Quantum Computation of Reactions on Surfaces
Using Local Embedding

Tanvi P. Gujarati,*† Mario Motta,† Triet Nguyen Friedhoff,‡ Julia E. Rice,† Nam Nguyen,*† Panagiotis Kl. Barkoutsos,§ Richard J. Thompson,∥ Tyler Smith,⊥ Marna Kagele,¶ Mark Brei,® Barbara A. Jones,† and Kristen Williams∥

†IBM Quantum, Almaden Research Center, San Jose, California 95120, USA
‡IBM Quantum, T. J. Watson Research Center, Yorktown Heights, New York 10598, USA
¶Integrated Vehicle Systems, Applied Mathematics, Boeing Research & Technology, Huntington Beach, CA, 92647
§IBM Quantum, IBM Research – Zurich, 8803 Rüschlikon, Switzerland
∥Integrated Vehicle Systems, Applied Mathematics, Boeing Research & Technology, Huntsville, AL, 35824
⊥Integrated Vehicle Systems, Applied Mathematics, Boeing Research & Technology, Orlando, FL, 32826
®Tech Vis and Integration, Global Technology, Boeing Research & Technology, Tukwila, WA 98108
@BSC Analytics, Chemical Technology, North Charleston, SC, 29456

E-mail: tgujarati@ibm.com; nam.h.nguyen5@boeing.com

Abstract

Quantum computational techniques have been proposed to model electronic systems. Despite encouraging preliminary results for small molecular species, the modeling
of complex material systems using these techniques is less understood and established. We outline a workflow for modeling chemical reactions on surfaces with quantum algorithms, and illustrate it for water dissociation on a magnesium surface. This is the first example, to the best of our knowledge, of modeling a reaction on a surface using a quantum computer. Two local embedding methods for systematic determination of active spaces are developed and compared. These methods are automated, systematically improvable and based on the physics of the system. To achieve this goal, they target a spatially localized region in which electron correlation effects are more important than in the rest of the system. To reduce finite-size effects, the local embedding methods are designed to enable Brillouin zone integration. Ground-state energies of the active-space projected Hamiltonians are computed with variational quantum algorithms suitable for near-term quantum computers, using classical simulators and quantum hardware, and the impact of various approximations is discussed. Results indicate that the system size which can be feasibly treated with quantum simulations is extended by using local embedding and Brillouin zone integration methods, as only a local region is correlated by a quantum simulation.

Introduction

In recent years, much effort has gone into identifying resource requirements and strategies for modeling complex molecular systems using quantum computing algorithms to identify avenues to achieve quantum advantage.\textsuperscript{1–3} One such potential direction is to identify and model chemical reactions that have significant scientific, as well as, industrial value. Accurately modeling chemical reactions using \textit{ab initio} methods can be proven useful for determining reaction rates and other thermodynamic properties, especially when performing experimental analysis of these reactions may be expensive and potentially dangerous. Chemical reactions often occur in complex environments, involving multiple chemical species, material surfaces or extensive bulk systems. Different considerations are required for studying these systems
when compared to molecular systems in vacuum. Density Functional Theory (DFT) methods have been predominantly used to study the complex environments and have been successful at modeling many large systems. However, DFT functionals are approximate and often fail at describing systems that have strong electronic correlations.

While exact diagonalization or Full Configuration Interaction (FCI) methods provide accurate estimates for these properties, the combinatorial scaling of these methods imposes severe restrictions on the size of systems that can be treated with such a high level of accuracy. Quantum computing algorithms have the potential to efficiently simulate correlated electronic systems from first principles through several classes of algorithms.\textsuperscript{4–7} Amongst them, Variational Quantum Algorithms (VQAs) are the best fit for near-term quantum processors; in particular, Variational Quantum Eigensolver\textsuperscript{8} (VQE) has been used extensively for the calculation of ground and excited states properties in electronic structure problems.\textsuperscript{9–16}

Although quantum computing algorithms hold promise, most of the current experimental demonstrations have focused on small molecular systems, spin systems or mean-field techniques.\textsuperscript{10,12–15,17,18} In the last few years, quantum algorithms and applications for material systems have started to emerge. Application of VQAs to the tight-binding Hamiltonian in absence of electron-electron correlations was studied\textsuperscript{19} and experimentally demonstrated with 18 qubits.\textsuperscript{20} Modifications to Unitary Coupled Cluster Singles and Doubles (UCCSD) variational ansatz to incorporate periodic boundary conditions\textsuperscript{21} and orbital optimization\textsuperscript{22} were examined. The UCCSD method adapted for periodic boundary conditions was used together with translational Quantum Subspace expansion methods.\textsuperscript{23,24} Quantum subspace expansion with unitary transformation of Hartree-Fock (HF) orbitals for a 1-D hydrogen chain was studied by Liu et al.\textsuperscript{25} In order to reduce the required quantum resources, variational quantum algorithms were developed for describing periodic systems using coarse-graining techniques.\textsuperscript{26,27} Quantum embedding theory in conjunction with quantum algorithms such as Quantum Phase Estimation (QPE) and variational algorithms was investigated for describing spin defects in semiconductors.\textsuperscript{28} Spin defects in diamond were investigated\textsuperscript{29} using
Green’s function embedding methods. Hamiltonian simulation in a plane-wave basis has been proposed to have better efficiency than a Gaussian basis.\textsuperscript{30} Variational algorithms using quantum neural network states were used for studying one-, two- and three-dimensional periodic systems.\textsuperscript{31} Apart from approaches that rely on \textit{ab initio} calculations, other quantum machine learning techniques were applied to the determination of properties of a periodic system.\textsuperscript{32,33}

In most of the studies listed above, there is a common thread of selecting a small sub-system from the full system since modeling the latter is prohibitive. The sub-system can then be treated more accurately with quantum algorithms. The rest of the system is either treated at a lower level of theory and combined using embedding schemes, subspace expansion methods, or coarse-graining techniques. Thus, the methods used for choosing and describing the subsystem systematically and accurately are extremely important. As we move from near-term quantum computers, with imperfect qubits and operations, to fault-tolerant quantum computation, we need to devise strategies that can scale and take advantage of the use of quantum resources for the description of larger sub-system(s) that are strongly correlated.

In this paper, we showcase an entire workflow for taking an industrially relevant chemical reaction in materials, and calculating important chemical properties efficiently with quantum computers. The workflow is demonstrated with an example which is relevant for the corrosion of magnesium in the presence of water. Magnesium and magnesium alloys are used extensively in electronic, aerospace, automobile, and defense sectors; understanding the corrosion mechanism has academic and industrial relevance. Prior studies in this field have relied on computing electronic and thermodynamic parameters using DFT methods.\textsuperscript{34–37} We build upon the DFT calculations and investigate the use of quantum algorithms to model a sub-system that is important for description of the reaction. Towards this end, we develop two methods for description of the sub-system that can be made more accurate systematically. We incorporate the use of \textbf{k}-point sampling to comprehensively describe this metallic material system. The expectation value of the sub-space Hamiltonian is approximated us-
Figure 1: Description of the chemical reaction and the workflow: a.) Reaction for splitting of H$_2$O on a magnesium surface including schematics of the optimized structures for the reactant and product. b.) Summary of the different steps involved in the workflow. Each step of the workflow is described in detail in the text.

Using variational quantum algorithms with multiple ans"atze, including wavefunctions provided by the Entanglement Forging (EF) formalism, which are especially suited for near-term quantum hardware.

