Hartree-Fock on a superconducting qubit quantum computer

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As the search continues for useful applications of noisy intermediate scale quantum devices, variational simulations of fermionic systems remain one of the most promising directions. Here, we perform a series of quantum simulations of chemistry which involve twice the number of qubits and more than ten times the number of gates as the largest prior experiments. We model the binding energy of H_6, H_8, H_{10} and H_{12} chains as well as the isomerization of diazene. We also demonstrate error-mitigation strategies based on N-representability which dramatically improve the effective fidelity of our experiments. Our parameterized ansatz circuits realize the Givens rotation approach to free fermion evolution, which we variationally optimize to prepare the Hartree-Fock wavefunction. This ubiquitous algorithmic primitive corresponds to a rotation of the orbital basis and is required by many proposals for correlated simulations of molecules and Hubbard models. Because free fermion evolutions are classically tractable to simulate, yet still generate highly entangled states over the computational basis, we use these experiments to benchmark the performance of our hardware while establishing a foundation for scaling up more complex correlated quantum simulations of chemistry.

I. INTRODUCTION

The prediction of molecular properties and chemical reactions from ab initio quantum mechanics has emerged as one of the most promising applications of quantum computing [1]. This is due both to the commercial value of accurate simulations as well as the relatively modest number of qubits required to represent interesting instances. However, as the age of quantum supremacy dawns [2], so has a more complete appreciation of the challenges required to scale such computations to the classically intractable regime using near-term intermediate scale quantum (NISQ) devices. Achieving that objective will require further algorithmic innovations, hardware with more qubits and low error rates, and more effective error-mitigation strategies. Here, we report a variational quantum eigensolver (VQE) [3] simulation of molecular systems with progress in all three directions.

We use the Google Sycamore quantum processor to simulate the binding energy of Hydrogen chains as large as H_{12}, as well as a chemical reaction mechanism (the isomerization of diazene). The Sycamore quantum processor consists of a two-dimensional array of 54 transmon qubits [2]. Each qubit is tunably coupled to four nearest neighbors in a rectangular lattice. Our largest simulations use a dozen qubits – twice the size as the largest prior quantum simulations of chemistry – and requires only nearest-neighbor coupling (depicted in Figure 1). Prior simulations of chemistry on superconducting qubit devices and trapped ion systems demonstrated the possibility of error mitigation through VQE [4–10], albeit on a small scale. We demonstrate that, to within the model, achieving chemical accuracy through VQE is possible for intermediate scale problems when combined with effective error mitigation strategies. Furthermore, we will ar-

gue that the circuit ansatz we use for VQE is especially appealing as a benchmark for chemistry.

We will simulate quantum chemistry in a second-quantized representation where the state of each of N qubits encodes the occupancy of an orbital basis function. We will use what are commonly referred to as core orbitals as the initial orbitals (shown for H_{12} on the left of Figure 1a), which are the eigenfunctions of the molecular Hamiltonian without the electron-electron interaction term. The goal of this experiment will be to use a quantum computer to implement the Hartree-Fock procedure, which is a method for obtaining the best single-particle orbital functions assuming each electron feels the average potential generated from all the other electrons. This assumption is enforced by constraining the wavefunction to be a product of one-particle functions which has been appropriately antisymmeterized to satisfy the Pauli exclusion principle. An initial guess for the Hartree-Fock state, from which we can optimize the orbitals, is obtained by filling the lowest energy $\eta/2$ orbitals, each with a spin-up electron and a spin-down electron, where η is the number of electrons. Since we simulate the singlet ground state for all molecules considered here, there is no spin component to the mean-field approximation; thus, we only need to explicitly simulate the $\eta/2$ spin-up electrons.

By performing a unitary rotation of the initial (core) orbital basis $\varphi_p(r)$, one can obtain a new valid set of orbitals $\widetilde{\varphi}_p(r)$ as a linear combination of the initial ones:

$$\widetilde{\varphi}_p(r) = \sum_{q=1}^{N} [e^\kappa]_{pq}\, \varphi_q(r)\,, \tag{1}$$

where κ is an $N \times N$ anti-Hermitian matrix and $[e^\kappa]_{pq}$ is the p, q element of the matrix exponential of κ. A surprising result due to Thouless [11] is that one can express the unitary that applies this basis rotation to the quantum state as time-evolution under a "free" (i.e., non-interacting) fermion Hamiltonian. Specifically, if we take $a_p^\dagger$ and a_p to be fermionic creation and annihilation operators for the core orbital $\varphi_p(r)$ then we can parameterize

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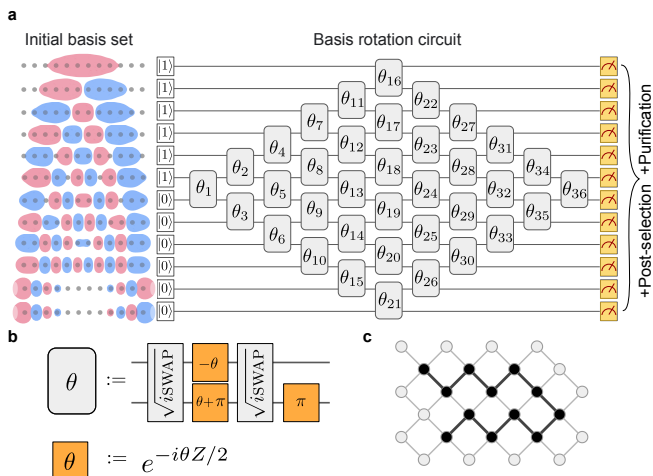Corresponding author (Ryan Babbush): babbush@google.com

FIG. 1. **Basis rotation circuit and compilation.** a) To the left of the circuit diagram are the initial orbitals for the H_{12} chain with atom spacings of 1.3 Å, obtained by diagonalizing Hamiltonian ignoring electron-electron interaction. The circuit diagram depicts the basis rotation ansatz for a linear chain of twelve Hydrogen atoms. Each grey box with a rotation angle θ represents a Givens rotation gate. b) Compilation of the Givens rotation gate to $\sqrt{i\text{SWAP}}$ gates and single-qubit gates that we can realize directly in hardware. The H_{12} circuit involves 72 $\sqrt{i\text{SWAP}}$ gates and 108 single-qubit Z rotation gates with a total of 36 variational parameters. c) Depiction of a twelve qubit line on a subgrid of the entire 54-qubit Sycamore device. All circuits only require gates between pairs of qubits which are adjacent in a linear topology.

$|\psi_\kappa\rangle$, an antisymmetric product state in the new basis $\widetilde{\varphi}_p(r)$, as free fermion dynamics from a computational basis state $|\eta\rangle = a_\eta^\dagger \cdots a_1^\dagger |0\rangle$ in the core orbital basis:

$$|\psi_\kappa\rangle = U_\kappa |\eta\rangle, \qquad U_\kappa = \exp\left(\sum_{p,q=1}^{N} \kappa_{pq} a_p^\dagger a_q\right). \quad (2)$$

Such states are referred to as Slater determinants.

To complete the Hartree-Fock procedure, we will perform VQE by optimizing over the parameters κ to minimize the energy of $|\psi_\kappa\rangle$. Thus, we define the Hartree-Fock state $|\psi_{\text{HF}}\rangle$ to be the lowest energy Slater determinant for the molecular Hamiltonian H, i.e.

$$|\psi_{\text{HF}}\rangle = |\psi_{\kappa^\star}\rangle \qquad \kappa^\star = \text{argmin}_\kappa \langle\psi_\kappa| H |\psi_\kappa\rangle. \quad (3)$$

We will apply U_κ to $|\eta\rangle$ using our quantum computer and then perform the optimization over κ through feedback from a classical optimization routine. The energy will decrease because the initial core orbitals were obtained by ignoring the electron-electron interaction. Since U_κ corresponds to free fermion evolution, its action on a product state can be simulated using classical computers in time $O(N^3)$. Despite that fact, we now argue that this is still a compelling experiment for a quantum computer.

The Hartree-Fock state is usually the initial state for classical correlated electronic structure calculations such

as coupled cluster and configuration interaction, as well as for many quantum algorithms for chemistry. Thus, often one chooses to work in the molecular orbital basis, which is defined so that the Hartree-Fock state is a computational basis state. However, the molecular orbital basis Hamiltonian has a large number of terms which can be challenging to simulate and measure with low complexity. Accordingly, the most efficient quantum algorithms for chemistry [12–15] require that one perform the simulation in more structured bases with asymptotically fewer terms [16–18], necessitating that $U_{\kappa^\star}$ is applied explicitly at the beginning of the computation. Even when simulating chemistry in an arbitrary basis, the most efficient strategies are based on a tensor factorization of the Hamiltonian which requires many applications of U_κ to simulate [19, 20]. Exploiting this tensor factorization with basis rotations is also key to the most efficient strategy for measuring $\langle H\rangle$ in variational algorithms, and requires implementing U_κ prior to measurement [21].

We use this variational ansatz based on basis rotations to benchmark the Sycamore processor for linear Hydrogen chains of length 6, 8, 10, and 12 and two pathways for diazene bond isomerization. We model Hydrogen chains of length N with N qubits. For diazene we require 10 qubits after pre-processing. The Hydrogen chains are a common benchmark in electronic structure [22] and the diazene bond isomerization provides a system where the required accuracy is more representative of typical electronic structure problems and has been used as a benchmark for coupled cluster [23]. For the diazene isomerization our goal is to resolve the energetic difference between the transition states of two competing mechanisms, requiring accuracy of about 40 milliHartree. This objective differs from prior quantum simulations of chemistry which have focused on bond dissociation curves.

One motivation for this work is to calibrate and validate the performance of our device in realizing an important algorithmic primitive for quantum chemistry and lattice model simulation. Our experiment is also appealing for benchmarking purposes since the circuits we explore generate highly entangled states but with special structure that enables the efficient measurement of fidelity and the determination of systematic errors. Further motivation is to implement the largest variational quantum simulation of chemistry so that we may better quantify the current gap between the capabilities of NISQ devices and real applications. Even though the Hartree-Fock ansatz is efficient to simulate classically, the circuits in our experiment are far more complex than prior experimental quantum simulations of chemistry. Finally, the structure of the Hartree-Fock state enables us to sample the energy and gradients of the variational ansatz with fewer measurements than would typically be required, allowing us to focus on other aspects of quantum simulating chemistry at scale, such as the effectiveness of various types of error-mitigation. Thus, our choice to focus on Hartree-Fock for this experiment embraces the notion that we should work towards valuable quantum
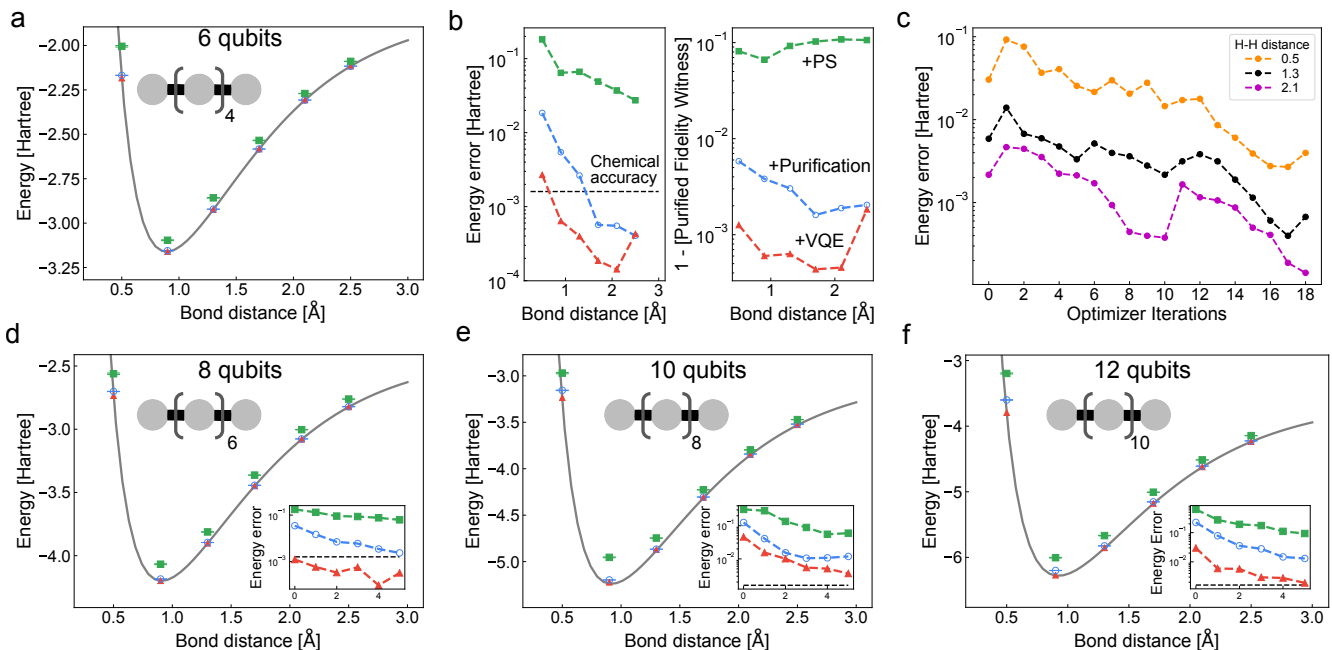
FIG. 2. **Static and VQE performance on Hydrogen chains.** Binding curve simulations for H_6, H_8, H_{10}, and H_{12} with various forms of error mitigation. Subfigures (a, d, e, f) compare Sycamore's performance with post-selection (green squares), purification (blue circles), and error mitigated combined with variational relaxation (red triangles). The green and blue points were calculated using the optimal basis rotation angles computed from a classical simulation; thus, the variational optimization shown here is only used to correct systematic errors in the circuit realization. Subfigure (b) contains the absolute error and infidelity for the H_6 system. For the non-purified points (green) we use a fidelity witness described in Appendix D. The "+PS" means applying post-selection to the raw data, "+Purification" means applying post-selection and McWeeny purification, and "+VQE" means post-selection, McWeeny purification, and variational relaxation. Subfigure (c) contains optimization traces for three H_6 geometries (bond distances of 0.5 Å, 1.3 Å, and 2.1 Å).

simulations of chemistry by first scaling up important components of the exact solution (e.g., error-mitigation strategies and basis rotations) in a fashion that enables us to completely understand and perfect those primitives.

