

Optimizing electronic structure simulations on a trapped-ion quantum computer using problem decomposition

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Quantum computers have the potential to advance material design and drug discovery by performing costly electronic structure calculations. A critical aspect of this application requires optimizing the limited resources of the quantum hardware. Here, we experimentally demonstrate an end-to-end pipeline that focuses on minimizing quantum resources while maintaining accuracy. Using density matrix embedding theory as a problem decomposition technique, and an ion-trap quantum computer, we simulate a ring of 10 hydrogen atoms without freezing any electrons. The originally 20-qubit system is decomposed into 10 two-qubit problems, making it amenable to currently available hardware. Combining this decomposition with a qubit coupled cluster circuit ansatz, circuit optimization, and density matrix purification, we accurately reproduce the potential energy curve in agreement with the full configuration interaction energy in the minimal basis set. Our experimental results are an early demonstration of the potential for problem decomposition to accurately simulate large molecules on quantum hardware.

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Electronic structure simulation is an essential tool for understanding the chemical properties of molecules. It is a basis for contemporary materials design and drug discovery. Performing accurate electronic structure simulations on classical computers requires a great amount of computational resources. In particular, they grow exponentially with the system size when employing the full configuration interaction (full CI) method, which calculates the exact solution of the electronic Schrödinger equation in a given basis set. Quantum computing, a computing paradigm that leverages the laws of quantum physics, has the potential to deliver scalable and accurate electronic structure calculations^{1,2} beyond the reach of classical computers.

Quantum computing technologies are rapidly advancing, and there has been major progress in simulating molecular systems in the past two decades^{3–13}. However, simulating the electronic structure of industrially relevant molecular systems on today's noisy, intermediate-scale quantum (NISQ) devices¹⁴ will require systematically scalable, robust methods that allow a given problem to be represented by a small number of qubits and shallow quantum circuits. The treatment of electron correlation is also necessary for applying electronic structure calculations to make accurate predictions about the process of a chemical reaction. Calculating the molecular energy remains a challenge, even for small systems, without limiting the number of configurations or the number of electrons active in performing the electronic structure calculations. Without being able to treat correlations in a scalable way, the stringent constraints of NISQ devices will inhibit their ability to perform high-accuracy simulations of larger molecular systems, particularly those systems where the electron correlation is strong.

Progress is being made on these issues as hardware develops. The largest calculation of the total energy including electron correlation to date is the simulation of BeH₂ using six qubits for the six-electron problem⁷. Note further that some of the authors of the present manuscript simulated a water molecule on a trapped-ion quantum computer. Using a small number of electron configurations that are known to contribute significantly to the total energy of the molecule, the energy estimates obtained were within the widely used measure for chemical accuracy (1.5936×10^{-3} hartrees) when compared to classically simulated results⁹. Other recent research¹³ simulated a chain of 12 hydrogen atoms using 12 qubits and the Hartree–Fock (HF) method. This is a system with 12 uncorrelated electrons and set the record in terms of the largest number of qubits used for a chemistry simulation.

To approach the simulation of larger molecules, problem decomposition techniques can be used to decompose a given molecular system into small subsystems, without sacrificing the accuracy of the electronic structure calculation for a wide class of chemical systems^{15–18}. These techniques admit a more compact representation of a molecule, enabling the explicit inclusion of more electrons in calculating correlation energies. Although the amount of reduction in the computational cost and resulting accuracy is dependent on the problem decomposition algorithm and the system being studied, these techniques have the potential to substantially reduce the qubit count requirements in electronic structure simulations^{19–27}.

Density matrix embedding theory (DMET)^{28,29} is one such problem decomposition method that has been used to study molecular systems, ranging from model systems such as a ring or a lattice of hydrogen atoms³⁰ to more-realistic organic molecules^{29,31}. It has also successfully been used in quantum simulations of the Hubbard model¹⁹. Despite the strength and wide applicability of DMET-based decomposition, complex molecular systems might require a different choice of problem decomposition technique.

In this work, we use DMET to demonstrate experimentally how, given a limited fragment size, we can extend the applicability of quantum hardware to larger systems with the aid of classical computations that implement problem decomposition—a schematic of the pipeline is shown in Fig. 1a. Our target system is a ring of ten hydrogen atoms where we take all electrons into account and do not use the frozen core approximation. We apply the DMET method to generate fragments and solve the electronic structure problem of the fragments using a quantum algorithm. The most appropriate algorithm for current hardware is the variational quantum eigensolver (VQE)⁴ whose advantage is enabling shallow circuits that can realistically be executed, at the expense of taking more measurements. We use the established qubit coupled-cluster method³² to generate the parametric ansatz required for running the VQE algorithm. To run our circuits, we use a trapped-ion quantum computer^{6,8,9}, a platform that allows for an efficient implementation of quantum circuits via complete qubit connectivity^{33–35}. We further employ a density matrix purification algorithm to post-process the experimentally determined results and mitigate residual error. Our results demonstrate the success of an end-to-end pipeline using problem decomposition to accurately solve a molecular problem.

Results and discussion

Numerical results of the DMET and the qubit coupled-cluster methods. We begin by describing our DMET-based methodology for simulating the electronic structure of a molecular system (see “Methods” section for further details). Consider a system described by a second-quantized Hamiltonian $\hat{H} = H^{1-e} + H^{2-e}$, where H^{1-e} is the one-electron interaction and H^{2-e} is the two-electron interaction of the entire molecule. In contrast to simulating the entire system using \hat{H} , in DMET, the system to be simulated is divided into small fragments. Each fragment is treated as an open quantum system, entangled with its surrounding environment, or bath. Here we use the mean-field, HF solution of the entire molecular system as a pre-processing step to find local orbitals that we use to fragment the molecule. Then, the following iterative process, which we call the DMET cycle, initiates. Once the cycle terminates, the electronic structure calculation of the entire molecule is complete. The DMET algorithm is shown in Fig. 1b.

