Numerical Simulations of Noisy Quantum Circuits for Computational Chemistry

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Abstract

The opportunities afforded by near-term quantum computers to calculate the ground-state properties of small molecules depend on the structure of the computational ansatz as well as the errors induced by device noise. Here we investigate the behavior of these noisy quantum circuits using numerical simulations to estimate the accuracy and fidelity of the prepared quantum states relative to the ground truth obtained by conventional means. We implement several different types of ansatz circuits derived from unitary coupled cluster theory for the purposes of estimating the ground-state energy of Sodium Hydride using the variational quantum eigensolver algorithm. We show how relative error in the energy and the fidelity scale with the levels of gate-based noise, the inter-molecular configuration, the ansatz circuit depth, and the parameter optimization methods.

Keywords: Variational Quantum Algorithms; Noise; Quantum Chemistry; Quantum Computing

1 Introduction

Computation is a staple of predicting the behaviors and properties of new chemicals and materials, and leading computational methods must take advantage of state-of-the-art computers to address the most challenging calculations. The advent of quantum computers has motivated the development and testing of new methods for solving familiar problems by using quantum mechanics itself to perform the computation [1, 2, 3, 4]. Current quantum computing methods range from fault-tolerant quantum error corrected algorithms that support arbitrarily long calculations to noisy intermediate-scale quantum (NISQ) algorithms that adapt to the error-prone devices available today [5]. We shall focus on the latter setting but we note the underlying quantum mechanical model affords novel opportunities to simulate the structure and dynamics of chemical systems within both regimes.

Among several approaches to NISQ algorithms, the family of variational methods have emerged in recent years as especially promising for testing the behavior of noisy quantum devices. Typified by the variational quantum eigensolver (VQE) [6], the
family of variational quantum algorithms uses tunable quantum circuits to prepare approximations to the quantum mechanical states of a model Hamiltonian [7]. The familiar variational principle offers a promise that the parameters which minimize the observed energy also prepare the best approximation to the Hamiltonian ground state, while modifications of this approach may be used to approximate higher energy eigenstates as well as other observables [8].

Multiple experimental investigations have tested the principles of VQE for recovering the electronic states of small molecular Hamiltonians [9, 10, 11, 12, 13]. Those results indicate that the choice of the parameterized quantum circuit, i.e., the ansatz, plays a significant role in the accuracy of the estimated energy as well as the complexity of finding the optimal parameters. In particular, development of an expressive and efficient ansatz is essential to temper the influence of noise and errors that arise during experimental implementation [14, 15, 16, 17, 18, 19, 20]. Many different techniques, including symmetry, constraints, and iterative approximations, have been used to further the construction of efficient ansatz circuits [21, 22, 23].

Despite the continuing improvement of such experimental demonstrations, there is an outstanding question as to how the fidelity of the prepared quantum state compares to the idealized pure state representation of the sought electronic ground state. All demonstrations to date are well within the range of conventional computation yet the leading observable for comparison is the energy estimate and not the state. By construction, the applied ansatz circuit has a best approximation to the true ground state of the given Hamiltonian operator, but the accuracy with which this state is found is not the leading metric for experimental validation. This is due primarily to the complexity of estimating the prepared state, which requires tomographic techniques for reconstructing the quantum state [24, 25].

Previously, Claudino et al. investigated the fidelity of several variational methods in approximating the ground state of few-electron molecular models [26]. Those results show that VQE methods with sophisticated ansatz circuits could approximate the ground electronic state with very high fidelity in the absence of circuit noise, depending on the ansatz and method of parameter selection. However, implementations on NISQ devices are prone to noise that leads to errors in state preparation, and there is an outstanding need to assess how noise influence circuit accuracy. The effects of noise and errors invalidate the pure-state representation used to motivate VQE methods and lead to significant sources of uncertainty in the prepared state.

Here we examine the accuracy and precision of the ansatz in several VQE methods by using numerical simulations of the noisy quantum circuits. This includes the nominal form of VQE with a one- and two-parameter ansatz circuits derived from unitary coupled cluster (UCC) theory as well as the more sophisticated ADAPT-VQE method using the singlet-adapted UCC operator pool. We investigate variations in parameter optimization due to noisy gate operations, testing both COBYLA and BFGS, and in all cases we consider the influence of gate noise on the estimated energy and prepared state fidelity. As a test case, we simulate VQE calculations of the expected ground state and energy for Sodium Hydride (NaH) and we compare with conventional electronic structure calculations.