II. METHODS

Variational algorithms are specified in the form of a functional minimization. This minimization has three main components: ansatz specification in the form of a parameterized quantum circuit (the function), observable estimation (the functional), and outer-loop optimization (the minimization). Each component is uniquely affected by our choice to simulate a model corresponding to free fermion wavefunctions. Symmetries built into this ansatz allow for reduction of the number of qubits required to simulate molecular systems, a reduction in the number of measurements needed to estimate the energy, and access to the gradient without additional measurements beyond those required for energy estimation. See Appendix A for details on how we realize Hartree-Fock with VQE.

Circuits. The unitary in Eq. (2) can be compiled exactly (without Trotterization) using a procedure based on Givens rotations. This strategy was first suggested

for quantum computing in work on linear optics in [24] and later in the context of fermionic simulations in [25]. Here, we implement these basis rotations using the optimal compilation of [26] that has gate depth $N/2$ and requires only $\eta(N-\eta)$ two qubit "Givens rotation" gates on a linearly connected architecture, giving one rotation for each element in the unitary basis change. These Givens rotation gates are implemented by decomposition into two $\sqrt{i\text{SWAP}}$ gates and three Rz gates. In Figure 1 we depict the basis change circuit for the H_{12} chain, which has a diamond shaped structure. We further review the compilation of these circuits in Appendix B.

Energy estimation. As described in Appendix A, the average energy of any molecular system can be evaluated with knowledge of the one-particle reduced density matrix (1-RDM), $\langle a_p^\dagger a_q \rangle$, and the two-particle reduced density matrix (2-RDM), $\langle a_p^\dagger a_q^\dagger a_r a_s \rangle$. In general, it is not possible to exactly reconstruct the 2-RDM from knowledge of just the 1-RDM. However, for single-Slater determinants (as in our Hartree-Fock experiment), the 2-RDM is completely determined by the 1-RDM [27]:

$$\langle a_p^\dagger a_q^\dagger a_r a_s \rangle = \langle a_p^\dagger a_s \rangle \langle a_q^\dagger a_r \rangle - \langle a_q^\dagger a_s \rangle \langle a_p^\dagger a_r \rangle. \quad (4)$$

Thus, in our experiment we only need to sample the 1-RDM to estimate the energy. As the 2-RDM has quadrat-
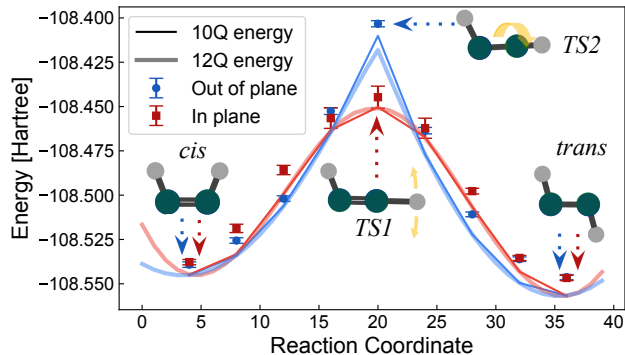
FIG. 3. **_VQE performance on distinguishing the mechanism of diazene isomerization._** Hartree-Fock curves for diazene isomerization between *cis* and *trans* configurations. $TS1$ and $TS2$ are the transition states for the in-plane and out-of-plane rotation of the Hydrogen, respectively. The yellow arrows on $TS1$ and $TS2$ indicate the corresponding reaction coordinate. The solid curve is the energy obtained from optimizing a 10-qubit problem generated by freezing the core orbitals generated from two self-consistent-field cycles. The transparent lines of the same color are the full 12 qubit system indicating that freezing the lowest two levels does not change the characteristics of the model chemistry. Nine points along the reaction paths are simulated on Sycamore using VQE. Error bars are based off the variance for each element of the 1-RDM without purification. If purification is applied the error bars become smaller than the markers. Each basis rotation for diazene contains 50 $\sqrt{i\text{SWAP}}$ gates and 80 Rz gates.

ically more elements than the 1-RDM, this is a significant simplification. We measure the 1-RDM using a protocol described in Appendix C. This protocol enables us to optimally parallelize measurement of all N^2 1-RDM elements with $N + 1$ distinct circuits. For each distinct circuit we make 250,000 measurements.

Error mitigation on the 1-RDM. We perform two types of error mitigation on our measured data: post-selection on particle number (conserved in basis rotations) and pure-state projection. To apply post-selection we modify our circuits by first rotating into a basis that diagonalizes $a_p^\dagger a_q + a_q^\dagger a_p$ for N different pairs of p and q so that these elements can be sampled at the same time as the total particle-number operator. Following the strategy in Appendix C, this is accomplished at the cost of two T gates and one $\sqrt{i\text{SWAP}}$ gate per pair of qubits. We then post-select to discard measurements where the total number of excitations changed from $\eta/2$.

For pure-state purification, we leverage the fact that the 1-RDM for any single-Slater determinant wavefunction $|\psi_\kappa\rangle$ has eigenvalues restricted to be 0 and 1 [28]. We perform projection back to the pure-set of 1-RDMs using a technique known as McWeeny purification [27]. Details on the procedure and sampling bounds for guaranteeing the procedure has a fixed-point 1-RDM corresponding to a Slater determinant can be found in Appendix E. While

McWeeny purification only works for Slater determinant wavefunctions, pure-state N-representability conditions are known for more general systems and we expect that those can be utilized in a more general context [29, 30].

Variational parameter optimization. A variety of circuit optimization techniques based on gradient- and gradient-free methods have been proposed in the context of NISQ algorithms. Here, we develop an optimization technique that exploits local gradient and Hessian information in a fashion which is unique to the Hartree-Fock model. It is based on a proposal for iterative construction of a wavefunction to satisfy the Brillouin condition for a single-particle model [31]. Our optimization protocol uses the property that at a local optima the commutator of the Hamiltonian H with respect to any generator of rotation G is zero (i.e. $\langle\psi|[H,G]|\psi\rangle = 0$) and the fact that sequential basis change circuits can be concatenated into a single basis change circuit (i.e. $U_a U_b = U_{ab}$). Using these relations and taking $G = \sum_{pq} \kappa_{pq} a_p^\dagger a_q$, as in our experiment, the double commutator $\langle\psi|[[H,G],G]|\psi\rangle$ determines an augmented Hessian (matrix of derivatives) which we can use to iteratively update the wavefunction such that the first order condition is approximately satisfied. Regularization is added by limiting the size of update parameters [32]. For details, see Appendix H.

III. RESULTS

Hydrogen chains. As a benchmark, we studied symmetrically stretched Hydrogen chains of length 6, 8, 10, and 12 atoms, as shown in Figure 2. The data from the quantum computer is plotted along with classical Hartree-Fock results, showing better and better agreement as we add post-selection, post-selection and purification, and then error mitigated variational relaxation. The 6- and 8-qubit data achieved chemical accuracy after VQE, and even the 12-qubit data follows the expected energy closely. The error data in Figure 2b and the other inserts are remarkable as they show a large and consistent decrease, about a factor of 100, when using these protocols. Figure 2c details the significant decrease in error using a modest number of VQE iterations.

A fidelity witness can be efficiently computed from the experimental data [33]; see Appendix D 2. This is a lower bound, and thus potentially loose when fidelity is small. However, Figure 2b demonstrates that this fidelity generally tracks the measured errors. Table I shows how fidelity increases as we add various forms of error mitigation, starting on the left column where the optimal angles are computed classically. Uncertainties in the last digit are indicated in the parenthesis and calculated in Appendix C 5. For all systems studied, we observe drastic fidelity improvements with combined error mitigation.

Diazene isomerization. We simulate two isomerization pathways for diazene, marking the first time that a chemical reaction mechanism has been predicted using a quantum computer. It is known that Hartree-Fock

system	raw	+post-selection	+purification	+VQE
H_6	0.674(2)	0.906(2)	0.9969(1)	0.99910(9)
H_8	0.464(2)	0.827(2)	0.9879(3)	0.99911(8)
H_{10}	0.316(2)	0.784(3)	0.9704(5)	0.9834(4)
H_{12}	0.010(2)	0.654(3)	0.9424(9)	0.9913(3)

TABLE I. **Average fidelity lower bounds for Hydrogen chain calculations.** We report values of the fidelity witness from [33], averaged across H-H separations of $\{0.5, 0.9, 1.3, 1.7, 2.1, 2.5\}$ Å, starting from circuits with the theoretically optimal variational parameters (κ). "Raw" corresponds to fidelities from constructing the 1-RDM without any error mitigation. "+Post-selection" corresponds to fidelities from constructing the 1-RDM with post-selection on particle number. "+Purification" corresponds to fidelities from constructing the 1-RDM with post-selection and applying purification as post-processing. Finally, "+VQE" corresponds to fidelities from using all previously mentioned error mitigation techniques in conjunction with variational relaxation. Note that for small values (such as the "raw" value for H_{12}) we expect the fidelity lower-bound is more likely to be loose.

theory reverses the order of the transition states; however, here we focus on the accuracy of the computation with respect to the simulated model. Correctly identifying this pathway requires resolving the energy gap of 40 milliHartree between the two transitions states. The pathways correspond to the motion of the Hydrogen in the process of converting *cis*-diazene to *trans*-diazene. One mechanism is in-plane rotation of a Hydrogen while the other is an out-of-plane rotation corresponding to rotation of the HNNH dihedral angle. Figure 3 contains VQE optimized data simulating nine points along the reaction coordinates for in-plane and out-of-plane rotation of Hydrogen. VQE produces 1-RDMs with average fidelity greater than 0.98 after error-mitigation. Once again, we see that our full error mitigation procedure significantly improves the accuracy of our calculation.

Our VQE calculations on diazene predicts the correct ordering of the transition states to within the chemical model with an energy gap of 41 ± 6 milliHartree while the true gap is 40.2 milliHartree. We provide a more detailed analysis of the error mitigation performance on the diazene circuits in Appendix F considering that the $\sqrt{i\text{SWAP}}$ gates we use have residual CPHASE($\pi/24$) and stochastic control angles for Rz gates. This simulation reinforces VQEs ability to mitigate systematic errors at the scale of 50 $\sqrt{i\text{SWAP}}$ gates and over 80 Rz gates.

IV. CONCLUSION

In this work we take a step towards answering the question of whether NISQ computers can offer quantum advantage for chemical simulation by studying VQE performance on basis rotation circuits that are widely used in quantum algorithms for fermionic simulation. The ansatz we consider affords us ways to minimize the resource requirements for VQE and study device performance for

circuits that are similar to those needed for full Hamiltonian simulation. These basis rotation circuits also make an attractive benchmark due to their prevalence, optimal known compilation, the ability to extract fidelity and fidelity witness values and the fact that they parameterize a continuous family of analytically solvable circuits demonstrating a high degree of entanglement.

We demonstrated the performance of two error mitigation techniques on basis rotation circuit fidelity. The first is post-selection on total occupation number when measuring all elements of the 1-RDM. This is accomplished by permuting the basis rotation circuit such that all measurements involve estimating nearest-neighbor observables and measuring each pair of observables such that the total occupation number is preserved. The second is the application of McWeeny purification as a post-processing step. The energy improvements by projecting back to the pure-state N-representable manifold is evidence that generalized pure-state N-representability conditions will be instrumental in making NISQ chemistry computations feasible. This underscores the importance of developing procedures for applying pure-state N-representability conditions in a more general context.