The DMET cycle begins by constructing the bath orbitals for each fragment. The bath orbitals describe the environment that is active for the electronic structure calculation of the fragment, by virtue of Schmidt decomposition³⁶. Note that, if the bath is large, the description of the bath can be greatly simplified. With the simple description of the bath, the Hamiltonian H^A for each fragment A, along with its specific bath B, is constructed according to the equation

$$H^A = H^{1-e,AB} + H^{2-e,AB} - \mu N^A, \quad (1)$$

where $H^{1-e,AB}$ denotes the one-electron interaction within and across the fragment and the bath, $H^{2-e,AB}$ denotes the two-electron interaction within and across the fragment and the bath, μ is the chemical potential, and N^A is the number of electrons in the fragment. See “Methods” section for more details. We use a quantum computer in the DMET calculation to accurately evaluate the minimal expectation value of H^A , as well as the number of electrons N^A in fragment A.

Once both the energy expectation value and the number of electrons for each fragment are computed, we combine them to compute the total system energy and check for self-consistency. In particular, we choose to compute the sum of the number of electrons in each fragment and check whether the sum is equal to the total number of electrons in the system. If the sum is within a

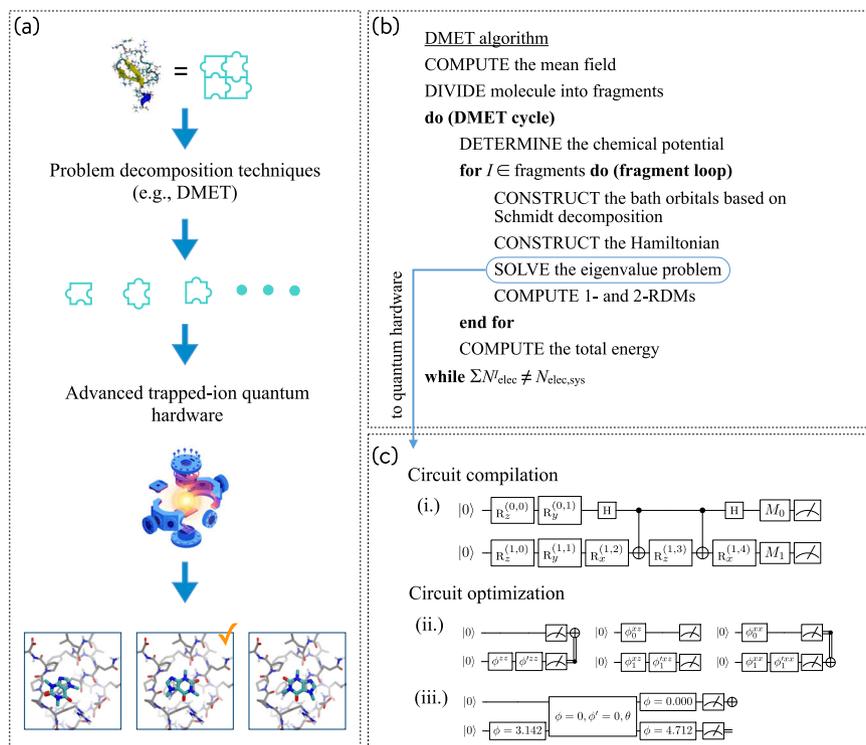


Fig. 1 Problem decomposition-based pipeline for efficient electronic structure simulation on a quantum computer. **a** Schematic illustration of the pipeline. **b** The density matrix embedding theory (DMET) algorithm. “1- and 2-RDMs” refers to one- and two-particle reduced density matrices. **c** Pre- and post-optimizing compilation circuits. (i) Pre-optimizing compilation input, with the gates M_0 and M_1 chosen appropriately for the different measurement bases. (ii) Post-optimizing compilation outputs for the three output circuits for ZZ (left), XZ (middle), and XX (right). Note that XZ and ZX result in the same circuit, outside of the relabeling of the qubit indices. See Supplementary Tables 3 and 4 for the numerical values of the gate parameters. (iii) Post-optimization circuits for YY, required for the classical post-processing of our simulation data. See Supplementary Table 5 for the numerical values of the gate parameters.

prespecified range with respect to the total number of electrons, the DMET cycle terminates. If the sum is not within the specified range, we run the DMET cycle again, with the chemical potential μ updated as the difference between the sum and the total number of electrons.

Our explicit example of calculating the electronic structure of a molecule using DMET is to simulate a ring of ten hydrogen atoms, H_{10} . For this molecule, we take advantage of its symmetry to create identical subproblems. This allows us to use a single fragment to solve for the entire system. If this symmetry was not present, we would need to solve each subproblem individually, which could be done in parallel. To minimize quantum resources, we choose to divide the molecule into ten one atom fragments, allocating two spin orbitals for the fragment and for the bath. This may be compared to a total of 20 spin orbitals in the simulation of the entire molecule, which shows a large reduction in the problem size: a 20-qubit problem is reduced to 10 two-qubit problems.

Classical simulations show that this decomposition reproduces full CI energy within chemical accuracy in all regions of the dissociation curve, except for the repulsive wall. This is consistent with the studies in ref. ²⁹, which also shows how correlations can be added to improve the approximation by increasing the fragment size, or by adding an additional self-consistency loop to optimize the correlation potential in the DMET approach. For the points along the dissociation curve that we will explore experimentally, we calculate the total energy per atom of the DMET fragments with a full CI solver and denote the results under DMET-FCI in Table 1.

To estimate the expectation value of the fragment energy and the number of particles per fragment on a quantum device, we use VQE⁴ with the qubit coupled-cluster (QCC) ansatz³². For all calculations, we use the symmetry-conserving Bravyi–Kitaev transformation (scBK)^{37,38} to transform from a fermion to a qubit basis. The QCC ansatz operator $\hat{U}(\boldsymbol{\tau})$ is specified according to the equation

$$\hat{U}(\boldsymbol{\tau}) = \prod_k^{n_g} \exp\left(-\frac{i\tau_k \hat{P}_k}{2}\right), \quad (2)$$

where τ_k is a variational parameter, n_g is the number of multi-qubit Pauli operators \hat{P}_k , defined as

$$\hat{P}_k = \bigotimes_j^{n_q} \hat{p}_j^{(k)} \quad \text{for } \hat{p}_j^{(k)} \in \{X, Y, Z, I\}, \quad (3)$$

where n_q is the number of qubits and X, Y, Z , and I are the Pauli matrices and a single-qubit identity operator, respectively. While the depth of the circuit rapidly increases as the size of the molecule increases, the QCC ansatz admits a low-depth quantum circuit compared to a widely used unitary coupled-cluster single and double ansatz. The details of the QCC circuit simulations can be found in Supplementary Note 1.

