assume that qubit-excitation evolutions come in spin-complement pairs. Hence, we append the spin-complementary of $\tilde{A}^{(m)}(\theta^{(m)})$, $\tilde{A}'^{(m)}(\theta'^{(m)})$ (step 5) to the ansatz. However, unlike the ADAPT-VQE, our algorithm assigns independent

variational parameters to the two spin-complement excitations. The reason for this is that qubit excitation evolutions do not account for the parity of the state. Hence, additional variational flexibility is required to obtain the correct relative sign between the two spin-complementary qubit excitation evolutions. Performing step 5 roughly halves the number of iterations required to construct an ansatz for a particular accuracy.

D. Classical numerical simulations

We perform classical numerical simulations of LiH and BeH₂, to compare the use of qubit and fermionic excitations (see Sec. II E) in the construction of molecular ansätze, and to benchmark the performance of the IQEB-VQE algorithm. Our numerical results are based on a custom code, designed to implement iterative VQE algorithms for arbitrary ansatz-element pools. The code is optimized to calculate analytically excitation-based statevectors (see Sec. II of the supplementary information). The code uses the *openfermion-psi4* [51] package to second-quantize the Hamiltonian, and subsequently to transform it to quantum-gate-operator representation. For all numerical results presented here, we use the Slater type orbital-3 Gaussians (STO-3G) spin-orbital basis set [52, 53], without assuming frozen orbitals. In this basis set, LiH (BeH₂), has 12 (14) spin-orbitals, which are represented by 12 (14) qubits. For the optimization of variational parameters, we use the gradient-descend Broyden Fletcher Goldfarb Shannon (BFGS) minimization method [54] from Scipy [55]. We also supply to the BFGS an analytically calculated energy gradient vector (see Sec. III of the supplementary information), for a faster optimization. We note that in the presence of high noise levels, gradient-descend minimizers are likely to struggle to find the global energy minimum [56, 57], while direct search minimizers [58] are likely to perform better [59, 60].

FIG. 3: Energy convergence for the ground states of the LiH and BeH₂ molecules in the STO-3G orbital basis set, at bond distances of 1.546Å and 1.316Å, respectively. The plot compares an ansatz of single and double qubit-excitation evolutions, to an ansatz of single and double fermionic-excitation evolutions.

E. Qubit versus fermionic excitations

Before we proceed to benchmarking the IQEB-VQE, we compare qubit and fermionic excitation evolutions in their ability to construct ansätze for molecular electronic wavefunctions. Comparing the IQEB-VQE and the ADAPT-VQE does not constitute a suitable comparison of the two types of excitation evolutions: The two algorithms use different ansatz growing strategies, and the ADAPT-VQE uses as ansatz elements spin-complement pairs of fermionic excitation evolutions, rather than independent fermionic excitation evolutions. Therefore, we perform numerical simulations of two simplified iterative-VQE algorithms. The two algorithms grow their ansätze based on an energy gradient hierarchy, similarly to the ADAPT-VQE, and differ only in their ansatz element pools of qubit and fermionic excitations, respectively.

The energy convergences of the two algorithms for LiH and BeH₂ are given in Fig. 3. The two algorithms converge remarkably similarly, with the one using fermionic excitation evolutions converging slightly faster for large ansatz sizes. Figure 3 suggests the remarkable result, that the more complex and physically motivated fermionic excitation evolutions have little or no advantage over the qubit excitation evolutions in approximating electronic wavefunctions. This means that the Pauli-*z* strings in equations (14) and (15), which compute the parity of the state and account for the anticommutation of the fermionic excitation operators, play little to no role in the variational flexibility of the ansatz on their own.

F. Dissociation curves

In this section, we benchmark the performance of the IQEB-VQE algorithm. In Figs. 4a,b we present energy dissociation curves for the LiH and BeH₂ molecules, obtained with the IQEB-VQE for $\epsilon = 10^{-6}$ Hartree and $\epsilon = 10^{-8}$ Hartree. We also include dissociation curves obtained with three other standard methods: the full-configuration-interaction (FCI) method [61]; the Hartree-Fock (HF) method [50]; and the VQE using an untrotterized UCCSD ansatz (UCCSD-VQE). In Figs. 4c,d the exact FCI energy is subtracted from the energies obtained with the other methods in order to compare their respective errors.