Finally, we were able to show further evidence that variational relaxation can effectively mitigate coherent errors arising in implementation of physical gates. The combination of these error mitigation techniques allowed us to unambiguously resolve a chemical mechanism to within the model chemistry using a quantum computation. It is still an open question whether NISQ devices will be able to simulate quantum chemistry systems in the classically intractable regime and it is likely that major innovations would be required to close that gap. However, we find the accuracy of these experiments and the effectiveness of these error-mitigation procedures to be an encouraging signal of progress in that direction.

Author Contributions

N. Rubin designed the experiment. C. Neill assisted with data collection. Z. Jiang, V. Smelyanskiy, and N. Wiebe assisted with analytical calculations and gate synthesis. N. Rubin and R. Babbush wrote the paper. Experiments were performed using a quantum processor that was recently developed and fabricated by a large effort involving the entire Google Quantum team.

Code Availability

The code used for this experiment and a tutorial for running it can be found in the open source library OpenFermion-Cirq, located at https://github.com/quantumlib/OpenFermion-Cirq/experiments/hfvqe [34].

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Appendix A: Hartree-Fock Theory via Canonical Transformations

In this section we derive Hartree-Fock theory from the perspective of canonical transformations. This derivation follows an original work by David Thouless [11] and is reproduced here due to its foundational importance to the formulation of this experiment. In Hartree-Fock theory one attempts to solve the time-independent Schrödinger equation using a state ansatz that is an antisymmeterized product of one-particle functions. Starting from an arbitrary orthogonal basis $\{\phi_i\}$ the goal is to variationally optimize the wavefunction

$$|\psi(r_1, ..., r_n)\rangle = (n!)^{-1/2} A_n (\chi_1(r_1)...\chi_n(r_n)) \tag{A1}$$

where A_n is the antisymmeterizer and $\chi_i(r) = \sum_j c_i^j \phi_j(r)$ in terms of the coefficients for χ. This antisymmeterized product of one-particle functions is commonly expressed in a more compact form as a determinant of a matrix whose elements are the functions $\chi_i(r_j)$ with i indexing the column and j indexing the row of this matrix. This representation of the antisymmeterized product through a determinant is why this wavefunction ansatz is commonly referred to as a Slater determinant.

The variational principle for the Schrödinger equation can be stated as

$$\langle \delta\psi | H | \psi \rangle = 0 \tag{A2}$$

which is a statement that the energy is stationary with respect to first order changes in the wavefunction. In second quantization a single antisymmeterized product of orbitals corresponds to a product of ladder operators acting on the vacuum to "create" a representation of the antisymmeterized wavefunction

$$\langle r | \psi \rangle = \langle r | \prod_{i=1}^{n} a_i^\dagger | 0 \rangle = \frac{1}{\sqrt{n!}} \text{Det} \left[\begin{pmatrix} \chi_1(r_1) & \cdots & \chi_1(r_n) \\ \vdots & \ddots & \vdots \\ \chi_n(r_1) & \cdots & \chi_n(r_n) \end{pmatrix} \right]. \tag{A3}$$

Assuming we are working in a fixed particle manifold and given the aforementioned complete set of one-particle functions is used as a basis we can index the functions used in the product wavefunction by i and those not used are labeled by a then any change in the wavefunction is generated by

$$\langle \delta\psi | = \langle \psi | a_i^\dagger a_a \zeta \tag{A4}$$

where ζ is the first order change to an orbital χ_i. This is because any unitary generator that has only indices $\{a\}$ or $\{i\}$ merely changes the phase on the state and thus is not observable [35]. Evaluating Eq. (A2) one arrives at an expression for the stationarity of the state

$$\langle \psi | a_i^\dagger a_a H | \psi \rangle = 0. \tag{A5}$$

All the quantities in Eq. (A5) can be evaluated using Wick's theorem given the initial state ψ is a product state and $a_r|0\rangle = 0$. This variational condition naturally leads to the *self-consistent-field* Hamiltonian commonly derived through a Lagrangian technique for the Hartree-Fock equations. In order to design a VQE style approach to solving the Hartree-Fock equations we take a different approach that leverages the fact that we can determine any basis rotation through a linear-depth quantum circuit. Thouless demonstrated [11] that any non-orthogonal product wavefunction can be obtained from a product wavefunction by a unitary generated by one-body fermionic operators of the form $a_p^\dagger a_q$. The underlying reason for why this is true is the fact that the one-body fermionic generators form a closed Lie-algebra. Given,

$$[a_p^\dagger a_q, a_r^\dagger a_s] = \delta_{q,r} a_p^\dagger a_s - \delta_{p,s} a_r^\dagger a_s \tag{A6}$$

the adjoint representation of any element of the algebra κ where

$$\kappa = \sum_{p,q} \kappa_{p,q} a_p^\dagger a_q, \tag{A7}$$

and its commutator with any other element can be efficiently represented as matrix that is $m \times m$ where m is the number of fermionic modes.

$$[\kappa, a_p^\dagger] = a_q^\dagger \kappa_{p,q} \quad , \quad [\kappa, a_p] = a_q \kappa_{p,q}^* \tag{A8}$$

Using the BCH expansion, we can express the similarity transformed ladder operators as

$$e^K a_p^\dagger e^{-K} = \sum_q a_q^\dagger u_{q,p} \ , \quad e^K a_p e^{-K} = \sum_q a_q u_{q,p}^* \tag{A9}$$

where u is the matrix given by the exponentiation of the coefficient matrix for the generator operator κ

$$u = e^\kappa \tag{A10}$$

which is the proof for Eq. (1). Any rotation of the underlying basis can now be represented as a similarity transformation of each fermionic mode

$$|\phi(\kappa)\rangle = e^K a_1^\dagger e^{-K} ... e^K a_n^\dagger e^{-K} |0\rangle = e^K |\psi\rangle. \tag{A11}$$

Thus any non-orthogonal state can be generated by implemented e^K as a circuit acting on an initial product state.

Given the Hartree-Fock wavefunction ansatz the energy is given by

$$E(\kappa) = \langle \phi(\kappa)|H|\phi(\kappa)\rangle = \langle\psi|e^K H e^{-K}|\psi\rangle. \tag{A12}$$

With the energy expressed in the form of Eq. (A12) it is not immediately clear that it can be evaluated without knowledge of the 2-RDM. To see this, employ the BCH expansion and notice that all nested commutator terms involve $a_p^\dagger a_q$-like terms and the original hamiltonian. The commutator of a two-mode number conserving fermionic operator with a four-mode number conserving fermionic operator produces a linear combination of four four-mode number conserving fermionic operators. Therefore, all terms in the expansion can be evaluated with knowledge of only the 2-RDM. If we start with a product state defined from an orthogonal set of states the 2-RDM can be constructed directly from the 1-RDM [27]

$$\begin{aligned}
{}^1D_i^j &= \langle\phi|a_j^\dagger a_i|\phi\rangle \\
{}^2D_{ij}^{pq} &= \langle\phi|a_p^\dagger a_q^\dagger a_j a_i|\phi\rangle = {}^1D_i^p \, {}^1D_j^q - {}^1D_i^q \, {}^1D_j^p
\end{aligned} \tag{A13}$$

This also demonstrates that we only need to measure the 1-RDM to evaluate the energy. The energy is evaluated as a function of the 1- and 2-RDM by

$$E(\kappa) = \sum_{ij} h_{ij} \langle\phi(\kappa)|a_i^\dagger a_j|\phi(\kappa)\rangle + \sum_{ijkl} V_{ijkl} \langle\phi(\kappa)|a_i^\dagger a_j^\dagger a_k a_l|\phi(\kappa)\rangle = \sum_{ij} h_{ij} \, {}^1D_j^i + \sum_{ijkl} V_{ijkl} \, {}^2D_{lk}^{ij} \tag{A14}$$

where h_{ij} and V_{ijkl}

$$h_{i,j} = \int dr \chi_i^*(r) \left(-\nabla^2(r) + \sum_A \frac{Z_A}{|r - R_A|} \right) \chi_j(r) \tag{A15}$$

$$V_{l,k}^{i,j} = \frac{1}{2} \int\int dr_1 dr_2 \chi_i^*(r_1)\chi_j^*(r_2) \left(|r_1 - r_2|^{-1} \right) \chi_k(r_2)\chi_l(r_1) \tag{A16}$$

are the molecular integrals in the original basis. Unless otherwise mentioned these orbitals are determined by diagonalizing the matrix of one-body integrals $h_{ij} = [\mathbf{h}]_{ij}$ described in the atomic orbital basis. In summary, to measure the energy of our system given basis rotation circuit ansatz we need the following steps:

1 Measure the entire 1-RDM.

2 Compute the 2-RDM by evaluating. Eq. (A13)

3 Compute the energy by evaluating. Eq. (A14)

1. Classical simulation of free-fermion circuits

Given a particular set of parameters $\{\kappa_{p,q}\}$ the 1-RDM resulting from a wavefunction $\psi = U(\kappa)\phi$, where ϕ is an initial product state, is

$$^1\tilde{D}_q^p = \langle\phi|e^{-K}a_p^\dagger e^K e^{-K} a_p e^K|\phi\rangle = \langle\phi|\sum_j u_{p,i} a_i^\dagger \sum_{q,j} u_{q,j}^* a_j|\phi\rangle = \sum_{ij} u_{p,i} u_{q,j}^* \langle\phi|a_i^\dagger a_j|\phi\rangle. \tag{A17}$$

With this 1-RDM one can evaluate the energy and gradients with respect to $\kappa_{p,q}$. This expression requires two matrix multiplications to evaluate along with the 1-RDM of the starting state.

Appendix B: Implementing the Basis Change Circuit and Circuit Concatenation

In order to implement the basis rotation circuits we leverage a number of recent works that provide asymptotically optimal circuit compilations. We review a circuit construction that is analogous to a QR decomposition as motivation before highlighting the salient features of the optimal circuit compilation. The basis rotation circuit is first expressed in fermionic modes which we then provide a compilation to the gate set used in this work. Our goal is to implement a unitary corresponding to

$$U(e^\kappa) = e^K \qquad\qquad K = \sum_{i,j} \kappa_{i,j} a_i^\dagger a_j \qquad\qquad \kappa^\dagger = -\kappa. \tag{B1}$$

Not all terms in K commute and thus naively one would expect an approximate method such as Trotterization to be required. In Reference [26] the connection of the QR decomposition of e^κ via Givens rotation to the sequence of untiaries $R_{pq}(u)$

$$R(u)_{pq} = e^{\log[u]_{pq}(a_p^\dagger a_q - a_q^\dagger a_p)} \tag{B2}$$

was established allowing for the exact evolution of the one-body component of the Hamiltonian without Trotter error and a circuit to implement any basis rotation–i.e. any Slater determinant. A unique feature of one-body rotations is that the map $U(e^\kappa)$ is a homomorphism under matrix multiplication

$$U(e^\kappa) \cdot U(e^{\kappa'}) = U(e^\kappa \cdot e^{\kappa'}) \tag{B3}$$

We use this homomorphism through the observation that

$$R_{pq}(\theta)U(u) = U(r_{pq}(\theta)u) \tag{B4}$$

where

$$r(\theta)_{p,q} = \begin{pmatrix} 1 & ... & 0 & ... & 0 & ... & 0 \\ \vdots & \ddots & \vdots & & \vdots & & \vdots \\ 0 & ... & \cos(\theta) & ... & -\sin(\theta) & ... & 0 \\ \vdots & & \vdots & & \vdots & & \vdots \\ 0 & ... & \sin(\theta) & ... & \cos(\theta) & ... & 0 \\ \vdots & & \vdots & & \vdots & \ddots & \vdots \\ 0 & ... & 0 & ... & 0 & ... & 1 \end{pmatrix} \tag{B5}$$

which given an appropriate selection of a sequence of $r_{p,q}(\theta)$ brings u into diagonal form

$$\prod_k R_k(\theta_k)U(u) = \sum_p e^{-i\phi_p a_p^\dagger a_p} = \sum_p e^{-i\phi_p}|p\rangle\langle p| \tag{B6}$$

The sequence of $R_k(\theta_k)$ can be determined by a QR decomposition of the matrix u. This was first recognized by Reck [24] and used in a variety of quantum optics experiments to implement universal unitary operations–limited to unitaries associated with one-body fermionic Hamiltonians. Jiang *et. al* and Kivlichan *et. al* [26, 36] point out that in a fixed particle manifold the circuit depth can be further minimized. This is clearly shown by considering the state in the basis that is being prepared through the Givens rotation network and back transforming to the original basis

$$|\psi(\kappa)\rangle = \prod_{i=1}^\eta \tilde{a}_i^\dagger|\text{vac}\rangle = \prod_{i=1}^\eta e^{-K}\tilde{a}_i^\dagger e^K|\text{vac}\rangle = \prod_{i=1}^\eta \sum_p [e^\kappa]_{i,p} a_p^\dagger|\text{vac}\rangle \tag{B7}$$

we only need the first η-columns of the matrix $[e^\kappa]$. Therefore, we can focus on Givens network elimination on these columns. Jiang *et al.* provide a further circuit minimization by noting that any rotation amongst the occupied orbitals merely shifts the observable by a global phase. Given a unitary V

$$\prod_{i=1}^\eta \sum_{j=1}^\eta V_{i,j}\tilde{a}_i^\dagger|\text{vac}\rangle = \det[V]\prod_{i=1}^\eta \tilde{a}_i^\dagger|\text{vac}\rangle \tag{B8}$$

FIG. 4. Givens rotation circuit for H_8 simulating a random basis transformation in the half filling sector. Each Givens rotation is compiled into $\sqrt{i\text{SWAP}}$ and Rz gates.

where the $\det[V]$ is a phase and thus not observable. The V can be chosen such that the lower left triangle or e^κ are zeroed out by Givens rotations. In chemistry parlance this is known as occupied-occupied orbital rotations and is known to be a redundant rotation. For restricted Hartree-Fock the number of non-redundant parameters in κ is equal to the number of occupied spatial orbitals times the number of virtual orbitals.

