Accuracy assessment of variational quantum computing Ansätze across a database of electronic structure problems

Ruhee D'Cunha and T. Daniel Crawford
Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

Mario Motta and Julia E. Rice
IBM Quantum, IBM Research Almaden, 650 Harry Road, San Jose, CA 95120, USA

Advances in quantum computation for electronic structure, and particularly heuristic quantum algorithms, create an ongoing need for databases to characterize and compare the performance of these methods. Here we present a database of electronic structure problems, containing energies, properties, and quantum circuits implementing the variational quantum eigensolver with different Ansätze developed for calculations on quantum hardware. We compare these results with those from unitary coupled-cluster with singles and doubles and full configuration interaction. This proposed database should be useful in the understanding and development of variational Ansätze, non-variational quantum algorithms, strategies to encode fermionic degrees of freedom to qubits, and error mitigation techniques for quantum hardware.

I. INTRODUCTION

Recent years have witnessed remarkable research in the simulation of many-body quantum systems by quantum computing algorithms [1–6]. A prominent application targeted by quantum algorithms is the electronic structure (ES) problem, namely solving for the ground- or low-lying eigenstates of the electronic Schrödinger equation for atoms, molecules, and materials. Research in this direction has delivered promising results in the calculation of potential energy curves, ground- and excited-state energies, and correlation functions [7–10] for various instances of the ES problem.

Notwithstanding these rapid developments, the behavior of quantum computing algorithms for the ES problem remains to be understood and established, and such a situation is due to several factors. For example: (1) different research groups demonstrate existing or novel algorithms on different instances of the ES problem, which makes comparative algorithm analysis difficult; (2) the design and implementation of novel quantum computing algorithms are often coupled to their demonstration on contemporary quantum hardware, which restricts the domain of potential applications to very small numbers of electrons and orbitals; (3) the limitations of classical simulators have similarly resulted in simulations mostly restricted to very small instances of the ES problem so that the observed algorithmic behavior is not guaranteed to generalize to larger or more complex instances; (4) even when quantum algorithms have known limitations, their numeric assessment is often limited by the immaturity of contemporary quantum computational platforms, which makes it difficult to gauge the severity of such limitations.

Overcoming these limiting factors can contribute to the understanding of the nature, performance, and limitations of quantum algorithms for the ES problem, and bring progress in their design and assessment. Useful steps towards this goal are: to establish a database of problems (i.e. a Hamiltonian and a set of target observables, the goal is to compute energies and target observables on the ground- or excited-states of the Hamiltonian) which researchers can use to test quantum algorithms; to propose a set of metrics to quantify algorithmic performance, and support an objective comparison of algorithmic behavior; to establish a database of results (i.e. quantum circuits out of which ground- or excited-state properties can be measured) which researchers can consult to compare quantum algorithms.

The proposed problems should be non-trivial (e.g. with more than 2 electrons and more than 2 spatial orbitals), to ensure meaningful assessments of algorithmic behavior. These problems should be studied with classical simulators of quantum devices and/or actual quantum devices. Using classical simulators, theoreticians can explore the properties of a methodology assuming an ideal or noisy quantum device. Experimentalists, on the other hand, can independently test a set of well-defined quantum circuits motivated by the solution of instances of the ES problem.

In this work, we present a set of instances of the ES problem, and perform an assessment of Ansätze used in variational ground-state quantum simulations [6, 11], using classical simulators of quantum hardware. In the assessment of quantum algorithms, where possible we will use the difference between the computed and exact (or full Configuration Interaction, FCI) ground-state energy as an indicator of algorithmic quality, along with quantities signaling the breaking of Hamiltonian symmetries, a conceptually important but often overlooked aspect of quantum simulations. We will use a variety of indicators of algorithmic cost, related to the optimization of variational parameters (number of variational parameters, cost of energy evaluation) and to the quantum circuits leading to the calculation of energies and properties (number of qubits, gates, circuit depth).
As illustrative applications, we employ the database presented here to test a new variational Ansatz termed *cascade* against existing methods, to compare open- and closed-shell implementations of the unitary coupled-cluster with singles and doubles [12, 13], and to compare two different strategies to encode fermionic degrees of freedom to qubits.

The remainder of this work is organized as follows: in Section II we describe the proposed database, and the algorithms we tested and compared; in Section III we present the results of this study; conclusions and perspectives for future work are described in Section V. A supplementary information (SI) contains additional computational and algorithmic details.

II. METHODS

In this section, we present the problems constituting the database studied in this work, and the metrics used to establish algorithm performance and computational cost.

A. Target problems

In this work, we focused on a set of four molecular species, namely BH, HF, BeH$_2$, and H$_2$O. The BH, HF, BeH and OH bond lengths $R$ varied between 0.7-3.5, 0.7-4.5, 0.7-4.5, and 0.7-3.3 Å respectively. These molecular species, proposed in previous work [8, 14], allow testing of quantum algorithms along the breaking of one (BH and HF) or two (BeH$_2$, and H$_2$O) covalent bonds, and in the presence of dominant dynamic (small $R$) or static (medium to large $R$) electronic correlation.

For each species, a restricted closed-shell Hartree-Fock calculation was performed, as specified in the SI. The core 1s orbital was frozen and the Born-Oppenheimer Hamiltonian

$$\hat{H} = E_0 + \sum_{pq \sigma \rho \sigma'} \langle pq | rs \rangle \left( \hat{c}^\dagger_{p\sigma} \hat{c}_{q\sigma'} + \text{H.c.} \right)$$

was computed, along with the number (of electrons), spin-$z$, and total spin operators

$$\hat{N} = N_f + \sum_{p \sigma} \hat{c}^\dagger_{p\sigma} \hat{c}_{p\sigma}, \quad \hat{S}_z = \sum_{p \sigma} (-1)^\sigma \hat{c}^\dagger_{p\sigma} \hat{c}_{p\sigma}, \quad \hat{S}^2 = \left[ \sum_p \hat{c}^\dagger_{p\sigma} \hat{c}_{p\sigma} \right] \left[ \sum_q \hat{c}^\dagger_{q\tau} \hat{c}_{q\tau} \right] + \hat{S}_z (\hat{S}_z + 1)$$

where $N_f = 2$ is the number of electrons in frozen (closed-shell) orbitals. In this study we focused on a minimal STO-6G basis, to ensure a number of orbitals and qubits were within reach of contemporary classical simulators of quantum circuits.