**Results**

**Chemical Reaction:**

Magnesium corrosion in water or an aqueous environment proceeds by an electrochemical reaction that produces magnesium hydroxide and hydrogen gas. While the overall Mg corrosion reaction is well known (see Eq. (1)), the detailed mechanisms of hydrogen evolution reactions on a magnesium surface is a topic of ongoing investigation.\textsuperscript{34–38}

\[
\text{Mg} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2 + \text{H}_2
\]  

(1)
Williams et al.\textsuperscript{35} proposed a detailed reaction scheme connecting the steps of initial water dissociation on Mg surface with the final step of H\textsubscript{2} evolution via a Tafel mechanism\textsuperscript{35,39} in the presence of adsorbed OH\textsubscript{ads} and H\textsubscript{ads} species using modeling based on DFT. The suggested reaction mechanism was shown to be a concerted reaction involving multiple water molecules. The first reaction studied in the process was splitting of a single H\textsubscript{2}O molecule creating adsorbed H\textsubscript{ads} and OH\textsubscript{ads} moiety:

\[
\text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg} (\text{OH}_{\text{ads}}) (\text{H}_{\text{ads}}) \tag{2}
\]

While many steps (detailed mechanism described in Supplementary Section S1) are involved in the study of the hydrogen evolution process, for this work we focus on modeling the chemical reaction given by Eq. (2) using the workflow described in Fig. (1 a.). This reaction is used to demonstrate the procedure of building on DFT results to describe periodic systems at a higher level of sophistication than DFT alone. In particular, we estimate the electronic energy difference (\(\Delta E\)) between the reactant and product

\[
\Delta E = E_{\text{product}} - E_{\text{reactant}} \tag{3}
\]

using quantum algorithms and compare the value with that determined from DFT alone. \(\Delta E\) is an important quantity since it is used in the determination of thermodynamic quantities such as the enthalpy or the Gibbs free energy of reaction.

**Classical Pre-processing:**

The steps in the workflow (see Fig. (1. b)) start with classical pre-processing. We obtained optimized geometries of the reactants and product using DFT with periodic boundary conditions. Schematics of these structures are shown in Fig. (1. a). In the optimized structure for the reactant, the water molecule is adsorbed on the surface with the oxygen atom situated 2.4 Å above an atop site. In the optimized structure for the product, the water molecule is
split such that OH$_{\text{ads}}$ and H$_{\text{ads}}$ species are co-adsorbed at nearest neighbor fcc sites.

The simplest calculations in periodic boundary conditions are carried out at the \( \Gamma \) (Gamma)-point, \( \mathbf{k} = \Gamma = \mathbf{0} \). The simplicity arises because the electron repulsion integral is a real-valued and 8-fold-symmetric tensor at the \( \Gamma \)-point as in molecular simulations, whereas for other \( \mathbf{k} \)-points in the Brillouin zone it is 4-fold-symmetric. However, \( \Gamma \)-point calculations often converge slowly and non-monotonically to the thermodynamic limit of infinite system size at zero temperature. Thus, it is important to sample over \( \mathbf{k} \)-points to get accurate estimates of the energies for periodic systems. Lin et al.\(^{40}\) proposed the use of twist-averaged boundary conditions for the computation of energies and other properties as averages. For example, the average of a generic operator \( B \) over a mesh of \( N_{k} \) \( \mathbf{k} \)-points in the Brillouin zone of the lattice is given by

\[
\langle B \rangle = \frac{1}{N_{k}} \sum_{i=1}^{N_{k}} B(\mathbf{k}_{i}) \tag{4}
\]

For properties involving kinetic energy, when compared to including only the \( \Gamma \)-point, twist-averaging results in faster convergence to the thermodynamic limit with the same computational complexity.

Using the optimized geometries, DFT calculations with Gaussian basis set were performed for the reactant and product using PySCF.\(^{41,42}\) The DFT calculations gave an electronic energy difference of \( \Delta E = -1.91 \) eV at the \( \Gamma \)-point. In comparison, the electronic energy difference in the study by Williams et al.\(^{35}\) was reported to be -1.78 eV. The difference in the two values can be explained by the fact that the optimized geometries, basis sets, and DFT exchange and correlation functionals used in both studies were different.

For the twist-averaged estimation, independent DFT calculations were performed at each \( \mathbf{k} \)-point of a \( 4 \times 4 \times 1 \) Monkhorst-Pack grid\(^{43}\) and Kohn-Sham orbitals were obtained. These orbitals were often de-localized over multiple atoms in the unit cell. Thus, localization\(^{44–49}\) of the Kohn-Sham orbitals was performed independently for the occupied and virtual orbitals using the Pipek-Mezey localization method.\(^{50}\)
Active Space Selection:

For certain chemical problems, reasonably accurate results can be achieved by correlating a limited number of electrons and orbitals through an active-space calculation. In general, an active space comprised of molecular orbitals in the valence space is most desirable. Further reductions are acceptable when based on chemical grounds. In particular, all statically correlated orbitals have to be included.

Previous work showed that, for some systems with small molecular adsorbates on metallic surfaces, electronic correlation is primarily associated to a few orbitals. These observations suggest the possibility of designing compact active spaces, to capture relevant patterns of electronic correlation. The construction of such active spaces should be automated, and physics-based. Furthermore, these active spaces should be systematically improvable, so that convergence of relevant properties can be assessed.

In this work, we designed and compared two strategies satisfying the above requirements. We selected active spaces using localized DFT orbitals projected onto a local active region for both reactant and product. Given the nature of the application, a reaction on a surface, it is natural to construct an active space that comprises not only the electrons and orbitals of the molecules directly participating in the reaction, but also includes electrons and orbitals localized around neighboring atoms on the surface. The active space, comprised of localized occupied and virtual orbitals, is then used in calculations with methods that allow for electronic excitations within this space. Details of the two methods used in construction of the active spaces describing the local embedding are given below and summarized in Fig. (2). Note that while zeroth order embedding is considered in this work, it can be easily extended to self-consistent embedding methods.

Method 1 - Based on Density Difference (DD): This method aims at ordering the localized Kohn-Sham orbitals according to their contribution to the active region. We determined the active region by computing the electron density difference between the full system and the adsorbate and slab treated separately. The effective local interaction region can be modelled
by constructing the difference of electron densities, $\rho_{DD}$, created due to the interaction of the adsorbate with the surface. By focusing on the orbitals that contribute to the change in electron density due to adsorption of the water, Eq.(5), we aim to capture the most important interactions.

\[ \rho_{DD}(x, y, z) = \rho_{Mg+H_2O}(x, y, z) - \rho_{H_2O}(x, y, z) - \rho_{Mg}(x, y, z) \]  \hspace{1cm} (5)

Integrated spatial overlap between the density of each localized Kohn-Sham orbital and the electron density difference, $\rho_{DD}(x, y, z)$, is then used for ordering occupied and virtual orbitals. The occupied orbitals sorted using this protocol can be picked with higher confidence than the virtual orbitals since all the electron densities in Eq. (5) are constructed from occupied orbitals. To refine the ordering of virtual orbitals, we selected the top five occupied orbitals (number of orbitals in the valence space of $H_2O$) and calculated the pairwise Coupled-Cluster Singles and Doubles (CCSD) energy contributions for each of the selected occupied orbital with every virtual orbital. The set of orbitals i.e. selected occupied and all virtual, were then ordered according to their pair-wise CCSD energies. Active orbitals were now chosen by systematically truncating the set of ordered orbitals as per the given computational budget. These steps are pictorially described in Fig. (2 a.)). Implementation of this method with DD and pair-wise CCSD is efficient in terms of the required classical resources and we observe systematic improvement in correlation energy with the inclusion of the orbitals sorted based on the procedure described above.

**Method 2 - Based on Density Difference and CCSD Natural Orbitals (DD+NO):** The rate of energy convergence as a function of active space size obtained in the above method can be further improved by constructing active spaces using natural orbitals. This method is the same as the DD-based method up to the step of sorting the occupied and virtual orbitals based on the electron density difference. Instead of the pair-wise CCSD calculations in the DD method, with the selected top five occupied orbitals taken together with all the virtual orbitals, we performed a larger CCSD calculation. Natural orbitals were then constructed.
Method 1: Density Difference (DD)

Method 2: Density Difference + Natural Orbitals (DD+NO)

Pair-wise CCSD (occ, vir)

Get systematic active spaces

Calculate density difference

Sort DFT orbs. based on DD

E.g. Sorted reactant occupied orbitals

CCSD

Evaluate CCSD Natural Orbitals

CCSD NOs

LUNO +1

LUNO

HONO -1

# active orbitals

Energy (Ha)

Figure 2: Two active space selection methods based on electron density differences

Top two blocks highlighted in green are common to both the methods. The two blocks on the left (in yellow) illustrate the steps used in the first method denoted by Density Difference (DD). The two block on the right (in orange) describe the steps taken in the second method denoted by Density Difference + Natural Orbitals (DD+NO).

by diagonalizing the CCSD one-particle density matrix. For the problems studied here, occupation numbers were either close to 2 or to 0, so we could unambiguously divide orbitals into high- and low-occupancy. On sorting the orbitals in decreasing order of occupation numbers, we identified the Highest Occupied Natural Orbital (HONO) as the last high-occupancy orbital and the Lowest Unoccupied Natural Orbital (LUNO) as the first low occupancy orbital. Active orbitals were constructed by hierarchically expanding the set of natural orbitals starting from the HONO and LUNO pair. The active space was then systematically truncated according to the resource budget available for quantum algorithms. These steps are pictorially described in Fig. (2 b.).