The remainder of the presentation is organized as follows: in Sec. 2, we present the background on the theory and methods for the VQE methods and ansatz circuits;
in Sec. 4, we present results from numerical simulations of the noisy ansatz circuits and we make comparisons with conventional solutions in terms of energy and state fidelity; and in Sec. 5, we discuss conclusions from our analysis.

2 Variational Quantum Eigensolver Methods

Within the context of computational chemistry, the non-relativistic, time-independent molecular Hamiltonian is

$$\hat{H}_{\text{mol}} = -\sum_i \frac{\nabla^2_{R_i}}{2M_i} - \sum_i \frac{\nabla^2_{r_i}}{2m_i} - \sum_{i,j} Z_i \left| R_i - r_j \right| + \sum_{i,j>i} \frac{Z_i Z_j}{\left| R_i - R_j \right|} + \sum_{i,j>i} \frac{1}{\left| r_i - r_j \right|}$$  \hspace{1cm} (1)

with $R_i$ the coordinate of the $i$-th nuclei of mass $M_i$ and charge $Z_i$ and with $r_i$ the coordinate of the $i$-th electron with mass $m_e = 1$ and charge $e = 1$. Under the Born-Openheimer approximation, the molecular Hamiltonian is decomposed into an electronic Hamiltonian and nuclear Hamiltonian. By adopting a spin-orbital basis $\{\varphi_p : p = 1, \ldots, N\}$ for the electronic degrees of freedom, the second-quantized form of the electronic Hamiltonian is expressed as

$$H(R) = \sum_{pq} h_{pq}(R)a^\dagger_p a_q + \frac{1}{2} \sum_{pqst} h_{pqst}(R)a^\dagger_p a^\dagger_q a_s a_t$$  \hspace{1cm} (2)

where the one-electron integrals

$$h_{pq}(R) = \int d\sigma \varphi^*_p(\sigma) \left( \frac{\nabla^2_{r}}{2} - \sum_i \frac{Z_i}{\left| R_i - r \right|} \right) \varphi_q(\sigma)$$  \hspace{1cm} (3)

and two-electron integrals

$$h_{pqst} = \int d\sigma_1 d\sigma_2 \frac{\varphi^*_p(\sigma_1)\varphi^*_q(\sigma_2)\varphi_s(\sigma_1)\varphi_t(\sigma_2)}{|r_1 - r_2|}$$  \hspace{1cm} (4)

are taken with respect to the variable $\sigma$ denoting both spin and position and depend on the nuclear coordinates $R$. The associated fermionic creation and annihilation operators satisfy the anti-commutation relations

$$\{a^\dagger_p, a_q\} = \delta_{p,q} \quad \text{and} \quad \{a_p, a_q\} = 0$$  \hspace{1cm} (5)

The fermionic representation of the Hamiltonian in (2) may be transformed into a qubit representation using the usual Pauli operators

$$X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$  \hspace{1cm} (6)

which satisfy $[X, Y] = -2iZ$. Several transformations into the qubit representation are known to satisfy the necessary fermionic commutation relations, and we employ the Jordan-Wigner transformation defined as

$$a^\dagger_p = \otimes_{i<p} Z_i \otimes \sigma^-_p, \quad \text{and} \quad a_p = \otimes_{i<p} Z_i \otimes \sigma^+_p$$  \hspace{1cm} (7)
in terms of the qubit raising and lower operations $\sigma_p^\pm = (X_p \pm iY_p)/\sqrt{2}$. The implementation of this transformation requires $n \geq N$ qubits, and the resulting representation of the fermionic Hamiltonian is

$$H(R) = \sum_j c_j(R)P_j$$

(8)

where $P_j$ denotes the $j$-th string of Pauli operators over $n$ qubits and $c_j(R)$ is the corresponding coefficient. The maximum number of terms in (8) is $4^n$ but, in practice, symmetries within the Hamiltonian significantly reduce the number of terms that have non-zero coefficients [27].