B. Qubit encodings

In the majority of quantum algorithms for contemporary devices, the Hamiltonian Eq. (1) and the auxiliary operators Eq. (2) are mapped onto linear combinations

$$\hat{H} = \sum_{i=0}^{n_q-1} c_i \sigma_{v_i w_i}, \quad \sigma_{v w} = \bigotimes_{k=0}^{n_q-1} \sigma_{v_k w_k}$$

of Pauli operators acting on a certain number $n_q$ of qubits. In Equation (3) $\sigma_{00,01,10,11} = 1, X, Z, Y$ is a single-qubit Pauli operator, $c_i$ a real-valued coefficient, and the summation ranges over $n_p$ terms.

The rationale behind this choice is that a Pauli operator acting on $k$ qubits can be exponentiated with a circuit of up to $4k - 1$ gates and measured using a single layer of $k$ single-qubit gates, which makes the representation (3) suitable for contemporary quantum devices.

In this study, we employed both first-quantization and second-quantization encodings. First-quantization establishes a one-to-one mapping between the Hilbert space spanned by a set of $K$ space- and spin-adapted configuration state functions (CSFs) and the Hilbert space of $n_q = \lceil \log_2 K \rceil$ qubits. Second-quantization establishes a one-to-one mapping between the Fock space of electrons in $M$ spatial orbitals and the Hilbert space of $n_q = 2M$ qubits. First-quantization encodings ensure access to automatically symmetry-adapted many-electron wavefunctions and require fewer qubits than their second-quantization counterparts, $\lceil \log_2 K \rceil \leq 2M$. Furthermore, first-quantization encodings lead to sparse
operators: such operators can be efficiently exponentiated [15], and the exponential operators can then be used to measure their expectation values with the quantum phase estimation algorithm [16]. Notwithstanding these desirable features of first-quantization encodings, the exponentiation of sparse operators and the use of such exponentials inside quantum phase estimation or variational algorithms are expensive operations, beyond the capabilities of contemporary quantum devices. On these devices, operators are more conveniently expressed as linear combinations of a certain number $n_p$ of Pauli operators acting on $n_q$ qubits. However, such representations lead to an $n_p$ that scales exponentially with $n_q$. Additional technical details are provided in the SI.

Second-quantization encodings give rise to a compact representation of the Hamiltonian and of auxiliary operators as linear combinations of a polynomial number of Pauli operators [17, 18], but allow the possibility that Hamiltonian symmetries are broken, for multiple reasons discussed in Section II D. The issue of symmetry-breaking can be alleviated in various ways. For example, one can restrain the expectation value of a target observable (e.g. spin) to a desired value by performing a variational optimization that includes a penalty term. While this strategy does not ensure access to an eigenstate of the target observable, deviations from an eigenstate can be assessed by computing variances, for example. Another way to alleviate symmetry-breaking is to project a wavefunction inside a target subspace of the Hilbert space. This projection removes symmetry-breaking by construction, and allows assessment of the severity of symmetry-breaking by computing the expectation value of the projector.

In this work, in second-quantization simulations, we alleviated symmetry-breaking by combining the parity mapping with the two-qubit and tapering techniques [19, 20]. The former removes two qubits to ensure conservation of the parity operators $(-1)^{\hat{S}_z}$ and $(-1)^{\hat{S}_y}$, and the latter identifies a subgroup of the molecular orbital symmetry group isomorphic to $\mathbb{Z}_2^k$ and removes $k$ qubits to ensure the simulated wavefunctions lie in a target irreducible representation of the identified abelian subgroup [19, 20]. The species studied here have molecular orbital symmetry groups ($C_{sv}$ for BH and HF, $D_{2oh}$ for BeH$_2$ and $C_2v$ for H$_2$O) isomorphic to $\mathbb{Z}_2 \times \mathbb{Z}_2$, so that the combined use of two-qubit reduction and tapering leads to $n_q = 2M - 4$ qubits for all molecules except BeH$_2$ where $n_q = 2M - 5$ qubits.

C. Target variational Ansätze

In this study, we elected to explore the behavior of the variational quantum eigensolver (VQE) algorithm [11], due to its widespread adoption in the community. This method defines a set of Ansatz states approximating the ground-state of a target Hamiltonian, of the form

$$|\Psi(\theta)\rangle = \hat{U}(\theta)|\Phi_0\rangle,$$  \hspace{1cm} (4)

where $\theta \in [0, 2\pi)^{n_\alpha}$ is an array of angles that define a parametrized quantum circuit $\hat{U}(\theta)$, applied to a register of $n_q$ qubits prepared in the standard initial state $|\Phi_0\rangle$, for example $|\Phi_0\rangle = |0\rangle^\otimes n_q$. The best approximation to the ground-state in the set of Ansatz states is found by minimizing the energy

$$E_{\text{VQE}}(\theta) = \langle \Psi(\theta)|\hat{H}|\Psi(\theta)\rangle$$  \hspace{1cm} (5)

as a function of the parameters $\theta$ using a classical optimization algorithm. Once the parameters are optimized, auxiliary observables can be measured (see Eq. (2)), yielding results

$$X_{\text{VQE}}(\theta) = \langle \Psi(\theta)|\hat{X}|\Psi(\theta)\rangle.$$  \hspace{1cm} (6)

This algorithmic workflow, termed variational quantum eigensolver (VQE) in the quantum simulation literature, is a heuristic technique for ground-state approximation. Its accuracy and computational cost, as discussed in Section II D, are determined by the details of the circuit $\hat{U}(\theta)$. In the remainder of this Section, we will present the Ansätze assessed in the present work.