Once the active spaces are determined, the orbitals that are not included in the active space remain frozen and an effective Hamiltonian in the active space is then constructed by projecting the Born-Oppenheimer Hamiltonian onto the Hilbert space defined by the orbitals.
We now compare the two active space selection methods based on local electron density differences. From a total of 588 orbitals used to describe the reactant and product in the GTH-DZV basis set, active spaces of up to 269 orbitals (5 selected occupied and all 264 virtual orbitals) were created. The energies of the reactant and product were determined from use of the CCSD method within the defined active space. In Fig. (3) energies of the reactant and product at the \( \Gamma \)-point using both the methods are shown in the left panel with increasing number of orbitals in the active space. In the right panel, the electronic energy difference between the product and reactant \( \Delta E \) for the two methods is shown. We see a monotonic reduction in the CCSD energies as the active space size increases for both methods. The DD+NO method has a faster convergence rate than the DD method as only 15-20 natural orbitals are needed before the convergence in energy differences is observed. For both the methods, DD and DD+NO, we see that the converged value of \( \Delta E \) is more negative than -1.91 eV obtained from the DFT calculations at the \( \Gamma \)-point.

For the rest of the calculations, i.e. studies with \( k \)-point sampling, we used active spaces obtained from the DD+NO method. The effective Hamiltonians in the DD+NO active

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Figure 3: **Comparison of the two active space selection methods** CCSD energies calculated in the active spaces defined by the two methods of active space selection, DD and DD+NO are shown for the reactant and product in the panel on the left. Panel on the right shows the energy difference \( \Delta E \) between the product and reactant obtained from the energies plotted in the left panel.
spaces are constructed independently for each \( k \)-point of the Monkhorst-Pack grid. The active-space Hamiltonian is described in the second-quantization picture. To simulate it using quantum algorithms on a quantum computer, we map this fermionic Hamiltonian to a qubit Hamiltonian by applying a fermion-to-qubit mapping.\(^{66–68}\) Given the computational restrictions for simulation of quantum algorithms on classical computers, we restrict the active space size to a maximum of 10 orbitals (with a matching number of occupied and virtual orbitals), equivalent to 18 qubits in the parity fermion-to-qubit mapping and 20 qubits in the Jordan-Wigner mapping. With an active space of 10 natural orbitals, convergence in energy differences is not achieved. However, the inclusion of about 15 natural orbitals provides an energy difference comparable in quality to the 269-orbital active space.

**Quantum algorithms in the active space:**

We used VQE and EF to perform higher accuracy calculations of the ground state energies for each system as a function of active space sizes. We chose to study these quantum algorithms to enable implementation on near-term quantum hardware. However, it should be noted that once the active-space Hamiltonian is obtained, other quantum algorithms, such as Quantum Phase Estimation (QPE), can be used in the future.

*Variational Quantum Eigensolver (VQE):* As the name suggests VQE is a technique that aims at finding the ground state wave-function, \( |\psi_0\rangle \), and energy, \( E_0 \), of a given Hamiltonian, \( H \), through variational optimization of a parameterized wavefunction ansatz, \( |\psi(\theta)\rangle \).

\[
E_{VQE} = \min_{\theta} \langle \psi(\theta) | H | \psi(\theta) \rangle
\]  

(6)

The energy of the Hamiltonian with respect to a given wave-function is evaluated on a quantum computer. The parameters of the wave-function are then optimized iteratively on a classical computer until convergence. While the VQE algorithm is straight-forward, the quality of the results, i.e. whether \( E_{VQE} \approx E_0 \), depends on the choice of the parameterized ansatz
as well as the nuances of the classical optimization procedure used. Literature\textsuperscript{12,22,69–71} indicates that VQE applied to small systems can obtain energies close to those of all excitations (Full CI) within the active space, commonly known as CASCI.

In this study, we analyze the performance of the VQE algorithm using two classes of ansätze: trotterized implementation of Unitary Coupled-Cluster Singles and Doubles (qUCCSD)\textsuperscript{70} and Qubit Coupled Cluster (QCC).\textsuperscript{72}

Figure 4: Energy difference in small active spaces $\Delta E$ evaluated for small active space sizes ranging from 2 to 10 CCSD natural orbitals obtained with the (DD+NO) method for the $\Gamma$-point (left), twist average over $2\times2\times1$ Monkhorst-Pack grid (center) and over $4\times4\times1$ grid (right) are shown. Corresponding DFT energy differences calculated with twist averaged $k$-point sampling are plotted for reference in grey and compared with the CASCI, CCSD and qUCCSD methods.

In Fig. (4) we compare the $\Delta E$ values obtained with the VQE-qUCCSD method against energies obtained via the CCSD and CASCI methods in small active space sizes. In this figure, we illustrate the impact of going beyond the $\Gamma$-point (left-most panel) with the inclusion of more $k$-points via the twist averaging method over a Monkhorst-Pack grid of $2 \times 2 \times 1$ (middle panel) and $4 \times 4 \times 1$ (right panel). We observe that the CASCI results, CCSD results and qUCCSD results are indistinguishable for all active space sizes and $k$-point calculations. Energy difference calculated using the DFT method for the full system and evaluated using the twist averaged method are reported for comparison. The $\Delta E$ values for all the methods including DFT vary significantly as more $k$-points are included, highlighting the importance of $k$-point sampling effects when investigating periodic systems.

VQE studies using qUCCSD ansätze show accurate results, comparable in value to the CCSD method, but they have very deep circuits that scale as $O(N^4)$ where $N$ are the
number of orbitals. Hence, they are difficult to simulate on the current quantum hardware.\textsuperscript{73}

Strategies to systematically construct the UCCSD ansatz have been recently explored.\textsuperscript{74} While promising, they are still expensive for simulations on the quantum hardware as these strategies rely on growing the UCCSD ansatz by one, or possibly a few, fermionic excitations at a time. This also results in a complicated circuit when mapped to qubits.

To overcome these restrictions, methods that rely on building an ansatz by systematically adding Pauli operator terms, as opposed to fermionic excitations, have been explored.\textsuperscript{72,75,76} These ansätze are described directly in the second quantized space. We investigate one such ansatz called Qubit Coupled Cluster (QCC) ansatz. Given a pool of ordered multi-qubit Pauli operators (or Pauli strings), the ansatz is constructed by successively adding exponentials of single Pauli operators according to their significance.

\textit{Entanglement Forging (EF):} Entanglement Forging\textsuperscript{18} is a quantum algorithm requiring only half the number of qubits compared to VQE with a Jordan-Wigner mapping. This algorithm uses classical post-processing to correlate weakly entangled subsystems of the full system. If the entanglement between the two sub-systems is weak, i.e. the Schmidt rank does not depend exponentially on the sub-system size, then classical post-processing of results obtained from many smaller quantum experiments using only half the number of qubits provides an efficient quantum algorithm to evaluate the properties of the full system. Ground states of many chemical systems have weak quantum entanglement between the spin-up and spin-down subsystems near equilibrium geometries, hence, they are suitable to be investigated with EF.