The variational quantum eigensolver (VQE) method estimates the minimal expectation value of a Hermitian operator with respect to a variable quantum circuit. The method relies on the variational principle, which states that only the lowest eigenstate of a non-negative operator can minimize the expectation value. Here, we use the the qubit representation of the electronic Hamiltonian as the operator of interest, such that the estimated energy expectation value is

$$E(R;\theta^*) = \min_\theta \langle \psi(\theta)|H(R)|\psi(\theta)\rangle$$

(9)

where $|\psi(\theta)\rangle = U(\theta)|\psi(0)\rangle$ is a variable pure quantum state prepared by a (unitary) ansatz operator $U(\theta)$. The parameter $\theta^*$ denotes the optimal value that minimizes the energy, and a generalization of $\theta$ may include multiple parameters within the ansatz.

The critical choice in applying the VQE method to a given Hamiltonian is selection of the ansatz operator $U(\theta)$ and the underlying reference state $\psi(0)$. The latter may be selected by using conventional approximations to the electronic ground state that are efficiently encoded as superpositions of binary states. For example, using the Hartree-Fock solution to the electronic Hamiltonian offers a convenient choice for the reference state, and the vacancy or occupation of a molecular orbital may be encoded by 0 or 1, respectively. The choice of the ansatz operator may also be drawn from conventional electronic structure theory, and many recent efforts have focused on unitary coupled cluster (UCC) theory to generate possible choices for the ansatz operator [27, 28]. The accuracy with which a given ansatz operator represents the true ground state of the Hamiltonian may be quantified using the fidelity

$$F = |\langle \Psi|U(\theta)|\psi(0)\rangle|^2$$

(10)

where $\Psi$ is the expected ground state in the qubit representation. We next review a family of ansatz operators derived from UCC theory.

2.1 Unitary Coupled Cluster Ansatz Operators

Consider the fermionic UCC ansatz operator [27]

$$U(\theta) = \exp \left( T(\theta) - T^\dagger(\theta) \right)$$

(11)
where

$$T(\theta) = \sum_{k=1}^{M} T_k(\theta)$$  \hspace{1cm} (12)$$

and $T_k(\theta)$ represents the $k$-th cluster operator of $M$ electrons excited. The unitary operator (11) may be approximated to first order by the finite series [29]

$$U(\theta) \approx \prod_{m=1}^{M} e^{\tau_m(\theta)}$$ \hspace{1cm} (13)$$

with $\tau_m(\theta) = T_m(\theta) - T_m^\dagger(\theta)$ and $M$ is the series limit. Terminating the series at $M = 2$ limits the theory to single and double excitations and yields what is known as the UCC singles and doubles (UCCSD) ansatz

$$U_{SD}(\theta) = e^{\tau_1(\theta)} e^{\tau_2(\theta)}$$ \hspace{1cm} (14)$$

where

$$T_1(\theta) = \sum_{i \in \text{occ}} \sum_{a \in \text{virt}} \theta_a^a i_i^a$$ \hspace{1cm} (15)$$

and

$$T_2(\theta) = \sum_{i,j \in \text{occ}} \sum_{a,b \in \text{virt}} \theta_a^b \theta_b^a i_{i,j}^a$$ \hspace{1cm} (16)$$

with $i_i^a = a_i^a a_i$, $i_{i,j}^a = a_i^a a_j^a a_i a_j$, and the vector $\theta$ defines the single- and double-excitation parameters $\theta_a^a$ and $\theta_a^b$, respectively, for excitations from occupied orbitals $i$ and $j$ to virtual orbitals $a$ and $b$ of the reference state.