1. Unitary coupled-cluster with singles and doubles

The quantum unitary coupled-cluster (q-UCC) method is based on the exponential Ansatz, i.e., the exact wavefunction is written as [21–26]

$$|\Psi_{gs}\rangle = e^{T-T^\dagger}|\Phi_0\rangle,$$  \hspace{1cm} (7)
where $\Phi_0$ is typically an independent-particle function (here, the Hartree-Fock state) and $\hat{T}$ is a cluster operator which, at the singles and doubles level (q-UCPSSD) is truncated to

$$
\hat{T} = \hat{T}_1 + \hat{T}_2 , \quad \hat{T}_1 = \sum_{i\sigma} t_{i\sigma}^{\alpha} \hat{c}_{i\alpha}^{\dagger} \hat{c}_{i\sigma}^{\phantom{\dagger}} , \quad \hat{T}_2 = \frac{1}{4} \sum_{abij\gamma\tau} t_{\gamma\tau}^{a\sigma b\sigma} \hat{c}_{a\sigma}^{\dagger} \hat{c}_{b\sigma}^{\phantom{\dagger}} \hat{c}_{j\tau}^{\dagger} \hat{c}_{i\gamma}^{\phantom{\dagger}},
$$

where $t_{i\sigma}^{\alpha}$ and $t_{a\sigma b\sigma}^{\gamma\tau}$ are a set of unknown cluster coefficients. We have adopted the convention that $i, j, k, l$ and $a, b, c, d$ refer to occupied and unoccupied orbitals in the reference state $\Phi_0$ respectively. It should be noted that the form Eq. (8), presented in previous literature [27] along with the corresponding quantum circuit, is an unrestricted Ansatz, which is not guaranteed to yield an eigenfunction of total spin.

If a closed-shell spin-adapted formalism is used, then, following Paldus [28] and Scuseria et al [12, 13], one needs

$$
t_{i\sigma}^{\alpha} = t_{i\beta}^{\alpha} = t_{i}^{\alpha},
$$

since the two other possible spin combinations are vanishing. Only 6 of the 16 possible spin combinations for the two-electron amplitudes are non-zero, namely

$$
t_{i\alpha j\beta}^{\alpha \beta} = t_{i\beta j\alpha}^{\alpha \beta} = t_{i\beta j\alpha}^{\beta \alpha} = \tilde{t}_{ij}^{ab}, \quad t_{i\alpha j\beta}^{\alpha \beta} = t_{i\beta j\alpha}^{\alpha \beta} = \tilde{t}_{ij}^{ab}, \quad t_{i\alpha j\beta}^{\alpha \beta} = t_{i\beta j\alpha}^{\alpha \beta} = \tilde{t}_{ij}^{ab}.
$$

Using the relations

$$
\tilde{t}_{ij}^{ab} = \tilde{t}_{ij}^{ba} + \tilde{t}_{ij}^{ab}, \quad \tilde{t}_{ij}^{ab} = -\tilde{t}_{ij}^{ba} = \tilde{t}_{ij}^{ab},
$$

one is left with only one set of independent two-electron amplitudes $\tilde{t}_{ij}^{ab}$ with $a \leq b$, $i \leq j$ and $(ai) \leq (bj)$. In addition to reducing the number of variational parameters, the use of a closed-shell spin-adapted formalism ensures that the cluster and total spin operators commute, $[\hat{T}, \hat{S}^2] = 0$. The exponential Eq. (7), however, cannot be implemented exactly at polynomial cost on a quantum computer. Instead, a Trotter approximation is required, which in turn leads to spin symmetry-breaking. The quantum circuits used to implement the q-UCPSSD Ansatz in a Jordan-Wigner representation are illustrated in Figure S3 of the SI.

2. Hardware-efficient $R_y$

![Quantum circuits implementing the linear- and full-connectivity $R_y$ Ansatz](image)

**FIG. 1.** Quantum circuits implementing the linear- and full-connectivity $R_y$ Ansatz, with $n_q = 4$ qubits and $n_r = 2$ repetitions (left, right respectively). The illustrated circuits have a computational basis state or a bit-string, i.e. a tensor product of the form $|x\rangle = \otimes_{k=1}^{n_q-1} |x_k\rangle$ with $x_k \in \{0, 1\}$, as initial state. $|0\rangle$ is the ground-state of a single qubit, and $|1\rangle$ can be prepared starting from a qubit in $|0\rangle$ by applying a single-qubit rotation of an angle $\pi$ around the $x$ axis of the Bloch sphere, $R_x(\pi) = \exp(-i\pi X/2)$.

Hardware-efficient Ansätze are families of wavefunctions designed with the primary goal to be compatible with the budget of contemporary quantum hardware in terms of available qubits, connectivity, native gates, and circuit depth. An example is the following $R_y$ Ansatz [8],

$$
|\Psi(\theta)\rangle = \prod_{k=1}^{n_q} \mathcal{R}(\theta_{k}^{n_q-1} \ldots \theta_{k}^{0}) \prod_{ij \in C} \mathcal{C}(\mathbf{NOT}_j) \mathcal{R}(\theta_{0}^{n_q-1} \ldots \theta_{0}^{0}) |\Phi_0\rangle , \quad \mathcal{R}(\theta_{i}^{n_q-i} \ldots \theta_{i}^{0}) = \prod_{i=0}^{n_q-i-1} R_{g,i}(\theta^i),
$$

where $|\Phi_0\rangle$ is an initial wavefunction (here, the restricted closed-shell Hartree-Fock state), $n_q$ is the number of qubits, $R_{g,i}(\theta) = \exp(-i\theta Y_i/2)$ is a $Y$-rotation (i.e. a rotation of an angle $\theta$ around the $y$ axis of qubit $i$’s Bloch sphere),
\(c_1\text{NOT}_j\) is a CNOT gate with control qubit \(i\) and target qubit \(j\), \(j\) a nearest-neighbor of \(i\), and \(n_r\) is an integer denoting the number of times a layer of entangling gates followed by a layer of \(Y\)-rotations is repeated.

In this study, we focused on the linear-connectivity and full-connectivity \(R_y\) Ansätze, given by

\[
C_{\text{linear}} = \{(i, i+1), i = 0 \ldots n_q - 2\}, \quad C_{\text{full}} = \{(i,j), i = 0 \ldots n_q - 1, i \leq j\}
\]

respectively. Examples of linear- and full-connectivity \(R_y\) Ansätze are shown in Figure 1. It is worth observing that other choices of connectivity are possible, and that Eq. (13) exemplifies two opposite regimes.