An example of an eight qubit half-filling circuit is given in Figure 4. When we are away from half filling the nice symmetry of the circuit is lost. For example, Figure 5 is Diazene which has 8-electrons in 12 orbitals.

FIG. 5. Givens rotation circuit for diazene prior to freezing the two lowest energy orbitals. Away from half filling the basis rotations have a parallelogram structure.

Appendix C: Optimal Measurement of the 1-RDM

In this section we present a methodology that allows us to measure the 1-RDM in $N+1$ measurement settings and no additional quantum resources. We will also discuss a method that allows us to perform post selection on all the Monte Carlo averaged terms at the cost of an additional row of $\sqrt{i\text{SWAP}}$ gates at the end of the circuit. The 1-RDM is an $N \times N$ hermitian positive semidefinite matrix with elements equal to the expectation values $\langle a_i^\dagger a_j \rangle$ where $\{i, j\}$ index the row and column of the matrix. The matrix of expectation values is depicted in Figure 6. As a motivator for our measurement protocol we start by describing circuits required to measure the diagonal elements of the 1-RDM of a six qubit system at half filling–i.e. $\langle a_i^\dagger a_i \rangle$.

1. Diagonal terms

Given a circuit U implementing the basis rotation e^κ the diagonal elements of the 1-RDM are obtained by measuring the Z expectation value on each qubit. The correspondence between $a_i^\dagger a_i$, measurement result M_i from qubit i, qubit operators is derived using the Jordan-Wigner transform

$$\langle a_i^\dagger a_i \rangle = \frac{I - \langle Z_i \rangle}{2} = \langle M_i \rangle \tag{C1}$$

where Z_i is the Z-qubit operator on qubit labeled i. The expectation value $\langle a_i^\dagger a_i \rangle$ is equivalent to the probability of measuring a 1 bit on qubit i–i.e $\langle M_i \rangle$. Because we are measuring in the computational basis we can post-select on the three excitations in the measurement result. This process is depicted in Figure 6.
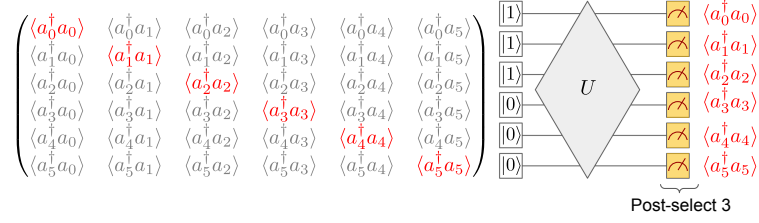
FIG. 6. Measurement circuit associated with estimating all diagonal elements of the 1-RDM simultaneously. The elements that are acquired with this circuit are highlighted in red.

2. One-off-diagonal terms

The hermiticity of the 1-RDM demands that $\langle a_i^\dagger a_{i+1}\rangle = \langle a_{i+1}^\dagger a_i\rangle^*$. The 1-RDM has no imaginary component because we use an initial basis built from real valued orbitals and the basis rotation circuit implements an element of $SO(N)$–i.e. the basis rotation circuit involves a unitary matrix with real values. Therefore, we only measure the real part of all one-off-diagonal terms $a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i$ which corresponds to $2\Re\langle a_i^\dagger a_{i+1}\rangle$. Using the Jordan-Wigner transform to map fermionic ladder operators to qubits

$$\langle a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i\rangle = \frac{1}{2}\left(\langle X_i X_{i+1}\rangle + \langle Y_i Y_{i+1}\rangle\right) = 2\Re\langle a_i^\dagger a_{i+1}\rangle \tag{C2}$$

we see that we must measure XX on all pairs and YY on all pairs. This can be accomplished with two circuits depicted in Figure 7.
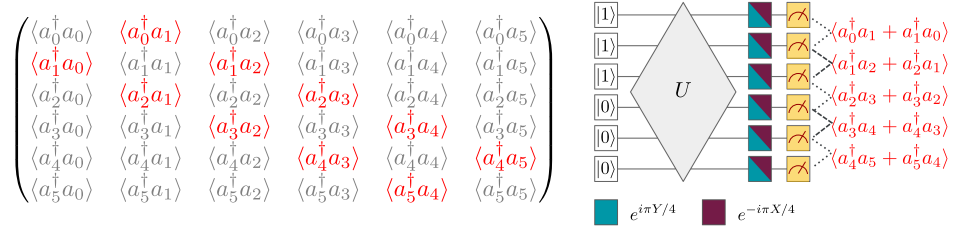
FIG. 7. The two circuits allowing for the measurement of all one-off-diagonal elements of the 1-RDM simultaneously. The teal circuit involves performing an Ry rotation (to measure in the X basis) at the end of the circuit while the purple circuit contains an Rx rotation (to measure in the Y basis). The 1-RDM elements that are acquired with these circuits are highlighted in red. We label which pairs contribute to which expectation values with grey dashed lines. The thinner dashes are for the even 1-RDM pairs while the thicker dashes are for the odd 1-RDM pairs. Because Ry and Rx operations do not preserve particle number we cannot post-select on total particle number with these measurement circuits.

3. General off-diagonal terms and virtual swapping

The label of each fermionic mode is an arbitrary choice, so we are free to reorder the labels such that measuring nearest-neighbor pairs of qubits corresponds to measuring different off-diagonal 1-RDM elements. Every relabeling of the qubits requires us to recompile the Givens rotation circuit. The structure of the circuit stays the same but the rotation angles are different. In this section we describe how to recompute the Givens rotation angles based on a new label ordering. Using the label sets $\{1, 3, 0, 5, 2, 4\}$ and $\{3, 5, 1, 4, 0, 2\}$ we are able to use the two measurementment circuits in Figure 7 to measure the remaining off-diagonal 1-RDM elements.

Formally, we build the new qubit labels by virutally swapping fermionic modes at the end of the original circuit implement e^κ. We note that performing nearest-neighbor fermionic swaps between adjacent pairs twice (even swaps and odd swaps) we obtain a new ordering of qubits. For example, consider six fermionic modes $\{0, 1, 2, 3, 4, 5\}$. Performing a set of fermionic swaps on modes labeled $\{(0, 1), (2, 3), (4, 5)\}$ followed by swaps on $\{(1, 2), (3, 4)\}$ leaves our mode ordering as $\{1, 3, 0, 5, 2, 4\}$. We can then perform X-Pauli and Y-Pauli measurements on each qubit to recover expectation values associated with

$$\{\Re(a_1^\dagger a_3 + a_3^\dagger a_1), \Re(a_3^\dagger a_0 + a_0^\dagger a_3), \Re(a_0^\dagger a_5 + a_5^\dagger a_0), \Re(a_5^\dagger a_2 + a_2^\dagger a_5), \Re(a_2^\dagger a_4 + a_4^\dagger a_2)\}. \tag{C3}$$
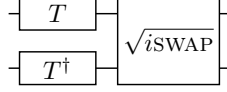
FIG. 8. Two-mode fermionic fast Fourier transform that diagonalizes the $XX + YY$ Hamiltonian.

This procedure can be repeated twice more to measure all the required two-body fermionic correlators to construct the 1-RDM. Though it appears that each new label set incurs additional circuit by requiring fermionic swaps between neighboring modes we can exploit the fact that one-body fermionic swaps generated by $\exp(-i\pi\text{FSWAP}/2)$ where FSWAP is

$$\text{FSWAP} = a_p^\dagger a_q + a_q^\dagger a_p - a_p^\dagger a_p - a_q^\dagger a_q. \tag{C4}$$

This one-body permutation can be viewed as a basis rotation which can be concatenated with the original circuit at no extra cost due to Eq. (B3). The swapping unitary simply shuffles the columns of e^κ that is used to generate the Givens rotation network. In conclusion we need $N/2$ circuits, where each of the $N/2$ circuits gets measured in two or three different ways, for an N-qubit system to measure the 1-RDM.

4. Off-diagonal terms with post-selection

The circuits depicted in Figure 7 did not allow for post-selection because the rotations to measure in the X-basis and Y-basis do not commute with the total number operator. In this section we design a basis rotation circuit that commutes with the total number operator and diagonalizes the $\frac{1}{2}(XX + YY)$ Hamiltonian. The diagonal form means that after performing the basis rotation we can measure in the computational basis to obtain expectation values $\frac{1}{2}\langle XX + YY \rangle$.

The circuit that diagonalizes $\frac{1}{2}(XX + YY)$ is described in Figure 8 and is denoted U_M below. Its commutation with the total number operator can be easy seen by recognizing that the T-gate ($\text{Rz}(\pi/4)$) commutes with the total number operator and so does the $\sqrt{i}\text{SWAP}$. Applying U_M to the $\frac{1}{2}(XX + YY)$ Hamiltonian

$$U_M \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} U_M^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{C5}$$

transforms the operator into a diagonal representation. Given an ordered pair of qubits $\{a, a+1\}$ the last matrix in (C5) is $\frac{1}{2}(Z_a - Z_{a+1})$ in qubit representation. Finally, we can relate the Z expectation values, the transformed $XX + YY$ expectation values, fermionic ladder operators, and binary measurements $\{M_a, M_{a+1}\}$ via

$$\langle U_m \left(a_a^\dagger a_{a+1} + a_{a+1}^\dagger a_a \right) U_m^\dagger \rangle = \langle U_m \frac{1}{2}(X_a X_{a+1} + Y_a Y_{a+1}) U_m^\dagger \rangle = \frac{1}{2}\langle Z_a - Z_{a+1} \rangle = \frac{1}{2}(M_{a+1} - M_a). \tag{C6}$$

The measurement circuit can only be applied to non-overlapping pairs and thus we can obtain estimates of $X_a X_{a+1} + Y_a Y_{a+1}$ for a values corresponding to even integers or a corresponding to odd integers. More concretely, we describe this process in Figure 9 for a six qubit problem.
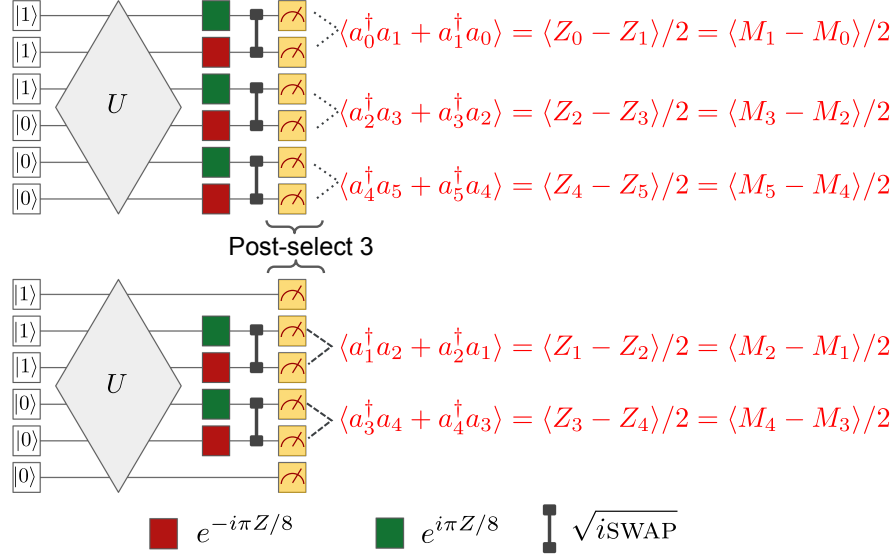
FIG. 9. Two circuit measuring the one-off-diagonal of the 1-RDM such that the total particle number can be measured simultaneously. This allows us to post select on the correct number of excitations in the measured bitstring. The top circuit measures the even pairs while the bottom circuit measures the odd pairs. Local Z expectation values are measured on all the qubits and used to construct the expectation value for $\langle a_i^\dagger a_{i+1} \rangle$.