We first consider an ansatz state that is a product state of n_q arbitrary single-qubit states, following the method described in the work of Ryabinkin et al.³⁹. We evaluate the expectation value of the mean-field Hamiltonian with respect to the ansatz state and use VQE, simulated on a classical computer, to minimize the

Table 1 Numerical and experimental values of the total energies per atom of the ring of ten hydrogen atoms (H₁₀).

R(A)	HF	FCI	DMET-FCI	DMET-QCC (T)	DMET-QCC (E)	DMET-QCC (P)
0.70	-0.454468	-0.462588	-0.460015	-0.460015	-0.461 ± 0.007	-0.464 ± 0.008
0.85	-0.509296	-0.519025	-0.516992	-0.516991	-0.521 ± 0.007	-0.522 ± 0.008
1.00	-0.526412	-0.538093	-0.536753	-0.536753	-0.536 ± 0.007	-0.538 ± 0.007
1.10	-0.527728	-0.541007	-0.540160	-0.540160	-0.539 ± 0.006	-0.540 ± 0.007
1.30	-0.518798	-0.536375	-0.536353	-0.536354	-0.536 ± 0.006	-0.536 ± 0.006
1.60	-0.494352	-0.522320	-0.522484	-0.522484	-0.521 ± 0.005	-0.522 ± 0.004
1.80	-0.476771	-0.514366	-0.514092	-0.514093	-0.512 ± 0.004	-0.515 ± 0.004
2.00	-0.460103	-0.508668	-0.508073	-0.508074	-0.507 ± 0.004	-0.507 ± 0.003
2.50	-0.425756	-0.501961	-0.501820	-0.501822	-0.500 ± 0.003	-0.502 ± 0.001
5.00	-0.368206	-0.499810	-0.499826	-0.499826	-0.499 ± 0.002	-0.49987 ± 0.00008

The total energies per atom (in hartrees) were calculated using the following methods: Hartree-Fock (HF), full configuration interaction (FCI), density matrix embedding theory (DMET) with the FCI solver (DMET-FCI), and DMET with the qubit coupled-cluster and variational quantum eigensolver (DMET-QCC). These methods are used for the H₁₀ molecule along the potential energy curve (R = 0.7, 0.85, 1.0, 1.1, 1.3, 1.6, 1.8, 2.0, 2.5, and 5.0 Å) of the symmetric expansion. For DMET-QCC, we report the theoretical (T), experimental (E), and post-processed (P) results. For the experimental and the post-processed results, we report the standard deviation of the energies, calculated using bootstrapping, which is described in the "Methods" section.

value. The variational parameters that result from the optimization correspond to the optimal wavefunction for the mean field. We next consider a QCC ansatz operator $\hat{U}(\tau)$ applied to the previously determined, mean-field optimized state. Note that we aim to minimize the expectation value of the fragment Hamiltonian with respect to the ansatz operator parameters τ . We find which \hat{P}_k to include in our ansatz by computing the derivative of the expectation value with respect to τ_k , which can be computed in a straightforward way when $\tau = \mathbf{0}$. We remove \hat{P}_k terms that have small derivative values. Applied to our example molecule H₁₀, we find that \hat{P}_k of XY and YX have large, identical derivative values. Note that we carry out the computation of the derivatives on a classical computer.

We now investigate the performance of DMET with the QCC ansatz, which we denote as DMET-QCC, on a classical computer. Specifically, we consider the potential energy curve of the symmetric expansion (i.e., increasing the bond length R while maintaining it for each pair of neighboring atoms) of H₁₀. We choose ten points ($R = 0.7, 0.85, 1.0, 1.1, 1.3, 1.6, 1.8, 2.0, 2.5, \text{ and } 5.0 \text{ \AA}$) along the potential energy curve and compare the total energies resulting from the two-qubit DMET-QCC ansatz with DMET-FCI, all calculated classically. The total energies per atom of the H₁₀ molecule are listed in Table 1, and the atomic coordinates can be found in Supplementary Data 1. We also include the results obtained from other known methods, such as HF and full CI. The DMET-QCC results almost exactly reproduce the DMET-FCI results indicating that the VQE and QCC methods accurately represent the fragments.

We next describe the simulation of our DMET method on a trapped-ion quantum computer. Instead of variationally optimizing the energies, then running through the DMET cycles, here we focus on the evaluation of the total energy from the quantum simulation for the classically precomputed optimal parameters. Note that for the DMET cycles, we require $\langle XX \rangle$, $\langle YY \rangle$, $\langle ZZ \rangle$, $\langle XZ \rangle$, $\langle ZX \rangle$, $\langle Z_0 \rangle$, $\langle Z_1 \rangle$, $\langle X_0 \rangle$, and $\langle X_1 \rangle$ to be simulated, where the subscripts denote the qubit index. See Supplementary Note 2 for details on the Hamiltonian and the DMET energy expressions used in the experiments.

Compiling the circuits for the trapped-ion hardware. The circuits are executed on IonQ's 11-qubit trapped-ion quantum computer, which is described in detail elsewhere⁴⁰. In the quantum computer, 15¹⁷¹Yb⁺ ions, aligned to form a linear crystal with spacing of about 4 μm, are suspended in a chip trap with a radial pseudopotential frequency of ~3.1 MHz. We cool the crystal to its motional ground state and use the 11 ions in the

middle as qubits, and initialize them to the $|0\rangle$ state. Two of these qubits are used in our experiment. Single- and two-qubit gate fidelities are nominally calibrated to greater than 99.5% and 96.5%, respectively. Counter-propagating laser beams capable of illuminating individual ions are used to implement quantum gates, leveraging the ion-ion coupling mediated by the collective radial motional modes. We read out the quantum state by fluorescing the ions using a detection laser.

The native gates available on the quantum computer are $R_\phi(\pi/2) := \exp(-i\sigma_\phi\pi/4)$ and $\phi\phi'(\pi/2) := \exp(-i\sigma_\phi\sigma_{\phi'}\pi/4)$, where $\sigma_\phi = \cos(\phi)X + \sin(\phi)Y$. We thus compile the DMET-QCC ansatz circuits discussed earlier using the native gates and optimize the circuits to reduce the number of quantum gates. Figure 1c shows the pre- and post-optimizing compilation quantum circuits. See "Methods" section for further details.