For both molecules, the IQEB-VQE achieves chemical accuracy over all investigated bond distances. This indicates that the IQEB-VQE successfully constructs accurate ansätze even for more strongly correlated states, further from the equilibrium bond distances. Meanwhile, the UCCSD-VQE fails to simulate BeH₂ at long bond distances (Fig. 4d). Furthermore, the IQEB-VQE method with $\epsilon = 10^{-6}$ is at least as accurate as the UCCSD, while using at least half the number of variational parameters. The reason for the superiority of the IQEB-VQE is that it constructs a problem tailored ansatz that includes only qubit excitations relevant to the approximation of the ground state of the system of interest. We also note that the IQEB-VQE with $\epsilon = 10^{-8}$ achieves, at least, two orders of magnitude higher accuracies than the UCCSD-VQE, while still requiring fewer parameters (Fig. 4e,f), and correspondingly shallower circuits.

FIG. 4: Energy dissociation curves for the LiH and BeH₂ molecules in the STO-3G orbital basis set. **(a,b)** Absolute energy as function of bond distance. **(c,d)** Energy error with respect to the exact FCI energy. **(e,f)** Number of ansatz variational parameters required to reach the energy accuracies in (c,d). The number of variational parameters for the UCCSD ansatz is 92 and 204 for LiH and BeH₂, respectively.

G. Energy convergence

In this section we compare the performance of the IQEB-VQE against the ADAPT-VQE and the qubit-ADAPT-VQE using energy convergence plots (Fig. 5) for the LiH and BeH₂ molecules. The plots are obtained for equilibrium bond distances of 1.546 Å and 1.316 Å, for LiH and BeH₂, respectively, as well as for bond distances of 3 Å, where correlation effects are stronger.

FIG. 5: Energy convergence plots for the ground states of LiH and BeH₂ in the STO-3G orbital basis set. The plots are obtained for equilibrium bond distances $r_{\text{Li-H}}^0 = 1.546\text{\AA}$ and $r_{\text{Be-H}}^0 = 1.316\text{\AA}$, and for bond distances $r_{\text{Li-H}}^1 = r_{\text{Be-H}}^1 = 3\text{\AA}$ where correlation effects should be significant. The *CNOT* counts in **e,f** are obtained assuming the use of the quantum circuits discussed in Sec. II B.

We compare the three algorithms in terms of three cost metrics; (1) the number of iterations, (2) the number of variational parameters, and (3) the number of *CNOT*s required to construct an ansatz for a desired accuracy. The number of iterations and the number of variational parameters determine the total number of quantum measurements and the run time of the algorithm (the number of iterations is the same as the number of variational parameters for

the ADAPT-VQE and the qubit-ADAPT-VQE, but not for the IQEB-VQE, where the number of iterations is less than the number of variational parameters). The $CNOT$ count of the ansatz circuit is approximately proportional to its depth. Hence, the $CNOT$ count can be used as a measure of the run time of the quantum subroutine of the VQE, which also reflects the error accumulated by the quantum hardware. Due to the limited coherence times of NISQ computers, the $CNOT$ count can be considered as a primary cost metric.

In Figs. 5a,b we notice that the IQEB-VQE and the ADAPT-VQE perform similarly in terms of the number of iterations. This indicates that the IQEB-VQE and the ADAPT-VQE use approximately the same number of qubit and fermionic excitation evolutions, respectively, when constructing their respective ansätze. This is expected as the two types of excitation evolutions perform similarly in constructing electronic wavefunction ansätze. Since qubit excitation evolutions are implemented by simpler circuits than fermionic excitation evolutions, the IQEB-VQE systematically outperforms the ADAPT-VQE in terms of ansatz circuit $CNOT$ count (Figs. 5e,f).

While the IQEB-VQE and the ADAPT-VQE require similar numbers of iterations (Fig. 5a,b), the IQEB-VQE requires up to twice as many variational parameters (Fig. 5e,f). This difference is due to the fact that the IQEB-VQE assigns one parameter to each qubit excitation evolutions in its ansatz, whereas the ADAPT-VQE assigns one parameter to a pair of spin-complement fermionic excitation evolutions.

In Figs. 5a,b,c,d, the IQEB-VQE converges faster, requiring systematically fewer iterations and variational parameters than the qubit-ADAPT-VQE. As suggested in Sec. IIB, this result is due to the fact that since single and double qubit excitation evolutions correspond to combinations of 2 and 8 Pauli string exponentials. Furthermore, in Figs. 5e,f the IQEB-VQE outperforms the qubit-ADAPT-VQE in constructing more $CNOT$ -efficient ansatz circuits, except for the initial low-accuracy iterations. Hence, the IQEB-VQE outperforms the qubit-ADAPT-VQE both in terms of circuit-efficiency and speed.