The ansatz operator in (14) may be transformed by the Jordan-Wigner transformation (7) to yield the individual terms

$$\tau_1(\theta) = \frac{i}{2} \sum_{i,a} \theta_a^a P_i^a$$ \hspace{1cm} (17)$$

and

$$\tau_2(\theta) = \frac{i}{8} \sum_{i,j,a,b} \theta_a^b \theta_b^a Q_{i,j}^a$$ \hspace{1cm} (18)$$

with

$$P_i^a = \bigotimes_{k=1}^{a-1} Z_k (X_a Y_i - Y_a X_i)$$ \hspace{1cm} (19)$$
and

\[
Q_{i,j}^{a,b} = \otimes_{k=i}^{a-1} Z_k \otimes_{\ell=j}^{b-1} Z_{\ell} \left( X_a X_b X_i Y_j + X_a Y_b Y_i Y_j + X_a X_b Y_i X_j + Y_a X_b Y_j Y_i - Y_a Y_b X_i X_j - Y_a X_b X_i Y_j - Y_a Y_b X_i X_j \right)
\]

where, under the $Z$ operator, occupied orbitals yield an eigenvalue $+1$ and virtual orbitals yield an eigenvalue $-1$ such that each operator $Q_{i,j}^{a,b}$ is determined by the single four-qubit Pauli string $X_a X_b X_i Y_j$.

The UCCSD operator serves as our starting point for developing various ansatz operators. First, we define a one-parameter ansatz operator derived from the UCCSD ansatz by considering only contribution from the doubles excitations in (21). For the four-qubit encoding of two-electrons described below, the resulting UCC doubles (UCCD) ansatz operator is reduced to

\[
U(\theta) = e^{i\theta Y_0 X_1 X_2 X_3}
\]

We also consider a singlet-adapted variation of the UCCSD ansatz for which the state is defined in a basis of restricted determinants. Specifically, we restrict the ansatz to basis states that are naturally eigenstates of the electron spin operator. Such states are formed from linear combinations of the corresponding excitation operators that conserve electron spin and obey the spin symmetry. These linear combinations are often referred to in chemistry as configuration state functions or symmetry-adapted basis functions. We defer the description of constructing these linear combinations to prior work [30]. Various details on both ansatz operators have been reported previously [10, 26].

An alternative to the fixed-depth ansatz operators above is an adaptive ansatz that changes the generating operator based on iterative evaluations of the energy estimate. Grimsley et al. first proposed the adaptive derivative-assembled pseudotrotter (ADAPT) ansatz motivated by UCC theory in which the unitary (11) is
expanded beyond first order [21]. They showed how the resulting operator expression guides iteratively growing an ansatz circuit until a desired convergence in the expectation value is obtained. The ADAPT method begins by decomposing the individual single- and double-excitations operators represented by (14) into a set known as the operator pool. Let \( T = \{ \hat{t}_a^i \} \cup \{ \hat{t}_{a,b}^{i,j} \} \) denote the operator pool derived from the UCCSD approximation. An exact ansatz operator may be expressed as

\[
U_{SD}(\theta) = \prod_k \prod_{i,a} \exp \left[ \theta_{i,k}^a (\hat{t}_a^i - \hat{t}_a^i) \right] \prod_{i,j,a,b} \exp \left[ \theta_{i,j,k}^{a,b} (\hat{t}_{a,b}^{i,j} - \hat{t}_{a,b}^{i,j}) \right] \tag{23}
\]

in which \( k \) indexes the different instances of each excitation operator.

The ADAPT method creates an approximation to (23) by selecting a subset of elements in the operator pool \( T \) to generate an ansatz operator. Operator selection is initialized with a starting ansatz operator which, for example, prepares the Hartree-Fock state for the given Hamiltonian. The selection then evaluates the commutator between each operator in the pool and the Hamiltonian with respect to the presently prepared state. The resulting vector of commutator evaluations defines a gradient that is steepest in the direction of the operator with the largest commutator. The operator corresponding to the largest commutator is then appended to the ansatz operator and, therefore, the ansatz circuit for the next evaluation of VQE. An associated parameter is introduced to tune the unitary rotation represented by the new operator, such that the number of optimized parameters grows with the size of the ansatz. When the norm of the gradient vector is less than a defined threshold, the algorithm converges and the lowest energy state is recovered.