Since the ground state of the system is unknown, in the EF protocol, the Schmidt decomposition of the ground state is represented by choosing the number of Schmidt coefficients to be a fixed integer. Unitary matrices that express the singular vectors are chosen to be parameterized quantum circuits. The values of the Schmidt coefficients and the angles in the circuits describing these unitary matrices are optimized iteratively using a classical optimization algorithm.
We show the Schmidt decomposition of the CASCI wave-function in an active spaces of 2 to 10 natural orbitals at the \( \Gamma \)-point in the Supplementary Fig. (S8). In all cases, only a few singular values contribute significantly to the Schmidt decomposition, providing affirmation that indeed the ground states for the reactant and product are weakly entangled between the spin-up and spin-down sectors. Illustrative studies with EF were performed at the \( \Gamma \)-point.

**Simulations with quantum hardware:**

We tested the performance of the VQE algorithm using the QCC ansatz on quantum hardware. For the HONO-LUNO active space, we can map the fermionic Hamiltonian to a qubit Hamiltonian using 2 qubits in the parity mapping. Simulations conducted on the classical simulators show the QCC ansatz with a single Pauli string can provide ground state energies that are within 1kcal/mol of the CASCI energies.

For the HONO-LUNO active space, twist average calculations of up to a \( 4 \times 4 \times 1 \) grid were performed on the quantum hardware. However, for larger active space sizes (from 4 to 10 orbitals) hardware calculations were performed at the \( \Gamma \)-point. While a QCC ansatz with up to 50 Pauli strings was studied on classical simulators, only ansätzte with two Pauli strings were tested on the hardware.

Having established the performance of the qUCCSD against the CASCI method, we now compare the performance of other quantum algorithms against qUCCSD energies for the active spaces with HONO-LUNO up to 10 active orbitals as a function of \( k \)-point sampling grids. For all active spaces and \( k \)-points, we included up to 50 Pauli strings in the QCC ansatz. While only 1 Pauli string is required for convergence in the case of active space with 2 orbitals, a QCC ansatz with more than 30 Pauli strings is required in all other cases. Refer to the Supplementary Section S4 to see the performance of the QCC ansatz for all active spaces and \( k \)-points as a function of the included Pauli strings for properties such as energy differences, number of particles, total spin \( S^2 \) and the z-component of the spin \( S_z \). Results for the 2 and 10 orbital active spaces are shown in Fig. (5). The left panel corresponds
to the HONO-LUNO active space which can be simulated with 2 qubits using VQE in the parity mapping and with 2 qubits using EF in the Jordan-Wigner mapping. The right panel corresponds to the active space with 10 orbitals which is equivalent to 18 qubits in the parity mapping for VQE and 10 qubits using EF. The results for the EF method were calculated with 4 Schmidt coefficients and simple representations of the $U$ and $V$ circuits using hop gates. Considering the symmetry between the spin-up and spin-down electrons we enforced $U = V$ in the EF implementation.

From the results presented in Fig. (5), we observe that the EF method and classical simulations with QCC ansatz can simulate the qUCCSD results exactly for the HONO-LUNO active space with $k$-point sampling of up to 16 $k$-points. The hardware experiments provide exact results to within the error bars for the HONO-LUNO active space and $k$-point sampling. For the active space with 10 orbitals, we observe the EF provides an energy difference that is less than 0.05 eVs away from the qUCCSD value. Similar results for the other active space sizes using the EF method are presented in the Supplementary section S5. The simulated QCC ansatz with up to 50 Pauli strings shown in the right panel for a 10
orbital active space is 0.3 eV lower than the qUCCSD value at the Γ-point and only 0.08 eV lower on inclusion of twist averaged sampling over 16 k-points. While the QCC ansatz with 2 Pauli strings does not provide convergence with respect to the number of Pauli strings, we find agreement between the hardware results and the expected energy difference obtained from the corresponding classical simulations of less than 1 kcal/mol.

**Discussion:**

We calculated the electronic energy difference between the reactant and product for water dissociation on a magnesium surface in active spaces constructed using two methods. We showed systematic convergence in energy differences with increasing active space sizes for both methods. In particular, convergence was reached with a number of orbitals in the tens, confirming that the embedding technique demonstrated here, using a selection of active space orbitals based on strongest inter-adsorbate interaction, is an effective method for modeling absorption of water on a metallic surface using current quantum hardware.

Our techniques make use of local electron density differences (DD) and natural orbitals. Our method using natural orbitals (Method 2) showed faster convergence compared to the other method based on localized Kohn-Sham orbitals. Similarly, previous studies\textsuperscript{77–79} show that natural orbitals lead to a faster convergence of CAS energies to the full basis limit, as they capture anti-bonding virtual orbitals as opposed to the Rydberg continuum.\textsuperscript{80} While the construction of active spaces using CCSD natural orbitals scales polynomially in system size using classical computers, it is expensive for large systems in practice. In this situation, where a CCSD calculation with the full set of virtual DFT orbitals is prohibitive, one can choose a subset of orbitals from the sorted list obtained after implementation of DD method (Method 1) to perform a CCSD natural orbital calculation that fits within the available resources.

We highlighted the importance of including the effects originating from periodic boundary
conditions by incorporating k-point sampling via the twist averaging method. It is important to point out that while twist-averaging removes size effects originating from the one-body part of the Hamiltonian, the residual size effects can only be removed by full Brillouin zone sampling,\textsuperscript{81–83} i.e. explicitly correlating all the k-points in the chosen mesh. Including full k-point sampling is considerably expensive for quantum algorithms and needs further investigation.

We used near-term quantum algorithms such as Variational Quantum Eigensolver (VQE) and Entanglement Forging (EF) to obtain energies within the carved active spaces. We showed that the results obtained with VQE using the Qubit Coupled Cluster (QCC) ansatz and EF with a few Schmidt coefficients provided satisfactory results when compared to the accurate qUCCSD ansatz. We also demonstrated results using the QCC ansatz on quantum hardware for a restricted set of Pauli strings. We note that in general, the QCC ansatz does not guarantee convergence to the exact ground state and alternatives such as qubit-adapt VQE\textsuperscript{76} may be considered. For EF, the results crucially depend on the choice of configurations included to represent Schmidt decomposition and the structure of the $U,V$ circuits describing the EF ansatz. Development of methods and techniques that provide a blueprint for selection of configurations and unitary circuits is important for investigating EF method for larger systems.

While the energy differences obtained at the equilibrium geometries of the reactant and product are important, obtaining energy differences between reactant and transition-states are important as well and more complex since the transition states are non-equilibrium structures. In general, extreme care in selection of active spaces and a thorough investigation for transition states is required. We focused on the reactant and product in this study; investigation of transition states as well as extensions to larger systems, remains for the future.

In conclusion, chemical reactions in material systems are an important application for quantum computers. However, in practice the size of the systems to be simulated can be
prohibitive on near-term hardware. Therefore, the development of efficient methods that enable the inspection of a subsystem with accuracy using a quantum computer is important. Towards this end, we defined an automated embedding protocol for studying chemical reactions on surfaces using quantum resources. We illustrated this procedure by studying one step relevant to the process of localized corrosion on magnesium surface, which is interesting from both an academic and industrial perspective. To the best of our knowledge, this is the first example of modeling a reaction on a surface using a quantum computer. The workflow involved a classical pre-processing DFT step, an active space selection step and investigations of quantum algorithms within the active spaces. We developed an automatic procedure for the determination of a systematically improvable small active space containing the most strongly correlated orbitals localized around the adsorbent and the neighboring surface atoms. Using the quantum computer, higher level calculations were performed in this active space to improve the description of the wavefunction. This protocol can be systematically improved and scaled to take advantage of new generations of quantum hardware. Such scaling could involve description of larger active spaces, inclusion of deeper circuits for improved expressivity, and more sophisticated embedding techniques.

**Methods**

**Geometry Optimization**

Geometry optimization in the plane-wave basis was performed using the Quantum ESPRESSO (QE) package. The \textit{hcp} Mg(0001) surface was modeled using a slab of four Mg layers with 16 atoms each and a slab thickness of 7.8 Å having 10.5 Å of vacuum separation between periodic images. Mg atoms in the two lowermost layers were kept fixed in their bulk-like positions, whereas the top two layers were free to relax, thus being able to respond to occurring forces due to surface effects or adsorption of the water molecule or its fragments.