We extract the expectation values of the Pauli terms using the three compiled, optimized circuits shown in Figure 1c(ii). We use the XX and ZZ circuits for $\langle XX \rangle$ and $\langle ZZ \rangle$, and the XZ circuit for $\langle XZ \rangle$ and $\langle ZX \rangle$, as the two pre-optimization circuits for $\langle XZ \rangle$ and $\langle ZX \rangle$ reduce to the same circuit upon optimizing compilation. The single-qubit Pauli terms $\langle X_0 \rangle$, $\langle X_1 \rangle$, $\langle Z_0 \rangle$, and $\langle Z_1 \rangle$, where B_i denotes the i th qubit's expectation value in the B basis, are computed using all of the statistics available from the three circuit executions. For instance, for $\langle X_0 \rangle$, we use the results from both $\langle XX \rangle$ and $\langle XZ \rangle$. Likewise, approaches are used for $\langle X_1 \rangle$, $\langle Z_0 \rangle$, and $\langle Z_1 \rangle$.

Experimental results. The total energies obtained from the quantum computer (points plotted in blue), along with the classically computed potential energies (lines), are shown in Fig. 2. We calculate the values of the error bars using the bootstrapping method described in the "Methods" section. The experimentally determined energies nearly coincide with the full CI energies (black line) and DMET-QCC reference values and agree within the margin of error.

To improve our experimental results, we perform classical post-processing using McWeeny's density matrix purification technique⁴¹ applied to the reduced density matrices (RDMs). Its effectiveness in improving energy estimation has been shown in ref. 13 for uncorrelated one-particle RDMs (1-RDM), and in ref. 10 for two-particle RDMs (2-RDM) of correlated two-electron systems. As in the latter case, ours is a two-electron system whose 2-RDM is the full density matrix P_{pqrs} . Only because of this aspect, we are able to purify our experiment iteratively using the following procedure: $P_{pqrs}^{\text{new}} = 3(P_{pqrs}^{\text{old}})^2 - 2(P_{pqrs}^{\text{old}})^3$ until the

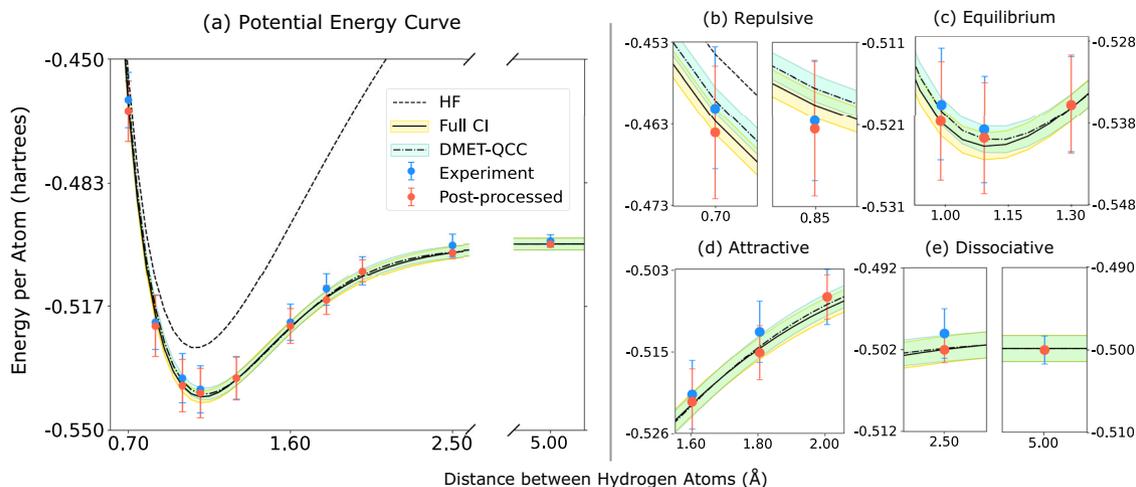


Fig. 2 The potential energy curve of the symmetric expansion of the ring of ten hydrogen atoms (H_{10}). For reference, we include classically simulated curves using several methods: Hartree-Fock (HF) shown with the dotted black line, full configuration interaction (full CI) shown with the solid black line, and density matrix embedding theory with the qubit coupled-cluster ansatz and variational quantum eigensolver (DMET-QCC) shown with the dashed black line. The full CI and DMET-QCC lines are surrounded by yellow and blue regions indicating chemical accuracy with respect to their values, and their overlap is indicated in green. The energies obtained by the experiment are shown in blue circles, and the post-processed energies are shown in red circles. The respective error bars for each are calculated using bootstrapping which is described in the “Methods” section. **a** The full potential energy curve. **b–e** A magnified view of the distinct energy regimes of the curve.

convergence criterion of $\text{Tr}(P_{pqrs}^2 - P_{pqrs}) < 1.0 \times 10^{-2}$ has been met, see “Methods” section for details.

We emphasize that this purification only works when applied to the 2-RDM for our system because our fragment only has two electrons—thus the 2-RDM happens to be the full density matrix, allowing idempotency to be imposed. To extend this method to larger correlated systems, we would need to purify our 2-RDMs using the more general n -representability conditions^{42–44}. This requires further study and is outside the scope of this work. Obtaining P_{pqrs} requires us to run an additional circuit, YY , on the trapped-ion quantum computer. The corresponding circuit is shown in Fig. 1c(iii.) comprising three single-qubit and one two-qubit native gate operations; see “Methods” section for details on the optimized compilation.

Table 1 and the points plotted in red in Fig. 2 show the post-processed total energies for all points, along with their respective errors. All points are in agreement with the simulated DMET-QCC values, and, with the exception of the repulsive wall and the point $R = 1.8 \text{ \AA}$, all values are within chemical accuracy. Again excluding the repulsive wall, the purification method improves the accuracy of the energy estimate for all points along the potential energy curve, and brings the point $R = 2.5 \text{ \AA}$ within chemical accuracy of DMET-QCC and full CI. This post-processing is enabled by the high quality of the two-qubit gates of the hardware; see Supplementary Note 3 for further details.

The level of accuracy in our results is due to the ability of the decomposition method to well approximate most of the curve, the success of the VQE algorithm and QCC circuit ansatz to express the fragments, and the small systematic errors of the hardware used in this experiment. We note that the error bars are quite large, which is a result of the limited sampling capacity. The achievable precision will increase as the availability of quantum resources grows. Simulating a molecule of this size was only possible by using problem decomposition to create fragments that would fit the hardware. This demonstrates how we can use classical methods to extend the applicability of quantum hardware that is limited in size, and scale the correlation captured in our fragments as hardware develops.