2.2 Ansatz Compilation

The above ansatz operators must be compiled into quantum circuits for execution. We use the XACC programming framework to synthesize circuits representing these ansatz operators. XACC provides a set of software methods to define and implement fermionic and spin transformations that reduce the operator expressions above into a sequence of discrete quantum gates [31]. In addition, the accompanying VQE and ADAPT-VQE methods orchestrate iterative execution of the ansatz and search through the corresponding parameter space. We defer details on the compilation methods to prior references [10]. The results include, for example, the compiled one-parameter UCCD ansatz from (22) decomposed into the sequence of one- and two-qubit gate operations shown in Fig. 1. Compiled circuits are then simulated and XACC facilitates this step as well. Here we perform numerical simulations that interface the compiled circuits with a simulator that otherwise faithfully execute the VQE and ADAPT-VQE methods. Details on the numerical simulations are reviewed below.

Given our interest in noisy quantum circuits, we have also investigated how compilation techniques may help mitigate such noise. Specifically, we consider randomized compiling to transform ansatz circuits by introducing independent, random single-qubit gates such that the output circuit is logically equivalent to the original [32]. Randomized compiling was developed to address coherent and correlated noise by effectively transforming the noise into a stochastic Pauli noise channel.
The technique is implemented by dividing gate sets into so-called ‘easy’ and ‘hard’ gates and then reorganizing the original circuit into clock cycles alternating between a round of easy and hard gates applied to disjoint qubits per cycle [32]. Each round of easy gates is conjugated by a twirling gate $T_k$ from a twirling gate set and an inverse operator $T_k^{-1}$. The original single qubit gates and the twirling gates are then compiled into new easy gate cycles. While randomized compiling can offer improvements in circuit performance [33], our investigation does not test such promises due to the selected noise model described next. Rather, we investigate the role that additional gates in the ansatz circuit have on the increased circuit depth and output state fidelity. We limit our analysis to random compiling of the UCCD ansatz circuit using the commercially available TrueQ software package [34].

3 Numerical Methods

For our numerical studies, we use the model of a two-electron Hamiltonian representing Sodium Hydride (NaH) within the frozen-core approximation and with the STO-3G basis set. We require $n = 4$ qubits to encode the two spin-orbitals using the Jordan Wigner transformation, and the corresponding Pauli representation of terms in the electronic Hamiltonian is summarized in Table 1. As described previously, we use the XACC framework to compile the ansatz circuits and perform optimization of the ansatz parameters with respect to the estimated energy. The compiled circuits are simulated numerically using the IBM aer simulator as the XACC qpu backend, and we integrate a noise model that describes each gate by a noisy operation.

In modeling noise in the quantum circuits, we assume a model by which each one- and two-qubit gates are followed by a depolarizing noise channel. The depolarizing noise model is a convenient device agnostic noise model that offers a coarse-grain representation for the loss of coherence caused by a noisy circuit, particularly for few-qubit numerical simulations [35]. Although it does not provide a fine-grain representation of the noise process, it has been used previously for accurately modeling the output from NISQ devices [36]. In addition, randomized compiling is known to yield a statistical model for the quantum circuit noise that is well approximated by the depolarizing model and motivates our use for the model here [37].

Within this model, the action of a single-qubit unitary gate $G$ acting on register element $j$ in the quantum state $\rho$ is simulated as

$$\xi^G_j(\rho) = (1 - p)\rho + p \sum_k \sigma^k_j \rho \sigma^k_j$$

with $\rho' = G\rho G^\dagger$, $\sigma^k_j \in X_j, Y_j, Z_j$, and the noise parameter $p \in [0, 1]$. Errors on a two-qubit gate acting on elements $i$ and $j$ are modeled similarly as $\xi^G_{i,j}(\rho) = \xi^I(\xi^G_i(\rho))$ with $I$ the identity operator. For our simulations, we use a gate set consisting of the single-qubit Pauli operator, the Hadamard gate, and single-qubit rotations with the two-qubit CNOT gate. These gates are decomposed by XACC into the OpenQASM representation [38]. Notably, OpenQASM gates that are diagonal in the computational basis, e.g., $Z$, are not modeled with noise, a consequence of using the IBM aer simulator. For our noise model, we use noise levels for the two-qubit CNOT gate that is always ten times the value of the single-qubit gate noise. This is
motivated by the difference in noise values observed in hardware. We use the same noise level for all single-qubit gates.