All calculations were performed with Perdew-Wang 91 gradient-corrected exchange–correlation
functional, along with scalar-relativistic, Vanderbilt ultra-soft pseudo-potential and a 30/360 Ry cutoff for wavefunction/density plane wave expansion. K-point convergence tests were performed for the optimized reactant and product geometries for grid density up to 8×8×1 (See Supplementary Section S2). From k-point sampling using plane-waves, a full sampling of 4×4×1 k-points was observed to be less than 1.6 kcal/mol away from the results of k-point sampling with 8×8×1 grid.

DFT calculations

With the optimized geometries obtained, we performed DFT calculations using an underlying single-particle basis of translational-symmetry-adapted linear combinations of Gaussian atomic orbitals (AOs):

$$\varphi_{k,p}(r) = \sum_{\mathbf{T}} e^{i\mathbf{k} \cdot \mathbf{T}} \chi_p(\mathbf{r} - \mathbf{T})$$

where $\mathbf{T} = \sum_{i=1}^{3} T_i \mathbf{a}_i$ is a lattice translation vector, $\mathbf{k} = \sum_{i=1}^{3} k_i \mathbf{b}_i$ is a crystal momentum vector in the first Brillouin zone, and $\chi_p$ is an orbital from an underlying Gaussian basis. The summation over $\mathbf{T}$ leads to a basis of translational-symmetry-adapted orbitals. In the basis (7), the Born-Oppenheimer Hamiltonian takes the form:

$$\hat{H} = E_0 + \sum_{\mathbf{k} \mathbf{p} \mathbf{r} \sigma \tau} h_{\mathbf{p} \mathbf{r}}(\mathbf{k}) \hat{a}^\dagger_{\mathbf{k} \mathbf{p} \sigma} \hat{a}_{\mathbf{k} \mathbf{r} \sigma} + \sum_{\mathbf{k}_p \mathbf{k}_q \mathbf{k}_r \mathbf{k}_s} \frac{(\mathbf{k}_p \mathbf{p} | \mathbf{k}_q \mathbf{q} \mathbf{s} \mathbf{s})}{2} \hat{a}^\dagger_{\mathbf{k}_p \mathbf{p} \sigma} \hat{a}_{\mathbf{k}_q \mathbf{q} \tau} \hat{a}_{\mathbf{k}_s \sigma} \hat{a}_{\mathbf{k}_r \tau}$$

The * symbol indicates crystal momentum conservation, $\mathbf{k}_p + \mathbf{k}_q - \mathbf{k}_r - \mathbf{k}_s = \mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector. The real-space grid density roughly corresponds to a kinetic energy cutoff in the plane-wave representation. To ensure that relatively low energy cutoffs can be used, core electrons are often replaced with separable norm-conserving Goedecker-Teter-Hutter (GTH) pseudo-potentials, that remove sharp nuclear densities, and Gaussian basis sets that are designed for use with these pseudo-potentials in solid-state calculations of DFT or HF type. In our work, we used the GTH-DZV basis of atomic orbitals, and
a Weigend auxiliary basis for the density fitting procedure, as implemented in the PySCF package.\textsuperscript{41,42}

The Hamiltonian in Eq. (8) includes explicit correlations between all \( k \)-points of a mesh sampled in the Brillouin zone. The twist-averaging method\textsuperscript{40} for sampling over \( k \)-points which was used in this work assumes that each \( k \)-point in the Brillouin zone can be treated independently.

The DFT calculations were performed with the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{93} functional approximation for exchange and correlation terms for each \( k \)-point of the Monkhorst-Pack grid.

Localization of the Kohn-Sham orbitals was performed independently for the occupied and virtual orbitals using the Pipek-Mezey localization method. Pipek-Mezey localization method maximizes the orbital dependent population charges on the atoms. The partial charges were calculated using the ‘meta-Löwdin’ orbital method.\textsuperscript{46,50}

**Active Space Selection**

Electron density difference defined in Eq. (5) for both geometries was calculated using results of DFT calculations performed for the full system as well as slab and water treated independently. The corresponding electron density differences obtained for the reactant and product are shown in Supplementary Section S3. Overlap, \( O_i(x, y, z) \), of each of the localized DFT orbitals indexed by \( i \) with the electron density difference was then calculated:

\[
O_i(x, y, z) = \left\{ \rho_{DD}(x, y, z) * \rho_{DFT_i}(x, y, z) \right\}^{\frac{1}{2}}
\]  

(9)

Occupied and virtual localized DFT orbitals were sorted independently based on the value of integrated overlap, \( \tilde{O}_i[\eta] \), as shown in Eq. (10). Here, parameter \( \eta \) was used as a threshold to truncate tails of the overlap function \( O_i(x, y, z) \) which may have a small but significant
contribution once it is integrated over the volume.

\[ \tilde{O}_i[\eta] = \int dxdydz \quad O_i(x, y, z) H(O_i(x, y, z) - \eta) \]  

In the above equation, \( H \) is the Heaviside step function used to truncate the contributions from the spatial overlap function that are smaller than \( \eta \). Value of the parameter \( \eta \) should be chosen such that it is neither too tight nor too loose. On scanning over a coarse range of values of \( \eta \) one finds the order of the sorted orbitals remains mostly constant for a wide range of values. On increasing the value of \( \eta \) further, orbitals that are spread across the metallic surface start dominating. Values of \( \eta \) corresponding the regime of stable orbital ordering is used in this study.

After selection of the active orbitals, the Born-Oppenheimer Hamiltonian was projected into the active space to get an effective Hamiltonian, thus, this formalism did not encounter double counting issues.

**Quantum Algorithms in Active Space:**

*Unitary Coupled Cluster Singles and Doubles ansatz:* Unitary coupled cluster singles and doubles (UCCSD) ansatz is obtained by applying the exponential of the \( T - T^\dagger \) operator, where \( T \) is the set of fermionic excitation operators containing single and double excitation from the occupied (indexed as \( j, k, \ldots \)) to the virtual orbitals (indexed as \( p, q, \ldots \)) as shown
below:

$$|\psi_{UCCSD}(\theta)\rangle = e^{T - T^\dagger}|\psi_{HF}\rangle$$

$$T = T_1 + T_2$$  

$$T_1 = \sum_{j,p} (\theta^R_{j,p} + i\theta^I_{j,p}) a_p^\dagger a_j$$  

$$T_2 = \sum_{j,k,p,q} (\theta^R_{j,k,p,q} + i\theta^I_{j,k,p,q}) a_p^\dagger a_q^\dagger a_k a_j$$

$$T_1 - T_1^\dagger = \sum_{j,p} \theta^R_{j,p} (a_p^\dagger a_j - a_j^\dagger a_p) + i\theta^I_{j,p} (a_p^\dagger a_j + a_j^\dagger a_p)$$

$$T_2 - T_2^\dagger = \sum_{j,k,p,q} \theta^R_{j,k,p,q} (a_p^\dagger a_q^\dagger a_k a_j - a_k^\dagger a_j^\dagger a_p a_q) + i\theta^I_{j,k,p,q} (a_p^\dagger a_q^\dagger a_k a_j + a_k^\dagger a_j^\dagger a_p a_q)$$

Here $a^\dagger$ and $a$ are fermionic creation and annihilation operators. The amplitude of the excitation are parameterized by $\theta = \{\theta^R_{j,p}, \theta^I_{j,p}, \theta^R_{j,k,p,q}, \theta^I_{j,k,p,q}\}$. For molecular systems, ground states can be described using wavefunctions that are purely real valued; implying that the parameterized amplitudes are real valued as well. In the case of periodic systems though, eigen-functions are complex values. The number of real parameters to be optimized in the UCCSD ansatz for periodic systems studied at each $k$-point, except for $\Gamma$-point, is twice that of UCCSD ansatz for molecular systems. For the implementation of this ansatz on a gate based quantum computer, we map the fermionic operators into qubit operators using a fermion-to-qubit mapping. Each fermionic excitation in the $T - T^\dagger$ operator after mapping is described by sum of multiple Pauli strings. UCCSD ansatz is simulated on the quantum computer by applying Trotter-Suzuki approximation or other product formulae (denoted as qUCCSD) to the $T - T^\dagger$ operator. This was implemented through Qiskit’s qUCCSD ansatz class with the appropriate modifications to include the imaginary parts of the wavefunction.