5. Computing error bars for elements of the 1-RDM

We use two methods to estimate error bars for all quantities in our experiments. The procedures differ in how the covariance between 1-RDM terms is estimated. In the first procedure, error bars are generated by estimating the covariance between terms in the 1-RDM at the same time as the mean estimation. Mean values of off-diagonal 1-RDM terms involve estimating the expectation values for $(Z_a - Z_b)/2$. Therefore, the covariance between two off-diagonal elements of the 1-RDM is

$$\text{Cov}\left[\frac{1}{2}\left(Z_a - Z_b\right), \frac{1}{2}\left(Z_p - Z_q\right)\right] = \frac{1}{4}\left(\text{Cov}\left[Z_a, Z_p\right] - \text{Cov}\left[Z_a, Z_q\right] - \text{Cov}\left[Z_b, Z_p\right] + \text{Cov}\left[Z_b, Z_q\right]\right) \tag{C7}$$

for all pair sets $\{(a,b), (p,q)\}$ measured simultaneously. All quantities can be estimated from the simultaneous measurement of all qubits. Therefore, for each circuit permutation we obtain two covariance matrix of size $N/2 \times N/2$ and $N/2 - 1 \times N/2 - 1$. For the circuit with no label permutation we also obtain the covariances for all $a_i^\dagger a_i$ terms.

In the second procedure for estimating covariance matrices we assume we are sampling from a pure Gaussian state. This assumption is applicable when the fidelity is high enough as any change to the covariance matrix would be a second order effect. For these states the 2-RDM is exactly described by the 1-RDM and therefore all covariances between the 1-RDM elements are perfectly defined by a non-linear function of the 1-RDM elements. For any wavefunction ψ corresponding to the output of a basis rotation circuit the covariance of 1-RDM elements computed from such a wavefunction are as follows:

$$\text{Cov}\left[a_i^\dagger a_j + a_j^\dagger a_i, a_p^\dagger a_q + a_q^\dagger a_p\right]_\psi = D_q^i \delta_p^j - D_q^i D_j^p + D_p^i \delta_q^j - D_p^i D_j^q + D_q^j \delta_p^i - D_q^j D_i^p + D_p^j \delta_q^i - D_p^j D_i^q. \tag{C8}$$

With the estimates of the covariances we are able to re-sample the 1-RDM assuming central-limit theorem statistics. We use a multinomial distribution where the mean values are $\langle a_{\sigma(i)}^\dagger a_{\sigma(i+1)} \rangle$ and the covariance matrix of the multinomial distribution is obtained by dividing the estimates of the covariance matrix above by $\alpha \times 250{,}000$. α is a number less than 1 reflecting the probability that a bitstring is rejected. α is estimated from prior N-qubit experiments. Once the new 1-RDM is obtained it can be purified, used to estimate a fidelity witness, and compute the energy. For all error bars we re-sample the 1-RDM 1000 times and compute a mean value and standard deviation from this set. All quantities estimated are sensitive to the N-representability of the resampled 1-RDM. We use the fixed trace positive projection described in [29] to ensure that each resampled 1-RDM is positive semidefinite and has the correct trace. The correct procedure is only applied when the resampled 1-RDM has eigenvalues below zero.

Appendix D: Computing the fidelity and a fidelity witness from the 1-RDM

1. Fidelity Witness

The class of quantum circuits simulating free-fermion dynamics have the special property that an efficient fidelity witness can be derived. The formal derivation for general free-fermion wavefunctions is described in Reference [33]. Here we adapt this result to the special case of particle conserving dynamics generated by one-body fermionic generators. A fidelity witness is an observable that provides a strict lower bound to the fidelity for all input states. The fidelity witness is efficient in the sense that for an L-qubit system only L^2 expectation values are required to evaluate the fidelity witness. Given that U is a unitary corresponding to a basis transformation circuit and $|\omega\rangle$ is the initial computational basis state corresponding to $\omega = (\omega_1, ..., \omega_L)$ any L-bit string which satisfies $n_j|\omega\rangle = \omega_j|\omega\rangle$ for $j = 1, ..., L$ allows us to define a basis state annihilator operator

$$n^{(\omega)} = \sum_{j=1}^{L} [(1 - \omega_j)n_j + \omega_j(\mathbb{I} - n_j)] = \sum_{j=1}^{L} [n_j - \omega_j n_j + \omega_j \mathbb{I} - \omega_j n_j] = \sum_{j=1}^{L} [n_j + \omega_j \mathbb{I} - 2\omega_j n_j] \tag{D1}$$

which satisfies $n^{(\omega)}|\omega\rangle = 0$. The computational basis state $|\omega\rangle$ is the zero energy eigenstate of n^ω and any other computational basis state an excitation from this state. The excitation energy is exactly the number of bits that are different from ω for each Fock basis state which can be computed by summing the resulting bit string from the XOR operation between the two Fock basis states being considered. The fidelty witness

$$\mathcal{W} = U\left(\mathbb{I} - n^\omega\right)U^\dagger \tag{D2}$$

can be evaluated with knowledge of the measured 1-RDM. To relate the fidelity witness to the 1-RDM it is important to note the following

$$\mathrm{Tr}\left[U\rho_p U^\dagger a_i^\dagger a_j\right] = \left[\mathbf{u}D\mathbf{u}^\dagger\right]_{i,j} \tag{D3}$$

where D is the matrix of expectation values $\langle \rho_p, a_i^\dagger a_j \rangle$ and $\mathbf{u} = e^\kappa$ because any one-body rotation on the state ρ_p can be equated to a similarity transform of the generating matrix for that one-body transformation. This is similar logic used in [37] to move one-body basis rotations at the end of the circuit into the Hamiltonian as an error mitigation technique. Using this relationship we can evaluate the fidelity witness with the following expression

$$F_{\mathcal{W}}(\rho_p) = 1 - \sum_{j=1}^{L} \left(\left[\mathbf{u}^\dagger \mathbf{D}\mathbf{u}\right]_{j,j} + \omega_j - 2\omega_j \left[\mathbf{u}^\dagger \mathbf{D}\mathbf{u}\right]_{j,j} \right) \tag{D4}$$

where $\mathbf{D}$ is the 1-RDM that is measured, $\mathbf{u} = e^\kappa$ is the unitary rotation representing the new Slater determinant.

2. Fidelity

Given an idempotent 1-RDM and the basis rotation unitary $u = e^\kappa$, the fidelity can be determined by the following procedure:

1. Perform an eigen decomposition on the purified 1-RDM and use the eigenvectors associated with eigenvalues equal to 1 as the columns of a unitary matrix v corresponding to the measured basis rotation.

2. Use the expression for the overlap between two basis rotation unitaries $|\langle\psi_u|\psi_v\rangle|^2 = |\det\left(v^\dagger u\right)|^2$ to compute the fidelity. The function det is the determinant of a matrix. This is the inner product between two Grassmann representatives and is independent of choice of orbitals.

Appendix E: Error mitigation through purification

A unique feature of the Slater determinant wavefunction ansatz is that their 1-RDMs are idempotent matrices. The manifold of states with idempotent 1-particle density matrices is significantly smaller than the space of possible wavefunctions. Thus our error mitigation strategy will rely on projecting the measured 1-RDM to the closest idempotent 1-RDM. This projection procedure can be represented by the following mathematical program

$$\min_{Tr[D]=\eta, D\succeq 0, D^2=D} ||D - \tilde{D}|| \tag{E1}$$

that seeks to determine a 1-RDM D that is close to the measured 1-RDM $\tilde{D}$ with has fixed trace, is positive semidefinite, and is a projector. A practical implementation of the the program in Eq. (E1) is challenging due to the idempotency constraint. Instead of solving Eq. (E1) directly we rely on an iterative procedure that under mild conditions projects a measured 1-RDM $\tilde{D}$ towards the set of idempotent matrices. This procedure is the McWeeny purification commonly used in linear scaling electronic structure techniques [27] and is defined by the iteration

$$D_{n+1} = 3D_n^2 - 2D_n^3. \tag{E2}$$

After each iteration the eigenvalues are closer to $\{0, 1\}$. Prior work [38] proposed to use McWeeny purification on the 2-RDM, but it is not clear what that accomplishes. This is because, in general, 2-RDMs are not idempotent matrices and applying pure-state purification requires more general pure-state N-representability conditions [30].

Here we will estimate the number of samples needed to ensure that the 1-RDMs can be faithfully reconstructed within arbitrarily small error using our protocol. This analysis assumes we sample from a perfect state and thus our goal is to provide evidence that McWeeny purification is convergent under sampling noise. Consider the purification process in Eq. (E2). Now let us assume that the principal eigenvalue of D is P_k. In absentia of numerical error we would have that $P_k = 1$ for Hartree-Fock theory. However, sampling error incurs an error in this eigenvalue such that

$$P_k = 1 + \Delta, \tag{E3}$$

where Δ is a random variable with mean 0 and variance σ^2. Further, let $\mu_k = \mathbb{E}(\Delta^k)$, where $\mu_2 = \sigma^2$ for example. Now given these quantities we wish to evaluate

$$\mathbb{E}(P_{k+1}) = \mathbb{E}(3P_k^2 - 2P_k^3) = 1 - 3\sigma^2 - 2\mu^3. \tag{E4}$$

Similarly we have that

$$\mathbb{E}(P_{k+1}^2) = 1 - 6\sigma^2 - 4\mu_3 + 9\mu_4 + 12\mu_5 + 4\mu_6. \tag{E5}$$

This implies that the variance is

$$\mathbb{V}(P_{k+1}) = \mathbb{E}(P_{k+1}^2) - \mathbb{E}(P_{k+1})^2 = 9(\mu_4 - \sigma^4) + 12(\mu_5 - \sigma^2\mu_3) + 4(\mu_6 - \mu_3^2). \tag{E6}$$

Further, let us assume that $\mu_j \leq \alpha_j \sigma^j$, for all j .

$$\mathbb{V}(P_{k+1}) \leq 9\sigma^4(\alpha_4 - 1) + 12|\sigma|^5(\alpha_5 + \alpha_3) + 4|\sigma|^6\alpha_6. \tag{E7}$$

Assuming that $\sigma \leq 1$ we have that

$$\mathbb{V}(P_{k+1}) \leq 9\sigma^4(\alpha_4 - 1) + 4|\sigma|^5(\alpha_6 + 3\alpha_5 + 3\alpha_3). \tag{E8}$$

It is clear from this recurrence relation that the variance for this method converges quadratically (assuming σ is sufficiently small). Specifically, we have that $\mathbb{V}(P_K) \leq \epsilon$ for $K \in \mathcal{O}(\log\log(1/\epsilon))$ if appropriate convergence criteria are met. A criterion for convergence is that $9\sigma^4(\alpha_4 - 1) + 4|\sigma|^5(\alpha_6 + 3\alpha_5 + 3\alpha_3) \leq \sigma^2$. This is guaranteed if,

$$\sigma^2 \leq \frac{1}{9(\alpha_4 - 1)}\left(1 - \frac{\beta\left(-\beta + \sqrt{\beta^2 + 36\alpha_4 - 36}\right)}{18(\alpha_4 - 1)}\right), \tag{E9}$$

where $\beta = 4(\alpha_6 + 3\alpha_5 + 3\alpha_3)$.

The precise values of α_j depend on the nature of the underlying distribution. However, if we assume that it is Gaussian then we have that $\alpha_{2j+1} = 0 \; \forall \; j$, $\alpha_4 = 3$, $\alpha_6 = 15$. Furthermore, we have under these Gaussian assumptions (for any $\sigma > 0$) that

$$\mathbb{V}(P_{k+1}) \leq 18\sigma^4 + 12\sigma^6. \tag{E10}$$

In this case, we find that the McWeeny iteration will converge if $\mathbb{V}(P_{k+1}) \leq \sigma^2$ which is implied by

$$\sigma^2 \leq \frac{-3}{20} + \frac{\sqrt{564}}{120} \approx 0.048. \tag{E11}$$

This relatively broad distribution implies that even if the uncertainty in the principal eigenvalue of the reconstructed RDM is large then the algorithm will with high probability converge to a pure state after a small number of iterations (if the underlying distribution is Gaussian). If the distribution is non-Gaussian then Eq. (E9) can be used to show convergence given that the moments of the distribution are appropriately small.

1. Errors in Eigenvalues

The errors in the eigenvalues of the RDM are easy to compute from known results. We have from Corollary 6.3.4 from [39] that if ρ is the true density operator and $\tilde{\rho} = \rho + sE$ for some matrix E of errors and some scalar $s \in [0,1]$ then the error in a particular eigenvalue is at most

$$|\lambda(\rho) - \lambda(\rho + sE)| \leq s\|E\|, \tag{E12}$$

where $\|E\|$ is the spectral norm of the error matrix. We are of course most interested in the case where $s = 1$, however below we will need the above formula for general values of s and so we give it for generality.