III. CONCLUSION

In this work, we investigated the use of qubit excitations to construct electronic VQE ansätze. We demonstrated numerically that an ansatz of qubit excitation evolutions can approximate a molecular electronic wavefunction comparably well to an ansatz of fermionic excitation evolutions. This similarity in encodability can be explained by the fact that, starting from the HF state, both fermionic and qubit excitation evolutions span the same Hilbert space, corresponding to real states with Hamming weight equal to the number of electrons. Our results suggest that, on their own, the Pauli- z strings, which measure the parity of the state and account for the anticommutation of the fermionic excitation operators, play little or no role in the variational flexibility of an electronic ansatz. Their practical functionality is limited to scenarios where measuring the parity can be used to form spin-complement pairs of fermionic excitation evolutions. Such spin-complement pairs can then be used to enforce parity conservation and reduce the number of variational parameters by up to a factor of 2 (as is done by the ADAPT-VQE). However, fermionic excitations are implemented by circuits whose size, in terms of $CNOT$ count, scales linearly (logarithmically) in the Jordan-Wigner (Bravyi-Kitaev) encoding with the system size, as opposed to qubit excitations, which enjoy the quantum-computational benefit of being implemented by fixed-size circuits. Therefore, for NIQS devices, where the number of CNOTs is a primary cost factor, qubit excitations are more suitable for constructing VQE electronic ansätze than fermionic excitations.

Motivated by the circuit efficiency of qubit excitations evolutions, we utilized them to construct the iterative qubit-excitation based variational quantum eigensolver (IQEB-VQE). The IQEB-VQE simulates molecular electronic ground states with a problem-tailored ansatz, grown iteratively by concatenating single and double qubit excitation evolutions. We benchmarked the performance of the IQEB-VQE with classical numerical simulations for the LiH and BeH₂ molecules. In particular, we compared the IQEB-VQE to other competitive iterative VQE algorithms, in particular the original ADAPT-VQE, and its more slowly converging, but more circuit-efficient younger cousin, the qubit-ADAPT-VQE. Compared to the ADAPT-VQE, the IQEB-VQE requires approximately twice as many variational parameters, but constructs systematically more *CNOT*-efficient ansätze, owing to the use of qubit excitation evolutions. We also found that the IQEB-VQE outperforms even the qubit-ADAPT-VQE, in constructing more *CNOT*-efficient ansätze. The primary reason for this is that qubit-excitation evolutions allow for efficient local circuit optimizations, whilst the more rudimentary Pauli string exponentials, utilized by the qubit-ADAPT-VQE, do not. Furthermore, the IQEB-VQE converges faster, requiring systematically fewer variational parameters, and correspondingly fewer iterations, than the qubit-ADAPT-VQE. These results imply that the IQEB-VQE is not only more circuit-efficient, but also faster than the qubit-ADAPT-VQE, which to our knowledge was previously the most circuit-efficient, scalable VQE algorithm for molecular simulations.

As further work, three potential upgrades to the IQEB-VQE can be considered. First, the ansatz element pool of the IQEB-VQE can be expanded to include non-symmetry-preserving terms as suggested in Ref. [62]. Potentially, this expanded pool could further improve the speed of convergence and boost the resilience to symmetry-breaking errors of the IQEB-VQE. Second, we suggest the use of methods from Ref. [40] to “prune”, from the already constructed ansatz, ansatz elements that have little contribution to the energy reduction. This could potentially optimize further the constructed ansatz. Third, we suggest the expansion of the IQEB-VQE functionality to enable estimations of energies of low lying excited states.

Finally, we note that there might be hardware-efficient ansätze that require shallower circuits than the ansätze constructed by the IQEB-VQE. However, as pointed out in the introduction of this paper, the classical optimization of such not-physically-motivated ansätze, is unlikely to be tractable for large molecules. To the best of our knowledge, the IQEB-VQE is the most circuit-efficient, scalable VQE algorithm for molecular simulations. We believe it represents a significant step towards implementing molecular simulations on NISQ computers.

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Figures

Figure 1

Circuit implementing the single qubit excitation evolution of equation (21).

Figure 2

Circuit implementing the double qubit excitation evolution of equation (22).

Figure 3

Energy convergence for the ground states of the LiH and BeH₂ molecules in the STO-3G orbital basis set (see Manuscript file for for figure caption)

Figure 4

Energy dissociation curves for the LiH and BeH₂ molecules in the STO-3G orbital basis set. (see Manuscript file for for figure caption)

Figure 5

Energy convergence plots for the ground states of LiH and BeH₂ in the STO-3G orbital basis set. (see Manuscript file for for figure caption)

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