The Qubit Coupled Cluster (QCC) ansatz is created by systematically adding exponen-
tials of Pauli strings from an ordered set of Pauli operators to the HF state. \cite{Rabyinkin2018, Rabyinkin2019}

\[ |\psi_{QCC}(\theta)\rangle = e^{i\theta_m P_m} e^{i\theta_{m-1} P_{m-1}} \cdots e^{i\theta_2 P_2} e^{i\theta_1 P_1} |\psi_{HF}\rangle \quad (17) \]

s.t. \[ P_k \in \{X, Y, Z, I\} \otimes M \quad (18) \]

In the above equation, \(X, Y, Z, I\) are Pauli operators and \(M\) is the dimension of the Hamiltonian in the second quantized Hilbert space. The Pauli strings \(P_k\) are ordered such that inclusion of the Pauli string \(P_1\) has the largest contribution to the correlation energy followed by \(P_2\) and so on. The stopping criterion \(m\) is decided based on how many strings can be robustly simulated by the noisy quantum hardware device or the energy convergence threshold. Strategies for ordering of the Pauli operators are described in detail in the works by Rabyinkin et al. \cite{Rabyinkin2018, Rabyinkin2019} While the strategies for ordering Pauli operators can be followed from these references, we chose to simplify our calculations by getting the sorted Pauli operators directly from the exact CASCI wave-function calculated on the classical computers using PySCF in the active space. The active space sizes studied in this work with quantum algorithms are still small enough to be investigated with exact diagonalization using classical machines. The configurations in the CASCI wave-function were ordered according to their contributions to the final state. On comparing the bit-string of a given configuration with the HF bit-string, the Pauli strings with \(X\), \(Y\) or \(I\) Pauli operators corresponding to the excitation were created. For each configuration, two Pauli operators were obtained to reflect the real and imaginary contributions to the wave-function after exponentiation.

The QCC ansatz was implemented using Qiskit. \cite{Qiskit} For all VQE simulations on the classical simulators, \texttt{L.BFGS.B}\textsuperscript{\cite{L-BFGS-B, L-BFGS-B}} optimizer was used.

\textit{Entanglement Forging (EF):} Consider a quantum system divided into subsystems (indexed by A and B, for simplicity \(\text{dim}(A) = \text{dim}(B) = N\)), then the wavefunction describing the full system can be expressed in terms of the two subsystems by looking at its Schmidt
decomposition.

|ψ_{A+B}\rangle = \sum_{x \in \{0,1\}^\otimes N} \lambda_x U|x\rangle_A \otimes V|x\rangle_B \quad (19)

where, $U$ and $V$ are unitary matrices and $\lambda$s are the Schmidt coefficients. The number of non-zero terms in this expansion is called the Schmidt rank and will determine the strength of entanglement between the two systems. When the entanglement is weak, only a few terms in this expansion contribute significantly. An expectation value, for example energy of the full system with Hamiltonian $H = \sum_{a,b=1}^h w_{a,b} P_a \otimes P_B$ for $P_{a,b} \in \{X,Y,Z,I\}^\otimes N$, can then be expressed as:

$$E = \sum_{a,b} \sum_{x,y} w_{a,b} \lambda_x \lambda_y \langle y|U^\dagger P_a U|x\rangle \langle y|V^\dagger P_b V|x\rangle \quad (20)$$

The expectation value for the full system $E$ scales quadratically with the Schmidt rank. The inner products expressed in Eq. (20) can be evaluated on the quantum computer with number of qubits that are half the number of qubits required for the full system.

The ground state wave-function of the system is not known a priori and thus just as in the VQE algorithm, a parameterized ansatz is used to model the Schmidt decomposed wavefunction described in Eq. (20). The variables of this ansatz are the configurations to be included in the Schmidt decomposition, the corresponding Schmidt coefficients as well as the unitary matrices $U$ and $V$ which are chosen as quantum circuits with parameterized rotation angles. We fix the number of terms and configurations used in the Schmidt decomposition. The corresponding Schmidt coefficients and parameterized angles are optimized using classical optimization methods.

In this work, we used EF algorithm coded using Qiskit to study the reactant and product systems in different active space sizes. Simultaneous Perturbation Stochastic Approximation (SPSA)\textsuperscript{97} optimizer was used to optimize the angles of the unitary $U$ and $V$. The Schmidt coefficients were optimized analytically.\textsuperscript{18} The choice of the selected configurations was guided by availability of the CASCI wavefunction; in absence of which one could use a CCSD or MP2 (2nd-order Möller-Plesset perturbation method) wavefunction. For implementation of
$U$ and $V$, we tested different circuit arrangements using hop gates and picked the ones giving the lowest energy. Details of the specific configurations or bit-strings used and the structure of the $U$ and $V$ circuits for all active space sizes are described in the Supplementary Section S5.

**Hardware Experiments:**

We performed hardware experiments using multiple IBM Quantum devices accessed via cloud, specifically, ibmq_lima, ibmq_guadalupe, ibmq_toronto, ibmq_casablanca, ibm_perth and ibm_lagos. For the HONO-LUNO active space full VQE optimization was performed for 16 $k$-points independently for the reactant and product geometries using COBYLA optimizer\textsuperscript{98} using one Pauli string which is sufficient (See Supplementary Fig. (S4)). Readout error mitigation as well as gate based zero noise extrapolation technique\textsuperscript{69} were used to mitigate the hardware noise.

While QCC ansatz with up to 50 Pauli strings was studied on classical simulators, for the hardware experiments ansatz with two Pauli strings were executed using parity mapping. Using circuit reduction techniques, we can exactly reduce the circuit corresponding to 2 Pauli string into circuits that act only on 2 qubits independent of the active space size. The simplified circuits are shown in Supplementary Fig. (S10). We used the optimized parameters obtained via classical simulators for these ansätze to estimate the optimal ground state energies on the quantum hardware and compare them with the expected results. Readout error mitigation and gate based zero noise extrapolation was used when applicable.

For the 2 orbital active space experiments with full VQE optimization as well as other experiments without optimization, 5 independent trials were conducted. For each set of optimal parameters obtained, additional stretched circuits with 3 times the original number of two qubit gates for zero noise extrapolation were run. Linear extrapolation results to the zero noise limit obtained from these 5 pairs of original and extrapolated circuits were then averaged over to report the final energies for a given active space size and $k$-point value.
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Supplementary Information for: Quantum Computation of Reactions on Surfaces Using Local Embedding

S1. Corrosion Reaction

The overall corrosion reaction\textsuperscript{S1,S2} in aqueous environments is given as:

\[ \text{Mg} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2 + \text{H}_2 \]  \hspace{1cm} (S1)

Eq. (S1) contains two partial equations corresponding to the oxidation of magnesium and reduction of water:

\[ \text{Mg} \rightleftharpoons \text{Mg}^{2+} + 2e^- \text{ (anodic)} \]  \hspace{1cm} (S2)

\[ 2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \text{ (cathodic)} \]  \hspace{1cm} (S3)

Williams et al.\textsuperscript{S1} proposed a detailed reaction scheme connecting the steps of initial water dissociation on Mg surface with the final step of H\textsubscript{2} evolution via Tafel mechanism\textsuperscript{S1,S3} in the presence of adsorbed OH\textsubscript{ads} and H\textsubscript{ads} species using modeling based on DFT. The suggested reaction mechanism was shown to be a concerted reaction involving multiple water molecules. The first reaction studied in the process was splitting of a single H\textsubscript{2}O molecule creating adsorbed H\textsubscript{ads} and OH\textsubscript{ads} moiety:

\[ \text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_{\text{ads}}(\text{H}_{\text{ads}}) \]  \hspace{1cm} (S4)

In the presence of multiple water molecules, the proposed reaction mechanisms consists of
three steps:

\[
\text{Mg} + 2 \text{H}_2\text{O} \longrightarrow \text{Mg(OH}_{\text{ads}})(\text{H}_{\text{ads}}) + \text{H}_2\text{O} \quad (S5)
\]

\[
\text{Mg(OH}_{\text{ads}})(\text{H}_{\text{ads}}) + \text{H}_2\text{O} \longrightarrow \text{Mg(OH}_{\text{ads}})_{2}(\text{H}_{\text{ads}})_{2} \quad (S6)
\]

\[
\text{Mg(OH}_{\text{ads}})_{2}(\text{H}_{\text{ads}})_{2} \longrightarrow \text{Mg(OH}_{\text{ads}})_{2} + \text{H}_2(\text{g}) \quad (S7)
\]

**S2. Geometry Optimization**

Density Functional Theory based energy difference between the product and reactant ground states as a function of the total \( k \)-points in Monkhorst-Pack densities of \( y \times y \times 1 \) for \( y \in \{1, 2, 4, 6, 8\} \) calculated using Quantum Espresso is shown in Fig. (S1). These calculations were performed using the plane wave basis set with full \( k \)-point sampling.