Now let E be a matrix consisting of M elements, each of which is independently distributed with zero mean and variances at most σ_M^2. We then have that

$$\mathbb{E}\left((\lambda(\rho) - \lambda(\rho + E))^2\right) \leq \mathbb{E}\left(\sum_{i,j}[E^2]_{i,j}\right) \leq M\sigma_M^2. \tag{E13}$$

Thus

$$\mathbb{V}(\lambda(\rho + E)) \leq M\sigma_M^2. \tag{E14}$$

Hence $\sigma^2 \leq M\sigma_M^2$, which allows the upper bounds in Eq. (E10) to be easily computed (under assumptions of Gaussianity). In particular, we then have convergence under the Gaussianity assumption if

$$\sigma_M^2 \leq \frac{1}{M}\left(\frac{-3}{20} + \frac{\sqrt{564}}{120}\right). \tag{E15}$$

Recall that the 1-RDM constists of $N(N+1)/2$ independent matrix elements, which implies that $M = N(N+1)/2$ in our case.

2. Errors in Eigenvectors

While the above criteria give conditions for the convergence of McWeeny purification starting from a sampled 1-RDM, there remains the question of whether the pure state that it converges to is ϵ-close to the true value. This is relevant because if the errors are large enough that an eigenvalue crossing occurs, then the purification process can fail to yield the desired state. Our aim here is to bound the distance between the eigenvectors.

First, rather than arguing about the difference in eigenvectors for ρ and $\rho + E$ we will instead consider R time slices and will be interested in the eigenvectors of $\rho(j) := \rho + (j/R)E$. Let the principal eigenvector of ρ be $|\lambda\rangle$ and more generally at step j let us denote the eigenvector to be $|\lambda(j)\rangle$ and the correspeonding eigenvalue to be $\lambda(j)$. We then have from first order perturbation theory, assuming that there is an eigenvalue gap that for any state $|\nu([j-1])\rangle$ that is orthogonal to $|\lambda([j-1])\rangle$,

$$\langle\nu(j-1)|\lambda(j)\rangle = \frac{1}{R}\frac{\langle\nu(j-1)|E|\lambda(j-1)\rangle}{\nu(j-1) - \lambda(j-1)} + O(1/R^2) \tag{E16}$$

Thus if we define $\gamma(j)$ to be the minimum eigenvalue gap between $|\lambda(j)\rangle$ and the remainder of the spectrum of $\rho(j)$ we have that

$$\sum_{\nu \neq \lambda}|\langle\nu(j-1)|\lambda(j)\rangle|^2 \leq \sum_{\nu \neq \lambda}\frac{1}{R^2}\frac{|\langle\nu(j-1)|E|\lambda(j-1)\rangle|^2}{(\lambda(j-1) - \nu(j-1))^2} + O(1/R^3)$$

$$\leq \sum_{\nu \neq \lambda}\frac{1}{\gamma^2(j-1)R^2}|\langle\nu(j-1)|E|\lambda(j-1)\rangle|^2 + O(1/R^3)$$

$$= \sum_{\nu \neq \lambda}\frac{1}{\gamma^2(j-1)R^2}\langle\lambda(j-1)|E|\nu(j-1)\rangle\langle\nu(j-1)|E|\lambda(j-1)\rangle|^2 + O(1/R^3)$$

$$= \frac{1}{\gamma^2(j-1)R^2}\left(\langle\lambda(j-1)|E^2|\lambda(j-1)\rangle - (\langle\lambda(j-1)|E|\lambda(j-1)\rangle)^2\right) + O(1/R^3)$$

$$\leq \frac{\|E^2\|}{\gamma^2(j-1)R^2} + O(1/R^3) \tag{E17}$$

It then follows from Eq. (E17) that

$$|\langle \lambda(j-1)|\lambda(j)\rangle - 1|^2 \leq \frac{\|E^2\|}{\gamma^2(j-1)R^2} + O(1/R^3) \tag{E18}$$

This gives us that, for the Euclidean distance between two vectors,

$$\||\lambda(j)\rangle - |\lambda(j-1)\rangle\| \leq \frac{\sqrt{2\|E^2\|}}{\gamma(j-1)R} + O(1/R^2). \tag{E19}$$

Next we have from the triangle inequality that for any integer R,

$$\||\lambda(R)\rangle - |\lambda(0)\rangle\| \leq \sum_{j=1}^{R} \||\lambda(j)\rangle - |\lambda(j-1)\rangle\| \leq \sum_{j=1}^{R} \frac{\sqrt{2\|E^2\|}}{\gamma(j-1)R} + O(1/R) \tag{E20}$$

In particular, this holds as we take $R \to \infty$, which yields

$$\lim_{R \to \infty} \sum_{j=1}^{R} \frac{\sqrt{2\|E^2\|}}{\gamma(j-1)R} + O(1/R) \leq \frac{\sqrt{2\|E^2\|}}{\gamma_{\min}} = \frac{\sqrt{2}\|E\|}{\gamma_{\min}}. \tag{E21}$$

Unfortunately, we do not know what $\gamma_{\min}$ is apriori, however we can bound it modulo some weak assumptions. Let $\|E\| \leq 1/4$, it is then straight forward to verify from Eq. (E12) that

$$\gamma_{\min} \geq 1 - 2\|E\|. \tag{E22}$$

Under the exact same assumptions we then have from a series expansion of the denominator that

$$\||\lambda(\rho)\rangle - |\lambda(\rho + E)\rangle\| \leq \sqrt{2}\|E\| (1 + 4\|E\|) \leq 2\sqrt{2}\|E\| \tag{E23}$$

As E is a sum of M elements each with zero mean and variance at most σ_M we then have under the above assumptions (and the additive property of variance) that

$$\mathbb{V}\||\lambda(\rho)\rangle - |\lambda(\rho + E)\rangle\| \leq 8M\sigma_M^2. \tag{E24}$$

Therefore if we demand that the variance is atmost ϵ^2 it suffices to pick

$$\sigma_M^2 = \frac{\epsilon^2}{8M}, \tag{E25}$$

which sets a sufficient condition on the number of samples of $N_{\text{samp}} \geq \frac{\epsilon}{2\sqrt{2M}}$. The remaining caveat is that in the above analysis we needed to assume that $\|E\| \leq 1/4$. If each of the entries of the matrix E are Gaussian random variables, for example, it then follows that regardless of the value of σ there will always be a tail probability that this eigenvalue condition is not met. We can bound the tail probability using Chebyshev's inequality. Using the exact same reasoning as in Eq. (E14) we have that

$$\mathbb{V}(\|E\|) \leq M\sigma_M^2. \tag{E26}$$

Thus the probability that $\|E\| \geq 1/4$ is

$$P \leq 16M\sigma_M^2 \sim 2\epsilon^2. \tag{E27}$$

Thus even under the pessimistic assumptions of Chebyshev's inequality, we have that the probability of failure is asymptotically negligible if σ_M is chosen in accordance with Eq. (E25). Note that the number of samples needed taken in this case is in $\Theta(\epsilon/N)$ as there are $M \in \Theta(N^2)$ independent matrix elements in the 1-RDM.

Appendix F: Effect of CPHASE and Givens Rotation Error

In this section we consider two known gate errors that occur in the Givens rotation circuits and attempt to analytically and numerically benchmark the effect of these errors. When implementing the $\sqrt{i\text{SWAP}}$ operation there is

a known $|11\rangle\langle11|$ phase error of approximately $\pi/24$. We model this phase error as a CPHASE($\pi/24$) gate that occurs directly after the $\sqrt{i\text{SWAP}}$ gate (Eq. (F1)). We find that the always on CPHASE($\pi/24$) has negligible effect on the outcome of the experiment while the stochastic Rz(θ) errors coherently corrupt the output of the circuit.

$$\sqrt{i\text{SWAP}} \approx \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 \\ 0 & \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & e^{i\pi/24} \end{pmatrix} = \text{CPHASE}(\pi/24)\sqrt{i\text{SWAP}} \tag{F1}$$

To benchmark the effect of the parasitic CPHASE we simulate the diazene experiment with this interaction turned on and evaluate the results with error mitigation. We can counteract the CPHASE($\pi/24$) by performing local Rz gates.
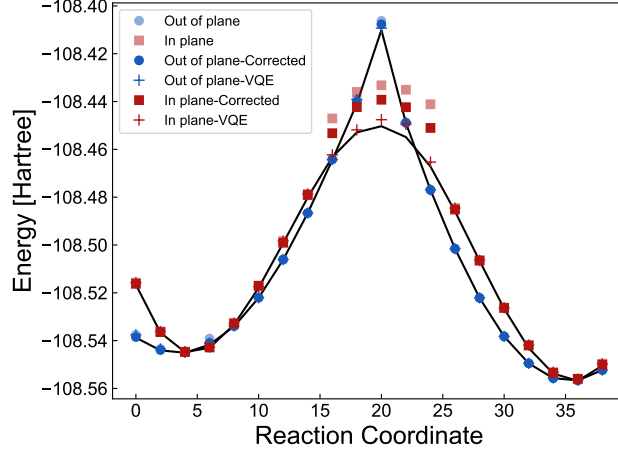

FIG. 10. Analysis of the diazene isomerization curve where the Givens rotations are corrupted by a parasitic CPHASE($\pi/24$). The light dots are the circuits executed without optimization, the darker dots are with an angle adjustment to counteract the known parasitic CPHASE, and the plus markers are VQE optimization of the CPHASE circuits.

Consider the imperfect gate

$$U_1 = \text{diag}(1, 1, 1, e^{-i\phi})\sqrt{i\text{SWAP}} \tag{F2}$$

we can use a different imperfect gate which differs only by single qubit phases,

$$U_2 = \text{diag}(1, e^{i\phi/2}, e^{i\phi/2}, 1)\sqrt{i\text{SWAP}}. \tag{F3}$$

The error associated with U_1 can be approximated by considering the Pauli expansion of the CPHASE part of U_1,

$$\text{diag}(1, 1, 1, e^{-i\phi}) \approx e^{-i\phi} \times \left(II + \frac{i\phi}{4}IZ + \frac{i\phi}{4}ZI - \frac{i\phi}{4}ZZ \right), \tag{F4}$$

and thus the error is approximately

$$\text{Err}_1 \approx 3\left(\frac{\phi}{4}\right)^2 = \frac{3}{16}\phi^2. \tag{F5}$$

Similarly for U_2

$$\text{diag}(1, e^{i\phi/2}, e^{i\phi/2}, 1) \approx e^{i\phi/4}\left(II - \frac{i\phi}{4}ZZ \right) \tag{F6}$$

with an associated Pauli error of

$$\text{Err}_2 \approx \frac{1}{16}\phi^2. \tag{F7}$$

Very crudely, since for $\sqrt{i\text{SWAP}}$ $\phi = \pi/24$, we expect Err_1 to be approximately 0.32% and Err_2 to be approximately 0.11%. This improvement is shown to be most beneficial for simulating the in plane rotations of diazene in Figure 10. The light dots are with the original CPHASE gate whereas the solid dots are with this local Rz correction. We also include a VQE optimization to numerically determine the noise floor for this experiment. This suggests that VQE + error mitigation can mitigate not only control error but more fundamental gate physics issues.