We also want to highlight that with the 2-RDM obtained in this experiment using the two-qubit gate for the $\langle YY \rangle$ term, we can successfully calculate other properties. Of interest is capturing the nature of the entanglement, which is the characteristic phenomenon of quantum simulation. We investigate two types of quantum entanglement by splitting the Hilbert space of the two-qubit system into two subsystems. The first method quantifies the entanglement between the molecular orbitals by splitting the first and second qubit and provides a metric to validate that the state prepared by the optimized circuits is entangled. The second method is to quantify the entanglement between the fragment and bath and reflects the structure of the DMET method. With the detailed analysis shown in Supplementary Note 4, we find that the experimental results reproduce the expected trend of the theoretical predictions, and indicate that our experiment has effectively prepared an entangled quantum state suitable for the problem decomposition method.

Conclusion

In this work, we have experimentally demonstrated an end-to-end pipeline using a PD technique to reduce the size of an electronic structure simulation, making a 20-qubit problem realizable on a trapped-ion NISQ device. Our method involves combining DMET and VQE with a QCC ansatz to compress the quantum simulation circuit for the electronic structure calculation, and circuit optimization techniques that target trapped-ion quantum computers. A density matrix purification method is then applied to mitigate residual errors. All of these steps successfully construct the potential energy curve of the ring of ten hydrogen atoms and serve as a proof of concept for the usefulness of problem decomposition to accurately and efficiently represent large molecules. Our results are in agreement with full CI, and almost all points are within the chemical accuracy of their DMET-QCC simulated values. This demonstrates that the approach employed herein can describe bond-breaking and bond-forming in molecular systems.

Computer-aided molecular design in both materials science and the life sciences is key to our attaining a sustainable future through the accurate prediction of chemical reactions, such as the

catalytic reaction of organometallic compounds in advanced materials innovation, enzymatic reactions in the life sciences, and the electrochemical reactions implemented in next-generation batteries. In a previous work by some authors of the present paper²⁶, it is shown that a quantum simulation of a typical, industrially relevant organometallic compound would require over 2000 qubits. Selecting the appropriate PD technique could result in the reduction of qubit requirements significantly. A reduction by a factor of five for industrially relevant systems is shown in another work²². This sort of reduction could place these simulations within the reach of near-future NISQ devices that have hundreds of qubits. The precise reduction in the amount of required resources can be both algorithm-dependent and application-dependent. For example, if we were to use the DMET algorithm as the PD technique, and if our target system were not symmetric, we would need to run quantum simulations for each fragment that the DMET algorithm would create. If we were to use a larger fragment size for greater accuracy, the quantum resource required to simulate the fragment would also become greater, but would always remain smaller than or equal in size to the case where the entire system was simulated without using any PD.

Our present work experimentally demonstrates the potential of problem decomposition methods as a preprocessing step to reduce the quantum resources required in simulating molecular systems while preserving accuracy. We were able to treat all electrons in the system, and include correlations as necessary to produce accurate results using subproblems that fit on hardware. This additional classical component allows us to apply results from quantum devices to a larger family of problems, which we believe will be a valuable tool for using quantum computers to enhance molecular design platforms.

Methods

The system Hamiltonian. The second-quantized electronic Hamiltonian can be written as

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} (pq|rs) \hat{a}_p^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_r, \quad (4)$$

where $p, q, r,$ and s are distributed over all spin orbitals, and \hat{a}_p^\dagger and \hat{a}_q are the corresponding creation and annihilation operators. The terms h_{pq} and $(pq|rs)$ are the one- and two-electron integrals (in chemists' notation), respectively. The evaluation of these integrals, as well as the HF and full CI calculations, are carried out using PySCF⁴⁵. The minimal basis set MINAO⁴⁶ is used in our calculation.

The electronic Hamiltonian is then transformed into the qubitized form by using scBK^{37,38}. The qubitized Hamiltonian can be written as

$$\hat{H} = \sum_p h_p^\alpha \sigma_p^\alpha + \sum_{pq} h_{pq} \sigma_p^\alpha \sigma_q^\beta + \sum_{pqr} h_{pqr} \sigma_p^\alpha \sigma_q^\beta \sigma_r^\gamma + \dots, \quad (5)$$

where p, q, r, \dots are distributed over all qubits, and $\sigma_p^\alpha \in \{\sigma_x, \sigma_y, \sigma_z, I\}$ acts on qubit p . The transformation of the electronic Hamiltonian into a qubit basis is performed using OpenFermion⁴⁷.

Density matrix embedding theory. Let us consider a molecular system divided into fragments, in which a small fragment A with N^A states is surrounded by a large bath B with N^B states. If the wavefunction of the entire system $|\Psi\rangle$ is known, Schmidt decomposition³⁶ can be applied, and we may write

$$\begin{aligned} |\Psi\rangle &= \sum_i^{N^A} \sum_j^{N^B} \psi_{ij} |\alpha_i\rangle |\beta_j\rangle \\ &= \sum_i^{N^A} |\alpha_i\rangle \left(\sum_j^{N^B} \psi_{ij} |\beta_j\rangle \right) \\ &= \sum_i |\alpha_i\rangle |\tilde{\chi}_i\rangle \\ &= \sum_{i'} \psi_{i'} |\alpha_i\rangle |\chi_{i'}\rangle, \end{aligned} \quad (6)$$

where

$$|\tilde{\chi}_i\rangle = \sum_j \psi_{ij} |\beta_j\rangle, \quad (7)$$

$|\alpha_i\rangle$ and $|\beta_j\rangle$ denote particular many-body bases and $|\chi_i\rangle$ is the orthogonal set of $|\tilde{\chi}_i\rangle$. The states $|\chi_i\rangle$ are the states of bath B; however, the number of states coincides with that of fragment A. This shows that, regardless of the size of bath B, only N^A states can be entangled with the fragment. This will reduce the size of the problem drastically for large-sized systems.