![Figure S1: Energy difference between the product and reactant as a function of number of \( k \)-points](https://example.com/figureS1)

**S3. Active Space Selection**

Electronic density difference obtained for the reactant and product systems based on the DFT calculations at the \( \Gamma \)-point using Gaussian basis set are shown in Fig. (S2). The
resultant plots are plotted with VESTA. 

**a.) Density Difference for Reactant**

**b.) Density Difference for Product**

Figure S2: Electronic density differences for the reactant and product systems as seen along the z-axis.

The top five orbitals selected from the ordered set of occupied orbitals produced after sorting based on electronic density differences for the reactant and product systems at the \( \Gamma \)-point are shown in Fig. (S3). All the occupied orbitals are localized around the surface moieties. Similar trend is observed for rest of the \( k \)-points as well.

**a.) Occupied orbitals selected for Reactant**

**b.) Occupied orbitals selected for Product**

Figure S3: Selected occupied orbitals for the reactant and product systems based on electronic density differences.
S4. VQE results with Qubit Coupled Cluster Ansatz

The VQE results obtained using the Qubit Coupled Cluster Ansatz with increasing number of Pauli strings for all \( k \)-points of a \( 4 \times 4 \times 1 \) Monkhorst-Pack grid are shown in Fig. (S4-S7). Each panel of Fig. (S4) shows the energy difference between the product and reactant minimum energy states in active space sizes increasing from 2 (top panel) to 10 (bottom panel) created using the electronic density difference + natural orbitals (DD+NO) method of active space selection. Similarly, Fig. (S5) shows the number of particles for the reactant (on left) and product (on right) with increasing active space sizes going from 2 (top) to 10 (bottom). Maximum deviation of \( 10^{-3} \) from the expected value is observed from these results. Results for other properties such as the z-component of the spin \( S_z \) in units of \( \hbar \) and total spin \( S^2 \) in units of \( \hbar^2 \) are shown in Fig. (S6) and Fig. (S7) respectively. The discrepancy in the total spin gets worse as the active space size increases. After addition of sufficient number of Pauli strings in the ansatz we expect the discrepancy to disappear.

S5. Entanglement Forging

In Fig. (S8) the singular values obtained from a Singular Value Decomposition of the CASCI (Complete Active Space Configuration Interaction) wavefunction by partitioning along the spin-up and spin-down sectors for each active space constructed from the DD+NO method for the reactant and product is shown. The results were evaluated at the \( \Gamma \)-point. Top panel is for the HONO-LUNO orbitals and the active space size increases by 2 orbitals with each panel going downwards up to 10. The singular values fall off quickly in all cases suggesting that the spin-up and spin-down subsystems in the ground state within each active space are weakly entangled.

In the Entanglement Forging (EF) algorithm, \(^{SS} |x\rangle_A \) and \( |x\rangle_B \) represents the N-qubit bit-string states or electronic configurations that describe a state of a bipartite \( (N + N) \)-qubit system \( |\psi_{A+B}\rangle \) (Eq. (19) in the main text). Since each bit-string describes electron occupa-
tions for spin-up and spin-down parts separately, the length of each bit-string corresponds to
the number of active orbitals. EF calculations at the \( \Gamma \)-point for active space sizes ranging
from two to ten active orbitals were performed. Table S1 (for reactant) and Table S2 (for
product) provide the details of the bit-strings used as well as the hop gate configuration
selected for the \( U \) and \( V \) unitary matrices. Each hop gate, \( h(\varphi) \), acts according to the
following matrix:

\[
h(\varphi) = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos(\varphi) & -\sin(\varphi) & 0 \\
0 & \sin(\varphi) & \cos(\varphi) & 0 \\
0 & 0 & 0 & -1
\end{bmatrix}
\]

While testing various ansätze for EF calculations, we systematically increased the number
of included bit strings from one to four, from a list of the most dominant bit strings obtained
from the full Configuration Interaction (CI) wavefunction in Jordan-Wigner (JW) transfor-
mation. For both reactant and product systems, each calculation includes the Hartree-Fock
state, e.g. \([1,1,0,0]\) for the case of four active orbitals. The obtained EF energies for each
systems are reported as well. While the EF energies for the reactant and product become
increasingly worse when compared to the CASCI energies as the active space size increases,
the values of \( \Delta E \) between the product and reactant compare well with the expected values
as shown in Fig. (S9). The CASCI energies are reported in Table S3 for the reactant and in
Table S4 for the product.

**S6. Details of Hardware Calculations**

Circuit reduction techniques employing exact circuit identities and Clifford transformations
were used to reduce the required circuit resources for the QCC ansätze with 2 Pauli strings
(for active space sizes of 4 and larger) and 1 Pauli string for the 2 orbital active space.
Details of this circuit reduction strategy can be found in a forthcoming manuscript.\textsuperscript{56}
Table S1: Entanglement forging set up and results for the reactant at the \( \Gamma \)-point in different active space sizes.

| # Active Orbitals | Bit Strings | Hop gates | EF energy (Ha) |
|-------------------|-------------|-----------|----------------|
| 2                 | [1,0]       | [0,1]     | -3981.02732    |
|                   | [0,1]       |           |                |
| 4                 | [1,1,0,0]   | [0,1], [2,3] | -3981.05119    |
|                   | [0,1,1,0]   |           |                |
|                   | [0,1,0,1]   |           |                |
|                   | [1,0,1,0]   |           |                |
| 6                 | [1, 1, 1, 0, 0, 0] | [0,1], [1,2], [2,0], [3,4], [4,5], [5,3] | -3981.05198    |
|                   | [0, 1, 1, 0, 1, 0] |           |                |
|                   | [0, 1, 1, 1, 0, 0] |           |                |
|                   | [1, 0, 1, 1, 0, 0] |           |                |
| 8                 | [1, 1, 1, 1, 0, 0, 0] | [3,4], [2,3], [4,5], [1,2], [5,6], [0,1], [6,7] | -3981.05609    |
|                   | [0, 1, 1, 1, 1, 0, 0] |           |                |
|                   | [1, 1, 0, 1, 0, 0, 1, 0] |           |                |
|                   | [1, 0, 1, 1, 1, 0, 0, 0] |           |                |
| 10                | [1, 1, 1, 1, 1, 0, 0, 0, 0] | [0,1], [0,2], [1,2], [1,3], [2,3], [2,4], [3,4], [5,6], [5,7], [6,7], [6,8], [7,8], [7,9], [8,9] | -3981.04709    |
|                   | [1, 1, 1, 1, 1, 0, 1, 0, 0, 0] |           |                |
|                   | [1, 0, 1, 1, 1, 0, 0, 1, 0, 0] |           |                |
|                   | [1, 1, 1, 1, 0, 1, 0, 0, 0, 0, 1] |           |                |

circuits which were run on the quantum hardware for different active space sizes are given in Fig. (S10).
Table S2: Entanglement forging set up and results for the product at the $\Gamma$-point in different active space sizes.