For different values of noise, we explore the influence of methodology on parameter optimization by comparing results from different optimizers. COBYLA and L-BFGS were chosen as gradient-free and gradient-based methods, respectively. Constrained optimization by linear approximation (COBYLA) constructs and optimizes a series of linear approximations to the objective function to compute parameter steps that minimize the objective function [39]. We use the third-party library implementation nlopt with a maximum number of iterations set to 1,000 with a convergence tolerance of 10^-4 [43]. By comparison, the low-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) method is a quasi-Newton method that uses the gradient and an approximate Hessian to determine steps in parameter space that minimize the objective function [41, 42]. We use the third-party library implementation mlpack with the central gradient method with a maximum number of iterations set to 500,000 with a convergence tolerance of 10^-6 [40].

The output of each simulation is a list of expectation values characterizing the Pauli strings with respect to the UCCD ansatz for r = 1.91438Å. We compare the statistics and behavior with respect to inter-nuclear configuration.

We conduct a range of studies of the above noise model applied to VQE and ADAPT-VQE simulations of the NaH molecule. We compare the statistics and fi-
delity of the expectation values of the noisy and noiseless simulations across different $R$ values and different optimizers. For the studies with VQE we study the simulations of the original circuit and compare them with the results of the randomly compiled circuits. The goal is to understand how noise affects these properties and if there are parameters that are more resilient to noise than others.

4 Results

We first present results from numerical simulations of the UCCD ansatz and its randomly compiled counterparts. Figures 2 and 3 show the simulated ground state energy for NaH and prepared state fidelity found using the optimization methods COBYLA and L-BFGS, respectively. The left columns of each figure include the results for the bare UCCD ansatz while the right column represents the average of 10 randomly compiled circuits. The simulated ground state energy predictably increases with increases in the depolarizing noise parameter $p$ across all $r$. The randomly compiled circuits result in slightly larger increase for the same noise level due to the presence of additional one-qubit gate. On average, the randomly compiled circuits consist of approximately 50% more single-qubit gates than the bare UCCD ansatz.

As seen in Fig. 4, the optimal ansatz parameter returned by each optimizer varies weakly from nearly 0 to 0.10 radians with $r$. There are noticeable differences in the parameters returned by L-BFGS and COBYLA with the latter showing a smoother variation with respect $r$, particularly at larger values. In addition, the variance in the optimal parameter is larger at these values of $r$ when using COBYLA. However, these variations in optimal parameter value do not change significantly the the energy expectation value or fidelity, as seen by comparing results between Fig. 2 and 3.
Figure 3. The top row presents the ground-state electronic energy of NaH calculated using VQE with UCCD ansatz (left) and average of 10 RC circuits (right, dashed line) while the bottom row presents the corresponding fidelity of the prepared quantum state with the ground state calculated using conventional methods. The parameters were chosen through the L-BFGS optimization routine.

Figure 4. The optimal values of the circuit parameter $\theta$ obtained from the VQE simulation of the UCCD ansatz and average of the simulation of 10 RC circuits as a function of the inter-molecular distance of NaH when using the COBYLA (top row) and L-BFGS (bottom row) optimization methods.
Figure 5 presents similar results for simulations using the singlet-adapted UCCSD ansatz. The left and right columns correspond to the COBYLA and L-BFGS optimizers, respectively. There is no significant difference between the results using different optimizer but, for a given value of the noise parameter, there is a significant increase in the energy and decrease in the fidelity compared with the UCCD ansatz results. Figure 5 shows that as $p$ increases, the estimated energy using singlet-adapted UCCSD ansatz increases much more than with UCCD. Similarly, the prepared state fidelity also decreases much more.

For our two-electron model of NaH, the singlet-adapted UCCSD ansatz uses two parameters denoted as $\theta_0$ and $\theta_1$, and we present the result of those parameter optimizations in the first and second rows, respectively, of Fig. 6. The left and right columns again correspond with the COBYLA and L-BFGS optimizers. Both optimizers search similar regions but there is noticeable variation in their results. In addition, as the noise level $p$ increases, the parameter search changes in tandem, with the $p = 0.01$ case for the $\theta_1$ parameter showing the most dramatic shift. However, recall that the estimated energy and fidelity shown in Fig. 5 are not significantly different. The increased sensitivity of the search method to the noise level is because the singlet-adapted UCCSD ansatz represent a much larger circuit relative to UCCD. While this sensitivity to the noise does effect the results from the optimizer, it does not translate into noticeable differences in the metrics of interest.