The exact wavefunction of the entire system $|\Psi\rangle$ is the eigenfunction of the Hamiltonian for the entire system H . The Hamiltonian H' of fragment A embedded in bath B can be defined using a projection operator P , that is,

$$H' = PHP, \quad (8)$$

where

$$P = \sum_{i'} |\alpha_i\rangle \langle \chi_{i'}| \langle \alpha_i| \langle \chi_{i'}|. \quad (9)$$

It is now evident that the electronic structure of the entire system can be described exactly by that of the fragments and their surrounding baths. The electronic structure calculation of the entire system can be solved using this smaller problem. However, the exact wavefunction of the molecular system is usually not known a priori; thus, the introduction of an approximation is necessary. The wavefunction of the entire system obtained by low-level, mean-field theory, such as the HF calculation, would be a straightforward approximation of the exact wavefunction of the entire system. Using a low-level wavefunction to construct a bath and solve the reduced problem employing a high-level theory is the principal idea behind the DMET.

The orbitals of the entire system are transformed into unentangled occupied orbitals, unentangled virtual orbitals, local fragment orbitals, and bath orbitals. The orbital space of the entire system is then greatly reduced, as only the local fragment and bath orbitals are employed for each high-level DMET fragment calculation.

Practically, we need to optimize the embedding of a bath. In DMET, a high-level calculation for each fragment is carried out individually until self-consistency has been attained according to a certain criterion: the sum of the 1-RDM of all of the fragments agrees with that of the low-level one for the entire system. The DMET energy is calculated using the 1-RDM and 2-RDM. The DMET algorithm used in this work, the single-shot algorithm²⁹, can be described as follows:

1. Calculate the wavefunction of the entire molecular system using a low-level method and then localize the orbitals to fragment the molecule.
2. Construct the bath orbitals so as to include the surrounding environmental effect.
3. Construct the Hamiltonian of a fragment (including environmental effect) and calculate the wavefunction using a method based on a high-level theory.
4. Calculate the fragment energy and the number of electrons for each fragment with the 1- and 2-RDMs from the wavefunction obtained in step 3.
5. Repeat steps 2–4 for each fragment and obtain the total energy and the high-level 1-RDM of the entire molecular system.
6. Repeat steps 2–5 until the sum of the number of electrons in the fragments agrees with the number of electrons for the entire system.

The initial step of a DMET calculation is to perform a mean-field HF calculation for the entire molecule. The localized orbitals are obtained by localizing the canonical orbitals from the HF calculation to determine how to fragment the molecules. The Meta-Löwdin localization scheme⁴⁸ is used in this work.

After the molecule is divided, the DMET cycle (steps 2–6) is initiated. The first step in the cycle is to obtain the bath orbitals \hat{a}_i^\dagger (the active orbitals in the electronic structure calculation used for fragments to describe environmental effects), and the environment density matrix of fragment A, $D^{\text{env},A}$, is calculated as follows:

$$D_{pq}^{\text{env},A} = \sum_{r \in \text{env}} C_{pr} C_{rq}^\dagger, \quad (10)$$

where C represents the molecular orbital coefficients obtained from the mean-field calculation of the entire molecule. Now, the embedding Hamiltonian $H^{\text{emb},A}$ can be constructed (step 3). It can be defined as

$$\begin{aligned} H^{\text{emb},A} &= \sum_{pq}^{L^A+L^B} \left[h_{pq} + \sum_{rs}^L (pq|rs) - (ps|rq) \right] D_{rs}^{\text{env}} \hat{a}_p^\dagger \hat{a}_q \\ &\quad - \delta\mu \sum_{p \in A} \hat{a}_p^\dagger \hat{a}_p + \sum_{pqrs}^{L^A+L^B} (pq|rs) \hat{a}_p^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_r, \end{aligned} \quad (11)$$

where the h_{pq} are the one-electron integrals, the $(pq|rs)$ are the two-electron integrals in chemists' notation, L^A is the number of orbitals in the fragment, L^B is the number of bath orbitals, L is the number of orbitals in the entire molecule, and $p, q, r,$ and s are general orbital indices. We introduce the chemical potential $\delta\mu$, which is optimized in the DMET cycle. Once the Hamiltonian $H^{\text{emb},A}$ has been obtained, the electronic structure calculation is performed for fragment A. We employ VQE with the QCC ansatz in this work. Following these calculations, the algorithm constructs the one- and two-particle density matrices, D^A and P^A ,

respectively, from the QCC wavefunction Ψ^A . The fragment energy E^A is calculated (step 4) from the RDMs as

$$E^A = \sum_{p \in A} \left(\frac{\sum_{rs}^L (pq|rs) - (ps|rq) D_{rs}^{env}}{2} \right) D_{qp}^A + \frac{1}{2} \sum_{qrs}^{LA+LB} (pq|rs) P_{qp|sr}^A. \quad (12)$$

Note that only the elements with fragment orbital indices ($p \in A$) are used for calculating the fragment energy. Here, the 1- and 2-RDMs are defined as

$$D_{qp}^A = \langle \hat{a}_p^\dagger \hat{a}_q \rangle \quad (13)$$

and

$$P_{qp|sr}^A = \langle \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \rangle, \quad (14)$$

respectively. The number of electrons N^A in fragment A is calculated (step 4) as

$$N^A = \sum_{p \in A} D_{pp}^A. \quad (15)$$

The DMET energy is calculated by summing the fragment energy for each fragment (step 5), which is obtained according to the equation

$$E^{\text{DMET}} = \sum_A E^A + E^{\text{nuc}}, \quad (16)$$

where E^{nuc} is the nuclear repulsion energy. The DMET cycle (steps 2–6) iterates until the number of electrons in the DMET calculation given by

$$N^{\text{frag}} = \sum_A N^A \quad (17)$$

converges to the total number of electrons in the molecule N^{tot} . Convergence is achieved by updating the chemical potential $\delta\mu$ according to the equation

$$\delta\mu = a(N^{\text{frag}} - N^{\text{tot}}), \quad (18)$$

where a is the positive number.

For the DMET calculation for the H_{10} ring, the high symmetry of the molecular structure allows us to reduce the calculation further. We calculate only a single fragment with the assumption that all of the fragments have both the same energy and number of electrons. The DMET total energy with only one fragment multiplied by 10 (the number of hydrogen atoms) coincides with the energy when using all fragments; thus, we treat only one fragment in the DMET calculation and simply multiply the energy and the number of electrons by 10.