3. Cascade

\[
|\psi(\theta)\rangle = \prod_{k=1}^{n_r} \mathcal{R}(\theta_k^{n_q-1} \ldots \theta_k^0) C \mathcal{R}(\theta_k^0 \ldots \theta_k^{n_q-1}) |\psi_0\rangle,
\]

where \(C = c_{n_q-2}\text{NOT}_{n_q-1} \ldots c_0\text{NOT}_1\) is a ladder of CNOT gates applied to adjacent qubits, and \(\mathcal{R}\) a product of \(Y\)-rotations, exactly as in the \(R_y\) Ansatz. As seen, the presence of \(C\) and \(C^\dagger\) ensures that \(\hat{U}(0) = \mathbb{I}\). Furthermore, as in other Ansätze [29, 30], given a wavefunction with \(n_r\) repetitions and optimized parameters \(\theta_{n_r}\), a wavefunction with \(n_r + 1\) repetitions can be initialized from the parameter configuration \(\theta_{n_r+1} = (\theta_{n_r}, 0)\) so that the VQE energy, unlike that from the \(R_y\) Ansatz, decreases monotonically with \(n_r\).

D. Metrics of algorithm performance

For the small problems studied here, the exact solution of the Schrödinger equation can be accessed using FCI. A natural metric to assess the accuracy of a variational simulation is therefore the difference between the computed and exact ground-state energy (in the same one-electron basis),

\[
\Delta E = E_{\text{VQE}}(\theta) - E_{\text{FCI}}.
\]

For larger problems, exact solutions are not available. A possible strategy to assess algorithmic performance in absence of FCI data is to synergistically deploy multiple independent numerical methods, and use agreement between different approaches as an indicator of accurate results or bias by common underlying approximations [31-34]. A related approach consists in taking methods other than FCI, when available, as reference. These methods should have a high level of accuracy established by numerical studies, as e.g. density matrix renormalization group (DMRG) [35].

Other metrics can be used along with Eq. (15). For example, the ES Hamiltonian has several symmetries, i.e. operators \(\hat{S}\) such that \([\hat{H}, \hat{S}] = 0\). In the presence of Hamiltonian symmetries, the search for Hamiltonian eigenfunctions has to be restricted to eigenspaces of Hamiltonian symmetries with known eigenvalues. Relevant Hamiltonian symmetries are the auxiliary operators Eq. (2) and, for the molecules studied in the present work, the group-state
lies in the eigenspaces of $\hat{S}_z$ and $\hat{S}_z^2$ with eigenvalue zero, and of $\hat{N}$ with eigenvalues 4 for BH and BeH$_2$ and 8 for HF and H$_2$O, since for all these species two electrons are in the frozen 1s orbital.

In general, a variational quantum simulation does not preserve Hamiltonian symmetries. To assess whether a variational simulation leads to symmetry-breaking, and to quantify its extent, we computed the deviations

$$\Delta N = N_{\text{VQE}}(\theta) - N_{\text{FCI}}, \quad \Delta S_z = S_z^{\text{VQE}}(\theta) - S_z^{\text{FCI}}, \quad \Delta S^2 = S^2_{\text{VQE}}(\theta) - S_{\text{FCI}}^2,$$

between the calculated and exact ground-state particle number, spin-$z$, and total spin.

In addition to the accuracy of a variational simulation, it is also important to quantify its computational cost. To this end we employed a tuple of values, namely: the number of qubits $n_q$, the number of repetitions $n_r$, the number of gates $n_g$, both (1 qubit, 2 qubit) and the depth $d$ of the variational circuit, the number of Pauli operators in the Hamiltonian $n_p$, and the number of variational parameters $n_{\theta}$. Note that the number of gates is not related to the hardware architecture, but rather reflects the number of gates in the circuit diagram. For example, full-$R_y$ will have many more gates when mapped to hardware with linear-connectivity.

### III. RESULTS

The overall strategy for the calculations performed in this work involved initial pre-processing by classical quantum chemistry codes on conventional computers as detailed in the SI, to generate optimized Hartree-Fock orbitals and Hamiltonian coefficients before performing computations with quantum simulators. The restricted Hartree-Fock (RHF) singlet state was chosen as the initial state for all of the calculations described here, since experience has indicated that this state is a good choice for various chemical problems [23].

Details about the molecular orbitals are in Figure S2 of the SI.

Having selected a set of single-electron orbitals for each studied species, we performed VQE computations with quantum simulators. We used IBM’s open-source Python library for quantum computing, Qiskit [36]. Qiskit provides tools for various tasks, for example creating quantum circuits and performing simulations. In particular, it contains an implementation of the VQE algorithm and a classical exact eigensolver algorithm (used to obtain the FCI energy) to compare results.

FIG. 3. Total energy, deviation between computed and exact total energy, electron number, total spin, and spin-$z$ (top to bottom) using the $R_y$ (with linear- and full-connectivity), cascade, and q-UCCSD Ansätze (left to right), for the BH molecule at the STO-6G level.
FIG. 4. Total energy, deviation between computed and exact total energy, electron number, total spin, and spin-\(z\) (top to bottom) using the \(R_y\) (with linear- and full-connectivity), cascade, and q-UCCSD Ansätze (left to right), for the HF molecule at the STO-6G level.

FIG. 5. Total energy, deviation between computed and exact total energy, electron number, total spin, and spin-\(z\) (top to bottom) using the \(R_y\) (with linear- and full-connectivity), cascade, and q-UCCSD Ansätze (left to right), for the BeH\(_2\) molecule at the STO-6G level.
Details about the natural orbitals from the classical exact eigensolver calculations are in Figure S2 of the SI.

We then minimized the expectation value of the Hamiltonian with respect to the parameters of our circuit. To carry out the minimization we employed the classical optimization method LBFGS [37, 38]. In many cases, to determine the lowest energy along the dissociation path, we performed multiple VQE calculations using different initial parameters. Once the VQE was complete, we obtained the optimized variational form and the estimate for the ground-state energy. In addition, we measured the set of auxiliary operators, see Eq. (2).