| # Active Orbitals | Bit Strings | Hop-gates | EF energy (Ha) |
|-------------------|-------------|-----------|----------------|
| 2                 | [1,0]       | [0,1]     | -3981.12598    |
|                   | [0,1]       |           |                |
| 4                 | [1,1,0,0]   | [0,1],[2,3]| -3981.13349    |
|                   | [0,1,1,0]   |           |                |
|                   | [0,1,0,1]   |           |                |
|                   | [1,0,0,1]   |           |                |
| 6                 | [1, 1, 1, 0, 0, 0] | [0,1], [1,2], [2,0], [3,4], [4,5], [5,3], [2,3] | -3981.15112    |
|                   | [0, 1, 1, 0, 1, 0] |           |                |
|                   | [0, 1, 1, 1, 0, 0] |           |                |
|                   | [1, 0, 1, 0, 0, 1] |           |                |
| 8                 | [1, 1, 1, 1, 0, 0, 0, 0] | [0,1], [2,3], [4,5], [6,7] | -3981.14932    |
|                   | [0, 1, 1, 1, 1, 0, 0, 0] |           |                |
|                   | [1, 1, 0, 1, 0, 1, 0, 0] |           |                |
|                   | [1, 1, 1, 0, 1, 0, 0, 0] |           |                |
| 10                | [1, 1, 1, 1, 0, 0, 0, 0, 0] | [0,1], [0,2], [1,2], [1,3], [2,3], [2,4], [3,4], [5,6], [5,7], [6,7], [6,8], [7,8], [7,9], [8,9] | -3981.15164    |
|                   | [1, 1, 1, 1, 1, 0, 0, 0, 0] |           |                |
|                   | [1, 0, 1, 1, 0, 1, 0, 0, 0] |           |                |
|                   | [1, 1, 1, 0, 1, 0, 0, 0, 0] |           |                |
Figure S4: Energy difference between the product and reactant as function of number of Pauli strings added to the QCC ansätz. Top panel corresponds to active space of HONO-LUNO orbitals. The active space size increases by 2 with each panel going downwards until the bottom panel with active space of 10 orbitals. Within each panel 16 curves represent the 16 \( k \)-points. One curve in each panel needs only half the number of Pauli strings since it describes higher symmetry \( \Gamma \)-point.
Figure S5: Number of particles for the reactant (left) and product (right) as function of number of Pauli strings added to the QCC ansatz. Top panel corresponds to active space of HONO-LUNO orbitals. The active space size increases by 2 with each panel going downwards. All 16 points are shown in each panel.
Figure S6: The z-component of the spin $S_z$ for the reactant (left) and product (right) as function of number of Pauli strings added to the QCC ansatz. Top panel corresponds to active space of HONO-LUNO orbitals. The active space size increases by 2 with each panel going downwards. All 16 points are shown in each panel.
Figure S7: The total spin $S^2$ for the reactant (left) and product (right) as function of number of Pauli strings added to the QCC ansatz. Top panel corresponds to active space of HONO-LUNO orbitals. The active space size increases by 2 with each panel going downwards. All 16 points are shown in each panel.
Figure S8: Singular values of the CASCI wavefunction for the reactant and product in increasing active space sizes going from 2 (top) to 10 (bottom) at the $\Gamma$-point. Inset in bottom two panels highlights the zoomed in results for small singular value indices.
Figure S9: Energy difference between the product and reactant using the EF and CASSCI method as a function of the active space size at the $\Gamma$-point.

Figure S10: Reduced circuits for the QCC ansatz in different active space sizes used for hardware experiments. Left circuits are for the reactant and the right for the product.
Table S3: CASCI energies in Hartree for the reactant system for active space sizes of 2 to 10 (along columns). Each row corresponds to a k-point of the $4 \times 4 \times 1$ Monkhorst-Pack grid. They are arranged such that top $y$ rows correspond to $y \times y \times 1$ k-points for $y \in \{1, 2, 4\}$.

| k-point | 2       | 4       | 6       | 8       | 10      |
|---------|---------|---------|---------|---------|---------|
| $\Gamma$ | -3981.02732 | -3981.06264 | -3981.07416 | -3981.10488 | -3981.13650 |
| k1     | -3980.73290 | -3980.76923 | -3980.80336 | -3980.81200 | -3980.84216 |
| k2     | -3980.73362 | -3980.76991 | -3980.80396 | -3980.81305 | -3980.84271 |
| k3     | -3980.73367 | -3980.76996 | -3980.80296 | -3980.81261 | -3980.84269 |
| k4     | -3980.94243 | -3980.97870 | -3981.01488 | -3981.02153 | -3981.05147 |
| k5     | -3980.94243 | -3980.97870 | -3981.01488 | -3981.02153 | -3981.05147 |
| k6     | -3980.94173 | -3980.97796 | -3981.01424 | -3981.02079 | -3981.05057 |
| k7     | -3980.85478 | -3980.89114 | -3980.92797 | -3980.93560 | -3980.96345 |
| k8     | -3980.85469 | -3980.89103 | -3980.92780 | -3980.93529 | -3980.96344 |
| k9     | -3980.94167 | -3980.97795 | -3981.01411 | -3981.02048 | -3981.05070 |
| k10    | -3980.85432 | -3980.89067 | -3980.92764 | -3980.93656 | -3980.96303 |
| k11    | -3980.85431 | -3980.89066 | -3980.92762 | -3980.93653 | -3980.96302 |
| k12    | -3980.94173 | -3980.97796 | -3981.01424 | -3981.02079 | -3981.05057 |
| k13    | -3980.94167 | -3980.97795 | -3981.01411 | -3981.02048 | -3981.05070 |
| k14    | -3980.85467 | -3980.89100 | -3980.92789 | -3980.93613 | -3980.96339 |
| k15    | -3980.85471 | -3980.89105 | -3980.92786 | -3980.93493 | -3980.96343 |
Table S4: CASCI energies in Hartree for the product system for active space sizes of 2 to 10 (along columns). Each row corresponds to a k-point of the $4 \times 4 \times 1$ Monkhorst-Pack grid. They are arranged such that top $y$ rows correspond to $y \times y \times 1$ k-points for $y \in \{1, 2, 4\}$

| k-point | 2       | 4       | 6       | 8       | 10      |
|---------|---------|---------|---------|---------|---------|
| $\Gamma$ | -3981.12598 | -3981.14553 | -3981.18386 | -3981.20901 | -3981.24312 |
| k1      | -3980.84116 | -3980.86099 | -3980.90073 | -3980.92480 | -3980.95919 |
| k2      | -3980.84021 | -3980.86008 | -3980.89705 | -3980.92330 | -3980.95759 |
| k3      | -3980.84122 | -3980.86071 | -3980.89915 | -3980.92476 | -3980.95931 |
| k4      | -3981.01493 | -3981.03404 | -3981.07256 | -3981.09781 | -3981.13191 |
| k5      | -3981.01493 | -3981.03404 | -3981.07256 | -3981.09781 | -3981.13191 |
| k6      | -3981.02091 | -3981.03972 | -3981.07846 | -3981.10327 | -3981.13760 |
| k7      | -3980.94182 | -3980.96125 | -3980.99898 | -3981.02423 | -3981.05856 |
| k8      | -3980.93851 | -3980.95933 | -3980.99836 | -3981.02129 | -3981.05546 |
| k9      | -3981.01783 | -3981.03635 | -3981.07467 | -3981.10059 | -3981.13482 |
| k10     | -3980.94069 | -3980.96021 | -3980.99808 | -3981.02322 | -3981.05760 |
| k11     | -3980.94069 | -3980.96021 | -3980.99808 | -3981.02322 | -3981.05760 |
| k12     | -3981.02091 | -3981.03972 | -3981.07846 | -3981.10327 | -3981.13760 |
| k13     | -3981.01783 | -3981.03634 | -3981.07466 | -3981.10059 | -3981.13482 |
| k14     | -3980.93851 | -3980.95933 | -3980.99835 | -3981.02129 | -3981.05546 |
| k15     | -3980.94182 | -3980.96125 | -3980.99898 | -3981.02423 | -3981.05856 |
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