To determine the error budget on the Rz rotation angles we can determine the degree of corruption from Gaussian noise on the control angle. Consider the Rz rotation

$$\text{Rz}(\theta, \delta\alpha) = e^{-iZ\theta(1+\delta\alpha)/2} \tag{F8}$$

where θ is the desired rotation angle and $\delta\alpha$ is a stochastic variable. We can build a simplified model of control angle error as Givens rotation error

$$G(\theta, \delta\alpha) = e^{\theta(1+\delta\alpha)\left(a_i^\dagger a_j - a_j^\dagger a_i\right)} \tag{F9}$$

which can be expressed as

$$G(\theta) = \sqrt{i\text{SWAP}}_{i,j}^\dagger e^{-i\theta(1+\delta\alpha)Z_i/2} e^{i\theta(1+\delta\alpha)Z_j/2} \sqrt{i\text{SWAP}}_{i,j}. \tag{F10}$$

For numerical simplicity we consider the effect on elements of the 1-RDM

$$G(-\theta, \delta\alpha, i, j)a_r^\dagger G(\theta, \delta\alpha, i, j) = \begin{cases} a_i^\dagger \cos(\theta(1+\delta\alpha)) + a_j^\dagger \sin(\theta(1+\delta\alpha)) & \text{if } r = i \\ a_j^\dagger \cos(\theta(1+\delta\alpha)) - a_i^\dagger \sin(\theta(1+\delta\alpha)) & \text{if } r = j \\ a_r^\dagger & \text{if } r \neq i \ \& \ r \neq j \end{cases} \tag{F11}$$

$$G(-\theta, \delta\alpha, i, j)a_s G(\theta, \delta\alpha, i, j) = \begin{cases} a_i \cos(\theta(1+\delta\alpha)) + a_j \sin(\theta(1+\delta\alpha)) & \text{if } s = i \\ a_j \cos(\theta(1+\delta\alpha)) - a_i \sin(\theta(1+\delta\alpha)) & \text{if } s = j \\ a_s & \text{if } s \neq i \ \& \ s \neq j \end{cases} \tag{F12}$$

We can determine the expected 1-RDM with respect to a Gaussian distribution of noise by integrating with respect to the perturbation

$$\rho(\delta\alpha) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(\delta\alpha)^2}{2\sigma^2}} \tag{F13}$$

$$\int_\infty^\infty \rho(\delta\alpha, \sigma)G(-\theta, \delta\alpha, i, j)a_r^\dagger G(\theta, \delta\alpha, i, j)d\delta\alpha = \begin{cases} a_i^\dagger \cos(\theta)e^{-\frac{\theta^2\sigma^2}{2}} + a_j^\dagger \sin(\theta)e^{-\frac{\theta^2\sigma^2}{2}} & \text{if } r = i \\ a_j^\dagger \cos(\theta)e^{-\frac{\theta^2\sigma^2}{2}} - a_i^\dagger \sin(\theta)e^{-\frac{\theta^2\sigma^2}{2}} & \text{if } r = j \\ a_r^\dagger & \text{if } r \neq i \ \& \ r \neq j \end{cases} \tag{F14}$$

$$\int_\infty^\infty \rho(\delta\alpha, \sigma)G(-\theta, \delta\alpha, i, j)a_s G(\theta, \delta\alpha, i, j)d\delta\alpha = \begin{cases} a_i \cos(\theta)e^{-\frac{\theta^2\sigma^2}{2}} + a_j \sin(\theta)e^{-\frac{\theta^2\sigma^2}{2}} & \text{if } s = i \\ a_j \cos(\theta)e^{-\frac{\theta^2\sigma^2}{2}} - a_i \sin(\theta)e^{-\frac{\theta^2\sigma^2}{2}} & \text{if } s = j \\ a_s & \text{if } s \neq i \ \& \ s \neq j \end{cases} \tag{F15}$$

Therefore, propagating the 1-RDM with stochastic Rz errors corresponds to evaluating the map in Eq. (F15). This calculation assumes that the stochasticity has a time-scale that is much faster than a single energy evaluation. We find that with $\sigma > 0.22$ purification projects to the wrong 1-RDM.

Appendix G: Gradient for the Basis Rotation Ansatz

Another benefit of restricting our ansatz to Slater determinants is the fact that the gradient with respect to the parameters is accessible via the elements of the 1-RDM. The gradient of the energy with respect to the parameters of a one-body generator $Z = \sum_{i<b} c_{b,i}\left(a_b^\dagger a_i - a_i^\dagger a_b\right)$ is

$$\frac{dE}{dc_{b,i}} = \langle\phi_0|\frac{de^{-Z}}{dc_{b,i}}He^Z|\phi_0\rangle + \langle\phi_0|e^{-Z}H\frac{de^Z}{dc_{b,i}}|\phi_0\rangle. \tag{G1}$$
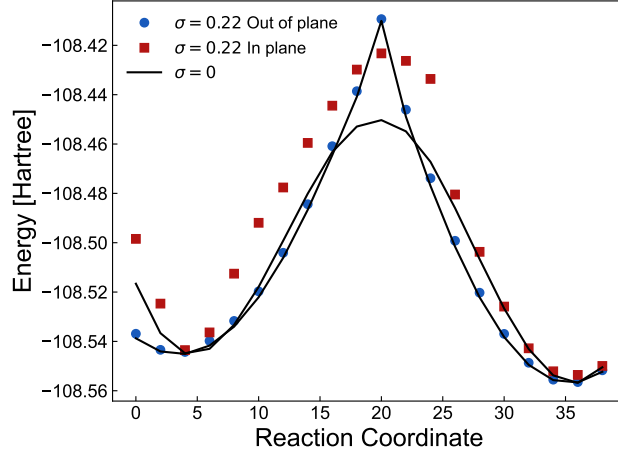
FIG. 11. Stochastic Rz simulation of diazene with $\sigma = 0.22$ radian fluctuation on the Givens rotation gates. The plotted points are after applying purification to the result 1-RDM

Due to the structure of this operator we expect the gradient to involve the commutator of the Hamiltonian with respect to the anithermitian operator that becomes the prefactor to the right gradient. We call this prefactor $\nabla f(Z)$ to indicate that it is a different operator from just the rotation generator associated with $c_{b,i}$.

$$\frac{dE}{dc_{b,i}} = \langle \phi_0 | e^{-Z} \left[H, \nabla f(Z)_{c_{b,i}} \right] e^Z | \phi_0 \rangle \tag{G2}$$

All quantities in the commutator above can be evaluated with knowledge of the 1-RDM when ϕ_0 is a computational basis state. In this work we utilized this gradient for a classical implementation and provide it here as justification for the ansatz and for future studies. The formal derivation of $\nabla f(Z)$ can be found in [40] and [41].

As a sketch for the form of $\nabla f(Z)$ consider the unitary performed in the Hartree-Fock experiment

$$U(c_{b,i}) = e^{\sum_{b,i} c_{b,i} E_{b,i}^-} = e^{\sum_{b,i} c_{b,i}(a_b^\dagger a_i - a_i^\dagger a_b)}. \tag{G3}$$

We now want to consider the energy derivative with respect to $c_{b,i}$. Using the formulas in [40] we obtain

$$\frac{dU(\mathbf{c})}{dc_{b,i}} = \left[\int_0^1 dx\, e^{x \sum_{b,i} c_{b,i} E_{b,i}^-} E_{b,i}^- e^{-x \sum_{b,i} c_{b,i} E_{b,i}^-} \right] e^{\sum_{b,i} c_{b,i} E_{b,i}^-}. \tag{G4}$$

In order to evaluate this integral we need to have an analytical form for the similarity transform of the integrand. The integrand can be expressed in series form with the Baker-Campbell-Hausdorff identity where each term involves nested commutators. Each nested commutator can be expressed more succinctly as the adjoint action of Z on $E_{b,i}^-$

$$\text{ad} \left(\sum_{b',i'} c_{b',i'} E_{b',i'}^- \right)^n \left(E_{b,i}^- \right). \tag{G5}$$

A general strategy for evaluating sums of adjoint actions is to represent the operator $\sum_{b',i'} c_{b',i'} E_{b',i'}^-$ in its eigenbasis and directly evaluate the commutator as a matrix power. In our case this would involve diagonalizing a large $2^n \times 2^n$ matrix. Fortunately, due to the connection between one-particle-basis rotations and rotations by one-body operators on the full Hilbert space we can find a $n \times n$ unitary that can diagonalize the matrix of $c_{b,i}$ coefficeints and represent the operator $E_{b,i}^-$ in this one-particle basis. Following this step of the derivation in [41] we form the $\mathbf{C}$ matrix of coefficients $c_{b,i}$ which is antihermitian and diagonalize. Therefore, $\mathbf{C}$ is represented in its eigenbasis as

$$i\mathbf{C} = i \sum_r \lambda_r \tilde{a}_r^\dagger \tilde{a}_r \tag{G6}$$

where λ are purely imaginary and we have used the fact that

$$\tilde{a}_p = \sum_q u_{p,q}^* a_q \quad , \quad \tilde{a}_p^\dagger = \sum_q u_{p,q} a_q^\dagger. \tag{G7}$$

We represent $E_{b,i}^-$ term in the basis that diagonalizes $i\mathbf{C}$

$$\mathbf{Y} = \sum_{k,l} Y_{kl} \tilde{a}_k^\dagger \tilde{a}_l \tag{G8}$$

$$Y_{kl} = \left(U^\dagger E_{b,i}^- U \right)_{k,l} \tag{G9}$$

here $E_{b,i}^-$ is an antisymmetric matrix with 1 at the (b,i) position and -1 at (i,b) position which is a representation of the operator $E_{b,i}^-$. Therefore,

$$\text{ad}\left(\sum_{b',i'} c_{b',i'} E_{b',i'}^- \right) \left(E_{b,i}^- \right) = \sum_{rkl} i\lambda_r Y_{kl} \left[\tilde{a}_r^\dagger \tilde{a}_r, \tilde{a}_k^\dagger \tilde{a}_l \right] \tag{G10}$$

$$= \sum_{rkl} i\lambda_r Y_{kl} \left(\tilde{a}_r^\dagger \tilde{a}_l \delta_k^r - \tilde{a}_k^\dagger \tilde{a}_r \delta_r^l \right) \tag{G11}$$

$$= i \sum_{kl} (\lambda_k - \lambda_l) Y_{kl} \tilde{a}_k^\dagger \tilde{a}_l. \tag{G12}$$

Furthermore, powers of the adjoint action are

$$\text{ad}\left(\sum_{b',i'} c_{b',i'} E_{b',i'}^- \right)^n \left(E_{b,i}^- \right) = i^n \sum_{kl} (\lambda_k - \lambda_l)^n Y_{kl} \tilde{a}_k^\dagger \tilde{a}_l. \tag{G13}$$

Armed with the adjoint power we can now evaluate the integrand of Eq. (G4) via fundamental theorem of calculus and arrive at an expression for the gradient

$$\frac{dU(\mathbf{c})}{dc_{b,i}} = \left[\sum_{kl} Y_{kl} \frac{e^{i(\lambda_k - \lambda_l)} - 1}{i(\lambda_k - \lambda_l)} \tilde{a}_k^\dagger \tilde{a}_l \right] e^{\sum_{b,i} c_{b,i} E_{b,i}^-} \tag{G14}$$

$$= \left(\sum_{k,l} \left[UMU^\dagger \right]_{kl} a_k^\dagger a_l \right) e^{\sum_{b,i} c_{b,i} E_{b,i}^-} \tag{G15}$$

where $M_{kl} = Y_{kl} \frac{e^{i(\lambda_k - \lambda_l)} - 1}{i(\lambda_k - \lambda_l)}$. The expression in the parenthesis is a new one-body operator that we previous denoted $\nabla f(Z)$.

Appendix H: Optimization Technique

The optimizer we use in the experiment is based on Kutzelnigg's approach to iteratively constructing a wavefunction that satisfies the Brillouin condition [31]. In the following section we include the derivation and modifications of this procedure from Reference [31] for completeness. This approach starts from the Lie-algebraic perspective on the variational principle. The generators for variations in a norm conserved wavefunction are elements of a complex Lie algebra. The variational principle which states

$$\delta \tilde{E} = \delta \langle \tilde{\psi} | H | \tilde{\psi} \rangle = 0 \tag{H1}$$

can be cast as stationarity with respect to a unitary group

$$U = e^R \quad R = -R^\dagger \tag{H2}$$

where R is an element of the Lie algebra $\mathcal{L}$ supporting H. Formulation of the variations in $\tilde{E}$ with respect to R is formulated using the BCH expansion

$$\tilde{E} \to \tilde{E}' = \tilde{E} + \langle \tilde{\psi} | [H, R] | \tilde{\psi} \rangle + \frac{1}{2} \langle \tilde{\psi} | [[H, R], R] | \tilde{\psi} \rangle + ... \tag{H3}$$

and thus stationarity with respect to infinitesimal variations in R implies

$$\langle \tilde{\psi} | [H, R] | \tilde{\psi} \rangle = 0 \ \ \forall R = -R^\dagger \tag{H4}$$

1. Iteratively constructing wavefunctions

Given an R that does not satisfy the first order stationarity condition Eq. (H4) we can propose a new wavefunction that is approximately stationary with respect to R.

$$A_R = \langle \phi | [H, R] | \phi \rangle \neq 0 \tag{H5}$$

We want to determine an update of the generator R such that the first order condition holds. We consider the update to the wavefunction

$$\psi = e^{-f_R R} \phi \tag{H6}$$

where f_r is a real number. Considering how the energy changes as a function of f_R

$$E_{f_R} = \langle \phi | e^{f_R R} H e^{-f_R R} | \phi \rangle \approx \langle \phi | H + f_R [H, R] + \frac{f_R^2}{2} [[H, R], R] | \phi \rangle \tag{H7}$$

In a similar fashion to deriving a Newton-Raphson update in optimization we can differentiate to find an f_R that approximately satisfies Eq. (H4).

$$\frac{dE_{f_R}}{df_R} = \langle \phi | [H, R] + \frac{f_R}{2} [[H, R], R] | \phi \rangle = 0 \qquad f_R = -A_R / B_{R,R} \qquad B_{R,R} = \langle \phi | [[H, R], R] | \phi \rangle \tag{H8}$$

Alternatively, one can determine the change in the stationary condition with respect to f_R

$$0 = \langle \phi | e^{f_R R} [H, R] e^{-f_R R} | \phi \rangle = \langle \phi | [H, R] + f_R [[H, R], R] + \frac{f_R^2}{2} [[[H, R], R], R] + ... | \phi \rangle \tag{H9}$$

and enforce the stationarity approximately by truncating at first order and solving for f_R

$$f_R = -A_R / B_{R,R} \tag{H10}$$

which provides the same type of update. The error in the residual for R, A_R, is now of the magnitude $O(f_R^2)$ at leading order. This update inspires a possible iterative procedure for improving the wavefunction that will quadratically converge to the correct state if we are in a convex region away from the exact solution [31].