A. Second-quantization simulations

In Figures 3, 4, 5, and 6 we computed ground-state potential energy dissociation curves for the BH, HF, BeH₂, and H₂O molecules respectively, using a second-quantization encoding.

For all the molecules, bond lengths, and Ansätze studied here, energies typically decreased monotonically with Ansatz depth \( n_r \). As naturally expected, the q-UCCSD Ansatz outperformed hardware-efficient Ansätze, since it was constructed starting from the natural excitations of the system (i.e. electronic transitions from occupied to virtual orbitals), rather than from application-agnostic circuits.

q-UCCSD calculations are spin-unrestricted, employ the primitive Trotter approximation to exponentiate the cluster operator, with exponentials of singles before exponentials of doubles. This choice led to a spin-contaminated solution for H₂O at large \( R \), see Fig. 6. In Section III A 1, we compared different implementations of q-UCCSD, and observed that a proper singlet wavefunction can be obtained without any accuracy losses by using a restricted closed-shell implementation of q-UCCSD, Suzuki approximation, doubles before singles and \( n_r = 2 \) repetitions.

It should also be noted that potential energy curves from shallow hardware-efficient Ansätze, though always lying below the Hartree-Fock energy, have cusps. Since calculations were carefully converged, these cusps are not a product of unconverged parameters, but rather a genuine limitation of the underlying Ansätze, which stands to impact the computation of energy gradients.

The most challenging regime is the intermediate dissociation region \(( R \simeq 2-3 \text{ Å})\), where the energies from hardware-efficient Ansätze are more than 100 milliHartree above the FCI value and clearly display cusps. Such artifacts were especially pronounced for the BeH₂ and H₂O molecules, where two bonds are broken simultaneously.

Interestingly, the linear-connectivity \( R_y \) Ansatz typically outperforms its full-connectivity counterpart, achieving...
more accurate results with fewer quantum resources. Furthermore, a cascade Ansatz with \( n_r \) repetitions performs approximately as well as a linear-connectivity \( R_y \) Ansatz with \( 2n_r \) repetitions.

It should be noted that an inaccurate performance by hardware-efficient Ansätze is accompanied by a pronounced breaking of the spin symmetry: the total spin of low-depth \( R_y \) Ansätze evolves from \( S^2 = 0 \) at short \( R \) towards a mixture of either the triplet or quintuplet value (\( S^2 = 2, 6 \).) Ansatz inaccuracy and symmetry-breaking, however, are not perfectly correlated. The largest deviations between VQE and FCI energies occur in the intermediate dissociation region, where symmetry-breaking starts to develop due to larger static correlation; on the other hand, spin symmetry-breaking is most pronounced at dissociation (\( R \geq 3\text{Å} \)), where the VQE energy is in better agreement with FCI. In the dissociation limit, multiple excited-states with higher spin have the same energy as the singlet. We attribute the combination of pronounced symmetry-breaking and high accuracy of energies in the dissociation limits to the fact that simulations target high-spin states nearly degenerate with the singlet ground-state.

1. Comparison of q-UCCSD implementations

In Figure 7 we compare the energies and total spins of restricted closed-shell and unrestricted q-UCCSD, approximated with primitive Trotter and second-order Suzuki product formulas and \( n_r = 1 \) steps, with singles followed by doubles and doubles followed by singles, for the \( \text{H}_2\text{O} \) molecule at the STO-6G level.

As seen, the unrestricted Ansatz yields lower energies at large \( R \), albeit with a significant spin contamination (a phenomenon analogous to the Coulson-Fischer [39] instability of mean-field theories). The restricted Ansatz, though leading to higher energies, features a modest spin contamination entirely caused by the Trotter approximation,

\[
e^{\hat{T} - \hat{T}^\dagger} = e^{\sum_\mu c_\mu (\hat{O}_\mu - \hat{O}_\mu^\dagger)} \approx \prod_\mu e^{\frac{t_\mu (\hat{O}_\mu - \hat{O}_\mu^\dagger)}{n_r}}, \quad e^{\frac{t_\mu (\hat{O}_\mu - \hat{O}_\mu^\dagger)}{n_r}} \approx \prod_i e^{\frac{t_\mu c_\mu \sigma_{\nu_i \omega_i}}{n_r}},
\]

(17)

where \( n_r \) is the number of Trotter steps and \( \sum_\epsilon c_\mu \sigma_{\nu_i \omega_i} \) is a qubit representation of \( \hat{O}_\mu - \hat{O}_\mu^\dagger \). Symmetry-breaking phenomena are milder when a second-order Suzuki product formula is used, and deviations with FCI are more modest when doubles are followed by singles. This is not unexpected, since the mean-field reference state couples with doubles due to Brillouin’s theorem.

Figure 8 shows \( n_r = 2 \) repetitions. As expected, the quality of restricted energies is very high, and the extent of spin contamination is considerably milder than in the case of an unrestricted implementation, and completely vanishes when doubles are followed by singles.

![FIG. 7. Deviation between computed and exact energy (top) and total spin (bottom), for the restricted closed-shell (left) and unrestricted (right) q-UCCSD Ansätze with \( n_r = 1 \) repetitions, for the \( \text{H}_2\text{O} \) molecule at the STO-6G level, using Trotter and Suzuki approximations (warm, cold colors) and with singles followed by doubles and doubles followed by singles (light, dark colors).](image-url)
FIG. 8. Deviation between computed and exact energy (top) and total spin (bottom), for the restricted closed-shell (left) and unrestricted (right) q-UCCSD Ansätze with \( n_r = 2 \) repetitions, for the H\(_2\)O molecule at the STO-6G level, using Trotter and Suzuki approximations (warm, cold colors) and with singles followed by doubles and doubles followed by singles (light, dark colors).