Figure 7 presents the results for the case of the ADAPT-VQE ansatz, which demonstrates the greatest increase in error with respect to the noise parameter.
Figure 6 The optimal values of the circuit parameters (top row) $\theta_0$ and (bottom row) $\theta_1$ for the singlet-adapted UCCSD ansatz as a function of obtained from VQE with respect to the NaH inter-molecular distance when using the COBYLA (left column) and L-BFGS (right column) optimization methods. Lines represent different values of the depolarizing noise parameter $p$ as defined in the text.

Figure 7 The top row presents the ground-state electronic energy of NaH calculated using ADAPT-VQE with Singlet-Adapted-UCCSD operators while the bottom row presents the corresponding fidelity of the prepared quantum state with the ground state calculated using conventional methods. The left and right columns distinguish between the parameters chosen through the COBYLA and L-BFGS optimization routines respectively. Lines represent different values of the depolarizing noise parameter $p$ as defined in the text.
As \( p \) increases, the error in the estimated energy for the ground state increases independent of the optimizer. The cause for this increase in error is apparent in Fig 8, which presents the number of parameters found to reach convergence of the ADAPT-VQE ansatz. The number of parameters fluctuates with coordinate \( r < 3.0 \) Å, and the parameters required for \( p = 0.01 \) is approximately an order of magnitude more than those found for UCCD and UCCSD. These parameterizations correspond with a much deeper circuit. There is some variation between the COBYLA and L-BFGS optimizers but we did not identify any specific trends.

The energy and fidelity shown in Fig. 7 follow the general trend of parameterization, namely, more parameters yield more error. Again, this corresponds with deeper circuits and therefore more noise. For some values of \( r \), the estimated error differs even though the circuit depth and value of \( p \) are the same. This is due to the presence of more CNOT gates which contribute more error within our model. Ansatz circuits with the same number of CNOT gates but a greater number of single-qubit gates resulted in marginal difference in error. This also indicates that the number of CNOT gates is the leading limit on how accurately the ansatz can describe the ground-state wavefunction.

5 Conclusions

Across all ansatz circuits, we find that a noiseless simulations always recover the ideal energy and a unit fidelity, while in the presence of noise, the depth of the ansatz circuit has the most important influence on the error in these quantities. Increases in gate depth of the ansatz necessarily increases the error in energy and lowers the fidelity and this is amplified at larger noise values. While different optimizers do yield different optimal parameters and number of parameters, these differences generally have on small influence on the outcomes. For example, prior work has confirmed that the energy surface characterizing the UCCD ansatz is relatively smooth [45], while our results presented here confirm similar behavior in the presence of noise.

The differences observed between the bare UCCD and UCCSD ansatz circuits versus the randomly compiled circuits reflect differences in their single-qubit gate depth while for the case of the ADAPT ansatz, it is the presence of two-qubit gates...
that make the most significant contribution. A leading feature of the ADAPT-VQE ansatz is that the ansatz grows iteratively to improve the accuracy of the computed energy. This feature allows for variability in the number of and types of gates that make up the ansatz. However, as shown here, variability in the ansatz circuit depth leads to fluctuations in the energy and fidelity that are not observed with the fixed ansatz.

Finally, we note that the ansatz produced by the ADAPT method often generate different ansatz for each internuclear configuration along with a different number of parameters. Some of these additional parameters appear nearly trivial as they correspond with small values of the optimal parameters. This raises questions about how the ADAPT method may be modified to ensure continuity in the ansatz circuit depth and parameter values. For example, intelligence pruning of the ADAPT ansatz may be beneficial with little loss of accuracy. We defer this point for later work.

6 Declarations

Availability of data and materials
The data and materials are available upon request.

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Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
J. W. and M. G. developed the methods, performed the experiment, processed the data, and composed the manuscript. D.C. developed the methods and composed the manuscript, P.C.L. processed the data and composed the manuscript. T.N. developed the methods, A.J.M. developed the methods, and T.S.H. processed the data and composed the manuscript.

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