The QCC method. An accurate and affordable description of the correlated wavefunction $|\Psi\rangle$ required to evaluate the energy of fragment A according to Eq. (12) is achieved using the QCC method³². Within the QCC approach, a mean-field wavefunction $|\Omega\rangle$ is determined and subsequently utilized in a heuristic³⁹ to construct a unitary operator ansatz $\hat{U}(\tau)$. This operator recovers the missing electron correlation for the mean-field state $|\Omega\rangle$ and results in the QCC wavefunction according to the equation

$$|\Psi(\tau, \Omega)\rangle = \hat{U}(\tau)|\Omega\rangle. \quad (19)$$

A parameterized mean-field wavefunction is defined as a tensor product of n_q single-qubit states and can be expressed as

$$|\Omega(\Gamma)\rangle = \bigotimes_j^{n_q} |\omega(\theta_j, \phi_j)\rangle, \quad (20)$$

where $\Gamma = \{\theta_j\}_{j=1}^{n_q} \cup \{\phi_j\}_{j=1}^{n_q}$ is the set of $2n_q$ mean-field parameters. Each single-qubit state is then represented in the qubit computational basis as

$$|\omega(\theta_j, \phi_j)\rangle = \cos\left(\frac{\theta_j}{2}\right)|0_j\rangle + e^{i\phi_j} \sin\left(\frac{\theta_j}{2}\right)|1_j\rangle, \quad (21)$$

and is characterized by the Bloch sphere polar and azimuthal angles θ_j and ϕ_j , respectively³². The mean-field energy functional is given by

$$E^{\text{MF}}(\Gamma) = \langle \Omega(\Gamma) | \hat{H} | \Omega(\Gamma) \rangle. \quad (22)$$

Minimization of Eq. (22) with respect to Γ gives the ground-state, mean-field energy E^{MF} and the corresponding optimal set of parameters Γ^{opt} . The QCC unitary operator ansatz $\hat{U}(\tau)$ takes the form

$$\hat{U}(\tau) = \prod_k^{n_g} \exp\left(-\frac{i\tau_k \hat{P}_k}{2}\right), \quad (23)$$

where \hat{P}_k is a multi-qubit Pauli operator defined as

$$\hat{P}_k = \bigotimes_j^{n_q} \hat{p}_j^{(k)} \text{ for } \hat{p}_j^{(k)} \in \{X, Y, Z, I\}, \quad (24)$$

τ_k is a variational parameter and n_g is the number of Pauli operators \hat{P}_k included in the ansatz. The QCC energy functional is defined as

$$E^{\text{QCC}}(\tau, \Gamma) = \langle \Omega(\Gamma) | \hat{U}^\dagger(\tau) \hat{H} \hat{U}(\tau) | \Omega(\Gamma) \rangle, \quad (25)$$

where $\tau = \{\tau_k\}_{k=1}^{n_g}$ is the set of n_g variational parameters. The heuristic screening procedure³⁹ is utilized to construct the set of operators $\{\hat{P}_k\}_{k=1}^{n_g}$ appearing in Eq. (23). This heuristic approach³² relies on the gradient of Eq. (25) with respect to τ_k evaluated using the optimal mean-field wavefunction (i.e., $\Gamma = \Gamma^{\text{opt}}$ and $\tau = \mathbf{0}$), the form of which is

$$\left. \frac{\partial E^{\text{QCC}}}{\partial \tau_k} \right|_{\tau=\mathbf{0}} = \frac{i}{2} \langle \Omega(\Gamma^{\text{opt}}) | [\hat{P}_k, \hat{H}] | \Omega(\Gamma^{\text{opt}}) \rangle, \quad (26)$$

where $[\hat{P}_k, \hat{H}] = \hat{P}_k \hat{H} - \hat{H} \hat{P}_k$. Equation (26) is quantified for a representative \hat{P}_k from each group of electron correlation generators contained in the direct interaction set (DIS)³⁹. The n_g representative generators from the DIS with the largest energy gradient magnitudes are utilized in Eq. (23). Minimization of the energy functional given by Eq. (25) with respect to τ gives the QCC ground-state energy E^{QCC} and the corresponding optimal set of parameters τ^{opt} . We note that, in the present work, the optimal mean-field parameter set Γ^{opt} is not relaxed during the minimization of Eq. (25). The parameter set T^{opt} of size $2n_q + n_g$ that specifies the ground-state QCC correlated wavefunction $|\Psi(T^{\text{opt}})\rangle$ is formed as the union of the separately optimized mean-field and QCC parameter sets: $T^{\text{opt}} = \Gamma^{\text{opt}} \cup \tau^{\text{opt}}$.

The DMET-QCC framework is applied to compute the energy of each point along the H_{10} potential energy curve (see Table 1 and Fig. 2). The pre-optimized quantum circuits utilized for the trapped-ion hardware experiments are constructed with T^{opt} obtained from classical DMET-QCC simulations of the embedding Hamiltonian for fragment A (see Eq. (11)). At each point, R along the potential energy curve, $\hat{H}^{\text{emb},A}(R)$, is a two-qubit operator ($n_q = 2$) after sCBK encoding and takes the form

$$\hat{H}^{\text{emb},A}(R) = a(R) + b(R)X_0X_1 + c(R)Z_0Z_1 + d(R)[X_0 + X_1] + e(R)[Z_0 + Z_1] + f(R)[X_0Z_1 + Z_0X_1]. \quad (27)$$

The inter-atom, spacing-dependent expansion coefficients of $\hat{H}^{\text{emb},A}(R)$ in Eq. (27) are provided in Supplementary Note 1 for each point along the H_{10} potential energy curve. ProjectQ⁴⁹ is employed to perform simulation on classical hardware. Further details of the DMET-QCC circuits and simulations can also be found in Supplementary Note 1.

Density matrix purification. We perform density matrix purification based on McWeeny's purification scheme⁴¹. This iterative method purifies the 2-RDM P_{pqrs} according to

$$P_{pqrs}^{\text{new}} = 3(P_{pqrs}^{\text{old}})^2 - 2(P_{pqrs}^{\text{old}})^3. \quad (28)$$

The iteration is continued until the convergence criterion

$$\text{Tr}(P_{pqrs}^2 - P_{pqrs}) < \epsilon \quad (29)$$

is met. In this work, $\epsilon = 1.0 \times 10^{-2}$ is used. Note that the change in the total energy is smaller than a millihartree when we changed the criterion to 1.0×10^{-7} . The tensor multiplication of P is defined as

$$A_{pqrs} = B_{pquv} \times C_{uvrs}, \quad (30)$$

where the Einstein summation is implied.