2. Comparison of calculations with highest \( n_r \).

Agreement with FCI within 1.6 milliHartree (1 kcal/mol) and smoother potential energy curves are only achieved by increasing \( n_r \) to the values listed in Table I. The energies of such Ansätze are shown in Figure 9. As seen, 1.6 milliHartree accuracy was reached for all molecules except for BeH\(_2\) with \( R_y \) Ansatz and full-connectivity, where even \( n_r = 10 \) repetitions lead to energies more than 1.6 milliHartree above FCI. To achieve 1.6 milliHartree accuracy, q-UCCSD calculations required \( n_r = 1 \) repetitions for BH, HF and \( n_r = 2 \) repetitions for BeH\(_2\), H\(_2\)O. This is because in the latter cases, two covalent bonds are broken simultaneously, and a second repetition of the q-UCCSD Ansatz includes the effect of disconnected quadruple excitations.

The computational cost of the second-quantization simulations is listed in Table II. The linear-connectivity \( R_y \), full-connectivity \( R_y \) and cascade Ansätze have \( n_\theta = n_q(n_r + 1) \), \( n_\theta(n_r + 1) \), \( n_q(2n_r + 1) \) parameters respectively, \( n_q = (n_\theta, n_q), (n_\theta, n_r(n_q - 1)n_q/2), (n_\theta, 2n_r n_q) \) single-qubit and CNOT gates respectively, and \( d = n_r(n_q + 1) + 1 \),

FIG. 9. Deviation between computed and exact total energy for the BH, HF, BeH\(_2\) and H\(_2\)O molecules at the STO-6G level (counterclockwise) using the \( R_y \) (with linear- and full-connectivity), cascade, and q-UCCSD Ansätze (red circles, orange squares, green crosses, and blue markers) with the highest computed number of repetitions.
TABLE I. Lowest number of repetitions \( n_r \) for which VQE energies are in agreement with FCI energies within 1.6 milliHartree (1 kcal/mole), for molecules and Ansätze studied with second-quantization simulations.

| Molecule | \( n_e (N_\alpha, N_\beta) \) | \( m \) | \( n_q \) | Ansatz \( n_\theta \) | \( n_g \) | \( d \) |
|----------|-------------------------------|------|------|----------------|------|------|
| BH       | (4,4)                         | 5    | 6    | 231            | 12   | (14,5) | 8    |
| HF       | (4,4)                         | 5    | 6    | 231            | 12   | (14,15) | 12   |
| BeH\(_2\) | (2,2)                         | 6    | 7    | 268            | 14   | (15,6) | 8    |
| H\(_2\)O | (3,3)                         | 5    | 6    | 216            | 12   | (15,15) | 12   |

TABLE II. Computational cost of second-quantization simulations carried out in the present work. \( n_e = (N_\alpha, N_\beta) \), \( m \), \( n_q \), and \( n_p \) denote numbers of active electrons (spin-up and -down), spatial orbitals, qubits, and Pauli operators in the Hamiltonian, respectively. \( n_\theta \), \( n_g \), and \( d \) denote numbers of parameters, gates (single- and two-qubit), and circuit depth. For simplicity, we illustrate the case of \( n_r = 1 \) repetitions. The full cost of the simulations can be obtained by combining these data with those in Table I.

\( n_r (n_q - 1) n_q / 2 + 1 \), \( n_r (2n_q + 1) + 1 \) respectively. For simplicity, we illustrate the case of \( n_r = 1 \) repetitions. However, note that the full cost of the simulations can be obtained by combining these data with those in Table I.

B. First-quantization simulations

We investigated two schemes for first-quantization simulations since the number of configuration state functions, \( K \), is unlikely to be a power of 2, a requirement for one-to-one mapping to qubits. In the “trimming” scheme, we chose \( n_q \) such that \( 2^{n_q} \) is the largest power of 2 less than \( K \). In the “padding” scheme, we chose \( n_q \) such that \( 2^{n_q} \) is the smallest power of 2 greater than \( K \). (See the Appendix for details on the two different schemes).

In Figure 10 we computed ground-state potential energy curves for the BH, HF, BeH\(_2\), and H\(_2\)O molecules (left to right), using the cascade Ansatz and the “trimming” scheme. Calculations carried out under such a scheme do not exhibit breaking of the particle number, spin, or point-group symmetry, and the trimming leads to further qubit reduction. As a result, cascade simulations with \( n_r = 3 \) or greater agree with the exact ground-state energy of the trimmed Hamiltonian within 25 microHartree, for all molecules and geometries. However, the trimming itself leads to a deviation between the FCI energy of the trimmed and that of the original first-quantized Hamiltonian, which is up to 3 milliHartree for BeH\(_2\) and up to 0.3 milliHartree for BH.

The computational cost of the first-quantization simulations shown in Figure 10 is listed in Table III. The number of qubits is less than in second-quantization, c.f. Table II. However, the Hamiltonian measurement is more expensive, a manifestation of the fact that expanding the first-quantization Hamiltonian in the Hilbert-Schmidt basis requires up to \( 4^{n_q} \) Pauli operators (see Appendix).
We illustrate the case of quantization encoding with padding and a cascade Ansatz optimized with the variation-after-projection scheme.

FIG. 10. Total energy, deviation between computed and exact energy, and energy error from the trimming procedure (top to bottom) for the BH, HF, BeH$_2$ and H$_2$O molecules at the STO-6G level (left to right) using the cascade Ansatz.

| molecule  | $n_e (N_\alpha, N_\beta)$ | $m$ | $n_q$ | $n_p$ | Ansatz | $n_q$ | $n_p$ | $d$ |
|-----------|---------------------------|-----|-------|-------|--------|-------|-------|-----|
| BH        | (4,4)                     | 5   | 4     | 136   | cascade (44, 40) | 41   |
| HF        | (4,4)                     | 5   | 3     | 36    | cascade (33, 20) | 31   |
| BeH$_2$   | (2,2)                     | 6   | 5     | 528   | cascade (55, 40) | 51   |
| H$_2$O    | (4,4)                     | 6   | 5     | 528   | cascade (55, 40) | 51   |

TABLE III. Computational cost of first-quantization simulations carried out in the present work, using the trimming scheme. $n_e = (N_\alpha + N_\beta)$, $m$, $n_q$, and $n_p$ denote numbers of active electrons (spin-up and -down) orbitals, qubits, and Pauli operators in the Hamiltonian, respectively. $n_p$, $n_q$, and $d$ denote numbers of parameters, gates (single- and two-qubit), and circuit depth. We illustrate the case of $n_r = 5$ repetitions.