One can use the above procedure where R is not an element of the operator basis $\{X_k\}$ of the Lie algebra $\mathcal{L}$

$$R = \sum_k c_k X \ , \ \ X \subset \mathcal{L} \tag{H11}$$

and to determine a set of c_k which approximately satisfy Eq. (H4).

$$0 \approx \langle \phi | [H, X_k] + \sum_l [[H, X_k], X_l] c_l | \phi \rangle \tag{H12}$$

Again, approximating the expansion in Eq. (H12) to first order we get a system of equations to solve for c_k that ensures the Brillouin condition is satisfied up to leading error of $\mathcal{O}(c_k^2)$.

In the context of a NISQ machine one needs to consider the family of generators $\{R\}$ that is tractable and the cost of the measurements associated with measuring A_R and $B_{k,l}$. In this work we use

$$A_{p,q} = \langle \psi | [H, a_{p,q}] | \psi \rangle \qquad B_{p,q;r,s} = \langle \psi | [[H, a_p^\dagger a_q], a_r^\dagger a_s] | \psi \rangle. \tag{H13}$$

Both the gradient and the Hessian term can be evaluated with knowledge of the 1-RDM under the assumption that ψ corresponds to a Slater determinant. The update parameters to κ, $f_{p,q}$ are computed by solving the augmented Hessian eigenvalue problem

$$\begin{pmatrix} 0 & \mathbf{A} \\ \mathbf{A}^\dagger & \mathbf{B} \end{pmatrix} \begin{pmatrix} 1 \\ f_{p,q} \end{pmatrix} = \epsilon \begin{pmatrix} 1 \\ f_{p,q} \end{pmatrix} \tag{H14}$$

which provides an optimal level shift to Newton's method

$$\mathbf{A} + (\mathbf{B} - \epsilon) f_{p,q} = 0. \tag{H15}$$

As described in [32] we add regularization by limiting the size of the update $f_{p,q}$ by rescaling under the condition that the max update is above a parameter γ

$$\begin{cases} f_{p,q} & \max(f_{p,q}) < \gamma \\ \frac{\gamma}{\max(f_{p,q})} f_{p,q} & \max(f_{p,q}) \geq \gamma \end{cases} \tag{H16}$$

The algorithm then dictates that the wavefunction is updated through Eq. (H6) which is yet another free-fermion wavefunction. We concatenate this basis rotation with the original using Eq. (B3) so the circuit depth remains constant. The optimization procedure is iterated for a fixed number of steps or the commutator $\langle [H, X_k] \rangle$ falls below a predefined threshold.

Appendix I: Additional Performance Analysis

In this section we examine the percentage of measurements rejected by post-selection as a function of system size and fidelity metrics across the systems studied in the Hydrogen chain and diazene experiments. In Table II we plot the ratio of the total number of circuit repetitions that result in the correct excitation number. As expected this ratio decreases with system size, almost perfectly tracking a joint readout fidelity of 95%. We believe the discrepency between the two 10-qubit experiments (H_{10} and diazene experiments) stems from the fact that the diazene circuits have more idle circuit moments where the qubits are free to decay.

Molecule	Post-selection Shot Ratio
H_6	0.764(7)
H_8	0.66(1)
H_{10}	0.56(1)
H_{12}	0.46(2)
diazene	0.44(1)

TABLE II. The average fraction of the 250,000 circuit repetitions used to measure observables for each circuit. The average is collected across all Hydrogen geometries and diazene geometries for every circuit required to estimate the 1-RDM for these systems.

Plotted another way, we can examine the distribution of local qubit expectation values $\langle M_i \rangle$ where M_i is the measurement result of qubit i. In Figure 12 we plot the integrated histogram of M_i–i.e. the probability of a 1 bit being measured from qubit i–(denoted P1) on all the qubits for all circuits in all Hydrogen chain experiments. This is compared to the theoretical value obtained by the perfect 1-RDM simulation described in Appendix A 1. The significant improvement in readout scatter from post-selection is a fundamental driver in the success of this experiment due to the sensitivity of quantum chemistry energies to electron number.
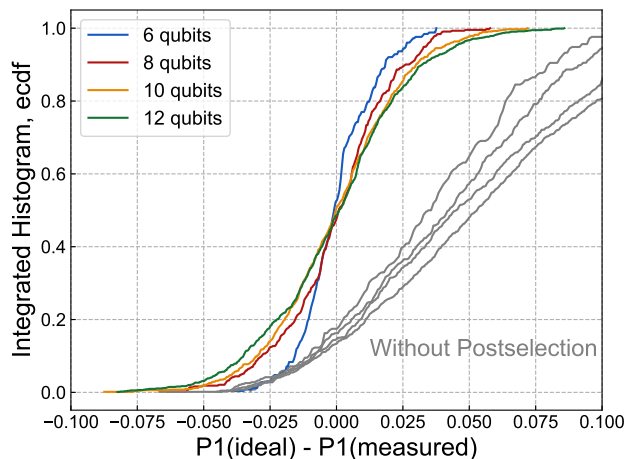

FIG. 12. Integrated histogram of readout performance with and without post-selection on photon number. Grey lines are the histograms of circuit measurements without post-selection.

In Figure 13 we plot the log-log scatter of absolute error and fidelity witness for all systems studied. The correlation in the fidelity and absolute energy error suggests that fidelity can be used as an optimization target for this system. This is a useful property when considering basis rotation states as targets for benchmarks and tune-up protocols.
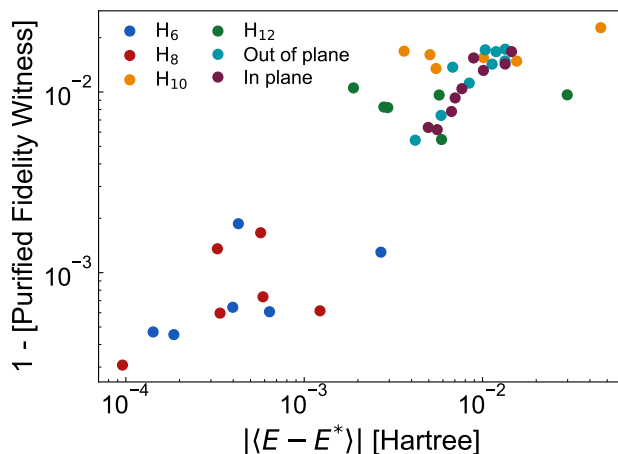

FIG. 13. Absolute error versus fidelity witness for VQE optimized with error mitigation for all experiments.

To better describe the consistent quality of VQE optimized 10 qubit calculations we tabulate the perceived fidelity calculated from purified 1-RDMs in all 10 qubit experiments: six H_{10} experiments and eighteen diazene points. On all but one experiment variational relaxation combined with other error mitigation techniques allows us to achieve $> 98.0\%$ average fidelity.
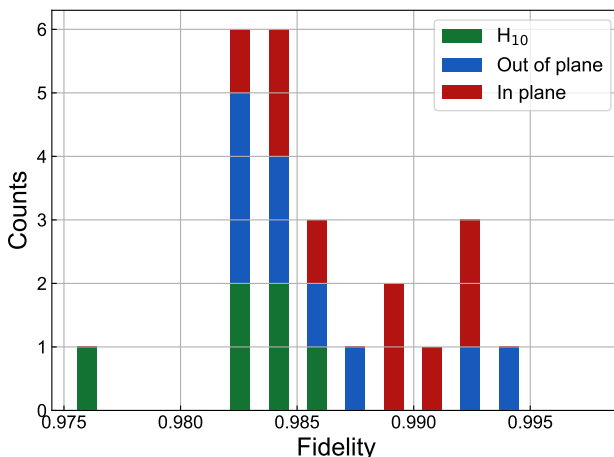

FIG. 14. **Fidelity of 10 qubit experiments:** A histogram of fidelity witness values associated with the VQE optimized 10 qubit systems.

Appendix J: Molecular geometries

For the Hydrogen chains OpenFermion [34] and Psi4 [42] were used to generate the integrals. All Hydrogen chains were computed at atom-atom separations of 0.5, 0.9, 1.3, 1.7, 2.1, and 2.5 Å. For the diazene curves we used Psi4 to map out the reaction coordinate for each isomerization mechanism by optimizing the geometries of the molecule while constraining either the dihedral angle or NNH angle to a fixed value. Table III and Table IV, below, contain the geometries we considered for out-of-plane rotation and in-plane rotation of the Hydrogen atom. To reduce diazene to a 10 qubit problem we perform two cycles of canonical Hartree-Fock self-consistent field and then integrate out the bottom two energy levels.

TABLE III. Out-of-plane rotation geometries

Internal coord.	Atom	Cartesian coordinates		
3.157	H	-0.00183	0.61231	-1.23326
	N	-0.00183	0.61231	-0.16961
	N	-0.00183	-0.56366	0.29317
	H	0.05269	-1.28820	-0.48362
26.315	H	-0.01473	0.61213	-1.23797
	N	-0.01473	0.61213	-0.17381
	N	-0.01473	-0.56586	0.29104
	H	0.42406	-1.25504	-0.39080
49.473	H	-0.02522	0.61175	-1.25087
	N	-0.02522	0.61175	-0.18596
	N	-0.02522	-0.57104	0.28761
	H	0.72616	-1.17742	-0.16152
72.631	H	-0.03098	0.60150	-1.29530
	N	-0.03098	0.60150	-0.23059
	N	-0.03098	-0.56623	0.30717
	H	0.89199	-1.09153	0.23125
95.641	H	-0.03338	0.62184	-1.24521
	N	-0.03338	0.62184	-0.18592
	N	-0.03338	-0.60178	0.24302
	H	0.96106	-0.90055	0.45184
117.611	H	-0.03017	0.62034	-1.22808
	N	-0.03017	0.62034	-0.16858
	N	-0.03017	-0.60975	0.20354
	H	0.86843	-0.76736	0.74227
139.581	H	-0.02217	0.61500	-1.22656
	N	-0.02217	0.61500	-0.16715
	N	-0.02217	-0.61052	0.18284
	H	0.63829	-0.67733	1.00847
161.551	H	-0.01085	0.61243	-1.22466
	N	-0.01085	0.61243	-0.16601
	N	-0.01085	-0.61150	0.16941
	H	0.31225	-0.62540	1.17746
183.522	H	0.00211	0.61159	-1.22471
	N	0.00211	0.61159	-0.16627
	N	0.00211	-0.61155	0.16640
	H	-0.06064	-0.61209	1.22297

TABLE IV. In-plane rotation geometries

Internal Coord.	Atom	Cartesian coordinates		
108.736	H	0.00000	0.61228	-1.23237
	N	0.00000	0.61228	-0.16925
	N	0.00000	-0.56613	0.29515
	H	0.00001	-1.25344	-0.51686
127.473	H	0.00000	0.61339	-1.24223
	N	0.00000	0.61339	-0.17528
	N	0.00000	-0.55235	0.28364
	H	0.00001	-1.46143	-0.26340
146.210	H	0.00000	0.61423	-1.26614
	N	0.00000	0.61423	-0.18644
	N	0.00000	-0.54592	0.27365
	H	0.00001	-1.56334	0.05447
164.947	H	0.00000	0.61854	-1.26711
	N	0.00000	0.61854	-0.18132
	N	0.00000	-0.55047	0.24812
	H	0.00000	-1.56434	0.33892
182.0	H	0.00000	0.62468	-1.24838
	N	0.00000	0.62468	-0.16646
	N	0.00000	-0.56138	0.21599
	H	0.00007	-1.50420	0.56008
200.526	H	-0.00002	0.63051	-1.22163
	N	-0.00002	0.63051	-0.14939
	N	-0.00002	-0.57522	0.18140
	H	0.00060	-1.39873	0.77683
219.052	H	-0.00004	0.63081	-1.20416
	N	-0.00004	0.63081	-0.14048
	N	-0.00004	-0.58876	0.15662
	H	0.00116	-1.21501	0.97997
237.578	H	-0.00005	0.62175	-1.20948
	N	-0.00005	0.62175	-0.14932
	N	-0.00005	-0.59932	0.15347
	H	0.00155	-0.93328	1.15189
256.105	H	-0.00004	0.61032	-1.22743
	N	-0.00004	0.61032	-0.16648
	N	-0.00004	-0.61200	0.16650
	H	0.00111	-0.58711	1.22715