Note that this purification technique can only be applied to two-electron systems^{10,13}. Although we here consider a ten-electron system, the RDM in our current work can be purified, as the fragment calculation for DMET involves a two-electron system. More analysis of the purification method applied to the experimental results can be found in Supplementary Note 4.

The Bootstrap method. The total energies and their statistical errors are calculated using an empirical bootstrapping method. We follow the procedure described in a previous work⁹. We start from the state preparation and measurement (SPAM)-corrected histograms for each Pauli operator (XX, YY, ZZ, XZ, and ZX), and construct a distribution of total energies.

The mean and the standard deviation (σ) are computed from the distribution of energies. The procedure of the bootstrapping method is as follows.

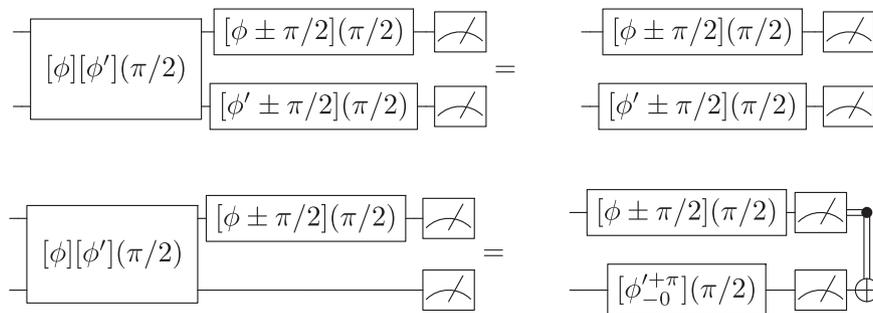


Fig. 3 Circuit optimization. The rules used to optimize the qubit coupled-cluster circuits for the ion trapped hardware.

1. Draw a random bootstrap sample of the same size as the original dataset with replacement of the data.
2. Construct a new histogram based on step 1.
3. Compute the expectation value of the Pauli terms using the new histogram.
4. Repeat steps 1–3 for each Pauli term and obtain all expectation values needed to construct RDMs.
5. Construct 1- and 2-RDMs.
6. Calculate the total energy.
7. Repeat steps 1–6 10,000 times and obtain a distribution of total energies.
8. Calculate the mean and the standard deviation from the distribution of energies constructed in step 7.

We follow this procedure to construct a histogram of possible measurements consistent with the empirical data. The calculated value of σ is represented using error bars. The mean of this distribution is the measured energy, and the 1σ error estimate is its standard deviation. The difference from the previous work⁹ is the construction of the RDMs (step 5), which is required for DMET energy calculation. Note that when we perform density matrix purification, we purify the 2-RDM between steps 5 and 6.

Circuit optimization and compiling. Our DMET-QCC ansatz circuits for H_{10} are written as a standard gate set that consists of controlled-NOT, $R_x(\theta) := \exp(-i\sigma_x\theta/2)$, $R_y := \exp(-i\sigma_y\theta/2)$, and $R_z := \exp(-i\sigma_z\theta/2)$ gates. To implement these circuits on a trapped-ion quantum computer, we transpile them so that the output circuits are encoded in the trapped-ion gate set. This set consists of $\phi\phi' := \exp(-i\sigma_\phi\sigma_{\phi'}\pi/4)$ and $\phi := \exp(-i\sigma_\phi\pi/4)$ gates, where $\sigma_\phi := \cos(\phi)\sigma_x + \sin(\phi)\sigma_y$. Further, we keep only three decimal digits after the decimal point in all our gate parameter specifications, commensurate with the machine's level of precision.

We combine the circuit compilation and optimization techniques reported in refs. ^{9,50,51} with the circuit optimization technique for the trapped-ion gate set shown in Fig. 3 to obtain the final, optimized circuits, amenable to implementation on a trapped-ion quantum computer. The pre- and post-optimization circuits are represented in Fig. 1c. Their gate parameters appear in Supplementary Tables 3 and 4.

Specifically, to perform the classical post-processing step, we obtain the $\langle YY \rangle$ expectation value from the trapped-ion quantum computer. The pre-optimization circuit is the same as that used to calculate any other expectation value, except the measurement basis transformation operations M_0 and M_1 in Fig. 1c(i) are $S^{\dagger}H$. The post-optimization circuit is shown in Fig. 1c(iii.). Note that we use a real degree of freedom in the two-qubit gate, that is, $\phi\phi'(\theta) := \exp(-i\sigma_\phi\sigma_{\phi'}\theta/2)$, as has been used elsewhere for efficient and high-fidelity simulations^{9,52}. The gate parameter values of θ for each point along the potential energy curve are shown in Supplementary Table 5.

Data availability

Atomic coordinates for the experimental points can be found in Supplementary Data 1. All other data that support the findings of this study are available from the corresponding author upon reasonable request.

Code availability

The code is available from the corresponding author upon reasonable request.

Received: 27 August 2021; Accepted: 26 October 2021;

Published online: 18 November 2021

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Acknowledgements

This work was supported as part of a joint development agreement between Dow and IQBit. We are grateful to Peter Margl from Dow for technical discussions. The authors thank Marko Bucyk at IQBit for his careful review and editing of the manuscript.

Author contributions

Y.K. and T.Y. designed the entire research project. N.A. and A.Z. coordinated the research project. Y.K. and T.Y. designed the simulation aspects of the research. Y.K., E.L., and M.P.C. performed the classical simulations. Y.K., E.L., M.P.C., L.H., and V.S. prepared the quantum circuits. Y.K., E.L., M.P.C., S.M., A.J.G., A.Z., and T.Y. analyzed the data of the simulations and hardware-related data. Y.N., S.J., and J.K. designed the hardware aspects of the research. Y.N. compiled and optimized the circuits for their execution on the hardware. A.O.M. and J.H.V.N. executed the circuits on the hardware. Y.N., A.O.M., and J.H.V.N. analyzed the hardware-specific data. Y.K., E.L., M.P.C., Y.N., S.M., A.J.G., S.J., N.A., A.Z., and T.Y. contributed to the writing of the manuscript.

Competing interests

The authors declare no competing interest.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s42005-021-00751-9>.

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Peer review information *Communications Physics* thanks the anonymous reviewers for their contribution to the peer review of this work.

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