FIG. 11. Total energy, deviation between computed and exact energy, and squared-norm of the physical component of the wavefunction (top to bottom) for the BH, HF, BeH$_2$ and H$_2$O molecules at the STO-6G level (left to right) using a first-quantization encoding with padding and a cascade Ansatz optimized with the variation-after-projection scheme.
In Figures 11 and 12 we computed ground-state potential energy curves for the BH, HF, BeH₂, and H₂O molecules (left to right), using the “padding” scheme, detailed in the Appendix, where \( K \leq 2^{n_e} \). Calculations carried out under such a scheme can exhibit breaking of the particle number, spin, or point-group symmetry and so spin projection is required, either before or after the optimization. These figures illustrate the cascade and linear-connectivity \( R_y \) Ansätze with the variation-after-projection optimization, since the variation-after-projection optimization was determined to be more effective than the projection-after-variation procedure. While the cascade calculations have an accuracy roughly comparable with that of the “trimmed” calculations shown in Figure 10, the \( R_y \) Ansatz reaches milliHartree accuracy featuring multiple cusps.

The squared-norm \( P \) of the physical component of the wavefunction reaches values as small as \( 2 \cdot 10^{-1} \) and \( 1 \cdot 10^{-2} \) for cascade and \( R_y \) respectively. Such a phenomenon indicates that, for both Ansätze, lowering the energy is accompanied by leakage of the wavefunction outside the physical subspace.

The computational cost of the first-quantization simulations shown in Figures 11 and 12 is listed in Table IV. The number of qubits is larger for the padding than for the trimming scheme (c.f. Table III). Consequently, the Hamiltonian measurement is more expensive than in both second-quantization and first-quantization with trimming.
IV. DATABASE

Having described a set of calculations pertaining to a number of heuristic Ansätze (linear-connectivity $R_y$, full-connectivity $R_y$, cascade) and compared the results with those of q-UCCSD and FCI, we outline the schema of a database which can store the results in a useful way and which can be extended to provide value to other researchers.

The schema is illustrated in Figure 13. The results in this study, organized with respect to this schema, can be publicly accessed on GitHub at [40]. Details of the format of the data within the folders can be found in the SI.

V. CONCLUSIONS AND FUTURE WORK

In this work, we assessed the performance of variational quantum computing Ansätze across a database of electronic structure problems. We used the proposed database to investigate the balance between computational cost, accuracy, and symmetry-breakings of hardware efficient Ansätze; to test a new variational Ansatz termed cascade; to compare implementations of q-UCCSD differing in representation of the cluster operator (unrestricted, restricted closed-shell) together with approximate implementation of the unitary coupled-cluster circuit (Trotter and Suzuki product formula, ordering of singles and doubles); and to compare first- and second-quantization strategies to encode fermionic degrees of freedom to qubits.

While this study offers a concrete and numerical assessment of computational cost and algorithmic performance, it should only be regarded as the starting point of a broader investigation. Possible extensions include: (i) with respect to algorithms: other variational Ansätze [30, 41, 42], algorithms other than VQE [41, 43–46]; (ii) with respect to electronic structure problems: open-shell systems (e.g. spin-unbalanced, radicals), non-minimal bases (e.g. Pople and/or correlation-consistent), different properties (e.g. electrostatic [10]); (iii) with respect to quantum computing: the use of classical software emulating decoherence and actual quantum devices, in either case focusing on the improvement brought by error mitigation techniques [47–50] to physically relevant observables (e.g. dissociation energies and spin).

The present study is accompanied by a database to integrate possible future extensions. We believe the present study will be a useful contribution in the understanding and development of quantum computing algorithms for electronic structure problems.

ACKNOWLEDGMENTS

MM and JER acknowledge the IBM Research Cognitive Computing Cluster service for providing resources that have contributed to the research results reported in this paper. RD and TDC were supported by the U.S. National Science Foundation through grant CHE-2154753.
Appendix A: First-quantization encoding

To carry out simulations in first-quantization, we introduce [51–55] a basis of Slater determinants \( \{x_i\}_{i=0}^{n_e} \) of \( n_e = N_\alpha + N_\beta \) electrons in \( M \) spatial orbitals (specifically the MOs from a restricted closed-shell HF simulation), i.e. of electronic configurations. We then select configurations in the same irrep of the molecular orbital symmetry group to which the HF state belongs, i.e. the totally symmetric irrep in the abelian point-group relevant to the present work. In the basis of such configurations, we construct the Hamiltonian and total spin matrices

\[
H_{ij} = \langle x_i | \hat{H} | x_j \rangle , \quad S_{ij} = \langle x_i | \hat{S}_z^2 | x_j \rangle .
\]

We diagonalize the total spin matrix obtaining a basis of configuration state functions (CSFs), \( S_{ij} \phi_{\mu} = s_\mu \phi_{\mu} \), out of which we select singlet CSFs (\( \mu \) such that \( s_\mu = 0 \)). Finally, we project the Hamiltonian matrix in the singlet subspace, constructing the operator

\[
\hat{H} = \left[ \sum_{\mu=0}^{K-1} |\phi_\mu\rangle \langle \phi_\mu| \right] \hat{H} \left[ \sum_{\nu=0}^{K-1} |\phi_\nu\rangle \langle \phi_\nu| \right].
\]

Where \( K \) is the number of singlet CSFs in the target irrep. In some cases, \( K = 2^n_q \) for some number of qubits \( n_q \), in which case \( \hat{H} \) can be represented as a qubit operator by expanding it on the Hilbert-Schmidt basis,

\[
\hat{H} = \sum_{vw} \sigma_w \frac{\text{Tr}[\sigma_v \hat{H}]}{2^n_q}.
\]

In general, \( 2^{n_q-1} < K < 2^n_q \) for some integer \( n_q \), and \( \hat{H} \) can be represented as a qubit operator in at least two ways:

1. "trimming" the matrix \( \langle \phi_\mu| \hat{H} |\phi_\nu\rangle \) removing a subset of \( K - 2^{n_q-1} \) CSFs. In the present work, we elected to compute the ground-state wavefunction of \( \hat{H} \), \( |\psi_0\rangle = \sum_\mu c_\mu |\phi_\mu\rangle \) and to remove the CSFs \( \phi_\mu \) with smallest coefficients in magnitude \( |c_\mu| \).

2. by introducing a set of \( 2^n_q - K \) additional basis functions, called "unphysical" basis function, padding the matrix \( \hat{H}_{\mu\nu} \) to produce a \( 2^n_q \times 2^n_q \) matrix, and introducing a projector onto the span of "physical" basis functions,

\[
J_{\mu\nu} = \begin{pmatrix} \hat{H} & 0 \\ 0 & \lambda \mathbb{I} \end{pmatrix}, \quad \Pi_{\mu\nu} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}.
\]

In this work, we chose \( \lambda = 10^4 \hbar \).

1. Variation-after-projection (VAP) and projection-after-variation (PAV) schemes

Second-quantization make use of the full Fock space of electrons in \( m \) spatial orbitals. As observed in Section III, this choice can lead to various symmetry-breaking phenomena, due to qubit wavefunctions having a component outside the target subspace (e.g. \( n_e = N_\alpha + N_\beta \), \( S_z = (N_\alpha - N_\beta)/2 \), and \( S^2 = S_z(S_z + 1)\hbar \)).

When first-quantization calculations are carried out within the "padding" scheme, a form of symmetry-breaking can occur, due to qubit wavefunctions having a component outside the "physical" subspace (the image of the projector \( \hat{\Pi} \)). To avoid such a symmetry-breaking, two schemes can be deployed:

1. Variation-after-projection (VAP) [56, 57]. The following cost function is optimized,

\[
E_{\text{vap}}(\theta) = \frac{\langle \Psi(\theta) | \hat{H} \hat{\Pi} \hat{\Pi} | \Psi(\theta) \rangle}{\langle \Psi(\theta) | \hat{\Pi} | \Psi(\theta) \rangle},
\]

i.e. the wavefunction \( |\Psi(\theta)\rangle \) is first projected in the physical subspace, and the energy is then optimized.

2. Projection-after-variation (PAV) [58–60]. The cost function

\[
E_{\text{pav}}(\theta) = \langle \Psi(\theta) | \hat{J} | \Psi(\theta) \rangle
\]

is optimized, and the energy is then computed with Eq. (A5), i.e. the energy is first optimized, and then re-evaluated over a projected wavefunction.
FIG. 14. Total energy, deviation between computed and exact energy, and squared-norm of the unphysical component of the wavefunction (top to bottom) for the BeH$_2$ molecule at the STO-6G level, using a first-quantization encoding with padding and a cascade Ansatz optimized with the projection-after-variation scheme.

In Section III we focused on the VAP scheme, as it yields more accurate results than PAV. The PAV scheme is illustrated in Figure 14 on the BeH$_2$ molecule and the cascade Ansatz. Comparison against the third column of Figure 11 clearly shows the greater accuracy of the VAP scheme. It should be noted, however, that both schemes may yield very inaccurate results when the qubit wavefunction lies predominantly outside the physical subspace, i.e. when $P = \langle \Psi(\theta)|\hat{\Pi}|\Psi(\theta)\rangle \ll 1$.

[1] I. M. Georgescu, S. Ashhab, and F. Nori, Rev. Mod. Phys 86, 153 (2014).
[2] Y. Cao, J. Romero, J. P. Olson, M. Degroote, P. D. Johnson, M. Kieferová, I. D. Kivlichan, T. Menke, B. Peropadre, N. P. Sawaya, et al., Chem. Rev 119, 10856 (2019).
[3] B. Bauer, S. Bravyi, M. Motta, and G. Kin-Lic Chan, Chem. Rev 120, 12685 (2020).
[4] S. McArdle, S. Endo, A. Aspuru-Guzik, S. C. Benjamin, and X. Yuan, Rev. Mod. Phys 92, 015003 (2020).
[5] M. Motta and J. E. Rice, WIREs Comput. Mol. Sci 12, e1580 (2021).
[6] M. Cerezo, A. Arrasmith, R. Babbush, S. C. Benjamin, S. Endo, K. Fujii, J. R. McClean, K. Mitarai, X. Yuan, L. Cincio, et al., Nat. Rev. Phys 3, 625–644 (2022).
[7] P. J. O’Malley, R. Babbush, I. D. Kivlichan, J. Romero, J. R. McClean, R. Barends, J. Kelly, P. Roushan, A. Tranter, N. Ding, et al., Phys. Rev. X 6, 031007 (2016).
[8] A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. M. Chow, and J. M. Gambetta, Nature 549, 242 (2017).
[9] F. Arute et al., Science 369, 1084 (2020).
[10] J. E. Rice, T. P. Gujarati, M. Motta, T. Y. Takeshita, E. Lee, J. A. Latone, and J. M. Garcia, J. Chem. Phys 154, 134115 (2021).
[11] A. Peruzzo, J. McClean, P. Shadbolt, M.-H. Yung, X.-Q. Zhou, P. J. Love, A. Aspuru-Guzik, and J. L. O’Brien, Nat. Commun 5, 4213 (2014).
[12] G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice, and H. F. Schaefer III, J. Chem. Phys 86, 2881 (1987).
[13] P. G. Szalay and J. Gauss, J. Chem. Phys 107, 9028 (1997).
[14] N. Gomes, F. Zhang, N. F. Berthusen, C.-Z. Wang, K.-M. Ho, P. P. Orth, and Y. Yao, J. Chem. Theory Comput 16, 6256 (2020).
[15] D. Aharonov and A. Ta-Shma, in Proc. ACM (2003) pp. 20–29.
[16] A. Y. Kitaev, arXiv quant-ph/9511026 (1995).
[17] J. T. Seeley, M. J. Richard, and P. J. Love, J. Chem. Phys 137, 224109 (2012).
[18] S. B. Bravyi and A. Y. Kitaev, Ann. Phys 298, 210 (2002).
