

# A quantum eigenvalue solver based on tensor networks

Oskar Leimkuhler<sup>1,2,3,\*</sup> and K. Birgitta Whaley<sup>1,2,3,†</sup>

<sup>1</sup>*Department of Chemistry, University of California, Berkeley*

<sup>2</sup>*Berkeley Quantum Information and Computation Center,  
University of California, Berkeley, CA 94720, USA*

<sup>3</sup>*Challenge Institute for Quantum Computation, University of California, Berkeley, CA 94720*

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We introduce a hybrid quantum-classical eigenvalue solver that constructs a wavefunction ansatz from a linear combination of matrix product states in rotated orbital bases, enabling the characterization of chemical ground states that are not subject to the constraint of a one-dimensional area law of entanglement. The energy is converged via a gradient-free generalized sweep algorithm based on quantum subspace diagonalization, with a potentially exponential speedup in the off-diagonal matrix element contractions upon translation into shallow quantum circuits of linear depth in the number of qubits. Chemical accuracy is attained in numerical experiments for both a stretched water molecule and an octahedral arrangement of hydrogen atoms, achieving substantially better correlation energies compared to a unitary coupled-cluster benchmark, with orders of magnitude reductions in quantum resource estimates and a surprisingly high tolerance to shot noise. This proof-of-concept study suggests a promising new avenue for scaling up simulations of strongly correlated chemical systems on near-term quantum hardware.

## I. INTRODUCTION

Following a century of developments in *ab initio* electronic structure theory since Hartree first introduced the self-consistent field [1], the chemical ground state problem remains intractable for large systems exhibiting strong electron correlation. In these cases a superposition of many Slater determinants may be necessary to characterize the ground state accurately, and the computation time and memory requirements on classical hardware can then scale exponentially with the system size, under a combinatorial explosion of the configuration space. In recent decades tensor network [2–4] methods such as the density matrix renormalization group (DMRG) [5–9] have emerged as powerful tools to partially tame, if not exactly break, this so-called ‘curse of dimensionality’. Tensor networks promise to efficiently represent some classes of many-body quantum states by exploiting the locality of correlations among the parts of the system. A necessary but not sufficient condition for a system to be efficiently described by a tensor network is that it obeys an area law of entanglement [10], meaning that entropy measures between certain partitions of the system scale only with the number of sites lying on the partition boundaries, as compared to volume law entanglement that scales with the total number of sites in the bulk. Tensor networks have proven very powerful in simulating one-dimensional lattice systems, for which the matrix product state (MPS) [11] ansatz offers attractive qualities such as flexibility, variationality, and systematic convergence with increasing bond dimension. While matrix product states have had some success in

quantum chemical settings [6–9, 12, 13], systems without a one-dimensional area law may require exponentially large bond dimensions, and even states that follow the law are not guaranteed to be efficiently simulable [14]. Extensions to two-dimensional connectivity known as projected-entangled pair states (PEPS) [15] have been proposed, but these are generically hard to contract even in terms of average-case complexity [16]. This reveals a broader challenge within the field of tensor networks, which is that generalizations beyond one-dimensional connectivity tend to incur exponentially hard classical contraction bottlenecks unless approximations or restrictions are applied [17].

Quantum computers [18, 19] present an alternative route to breaking the curse of dimensionality by encoding highly correlated ground states in entangled registers of qubits. An ideal quantum computer could in principle represent a state with arbitrarily large entanglement with no increase in the space requirement, and useful properties such as ground state energies may then be extracted via quantum phase estimation [20, 21]. Given the significant technical challenges associated with preserving and manipulating an array of entangled qubits, algorithms designed for the current generation of noisy intermediate-scale quantum (NISQ) processors must utilize as little quantum resource as possible. Hybrid quantum-classical algorithms, such as the variational quantum eigensolver (VQE) and its contemporary variants [22–26], aim to achieve practical ground state energy estimates with extremely low depth quantum circuits at the expense of a greater measurement cost. While VQE algorithms have shown promise for achieving practical quantum advantage in quantum chemistry, the most widely studied ansätze based on single-reference unitary coupled cluster with single and double excitations (UCCSD – we shall refer to related approaches as UCC-type) suffer from poor treatment of strong correlation, expensive gradient cal-

\* ol22@berkeley.edu

† whaley@berkeley.edu

culations, and barren plateaus in the training landscape [23]. The lack of strong correlation can be ameliorated by multi-reference methods such as the recently developed non-orthogonal quantum eigensolver (NOQE) [27], which promises a quantum advantage for systems with finite numbers of radical sites exhibiting both weak and strong electron correlation. Furthermore, optimizing the UCCSD ansatz requires a two-qubit gate count per QPU call of  $O(N^4)$ , where  $N$  is the number of molecular orbitals, which may be prohibitively expensive for medium-sized or large systems. While tensorial decompositions offer lower order polynomial scaling in practice [27, 28], and there is numerical evidence that adaptive methods such as ADAPT-VQE [24] can reduce gate counts considerably, these cost reductions are system dependent and the worst-case scaling for the most challenging systems may still be quartic in  $N$ .

Given that quantum circuits are tensor networks with unitary constraints, several recent works [29–34] have suggested that classical tensor network methods may be adapted to generate more compact and robustly trainable quantum circuit ansätze, so that quantum computers may help to resolve the computational bottlenecks in the contraction of higher-dimensional tensor networks. Here we present a new hybrid quantum-classical algorithm, which we call a tensor network quantum eigensolver (TNQE), that solves for chemical ground state energies by constructing a highly compact trial wavefunction from a superposition of  $M$  matrix product states of fixed bond dimension  $\chi$  in rotated orbital bases. We show that computing expectation values with such a construction by classical tensor network contraction is exponentially costly in the general case, but is however easily translated into quantum circuits of depth  $O(N)$ . This algorithm belongs to the emerging family of quantum subspace diagonalization (QSD) methods [27, 35–39], which use a QPU to evaluate the Hamiltonian and overlap matrix elements within a subspace of low energy state vectors, and as such may also be extendable to the calculation of low-lying excited states.

We are aware of several existing proposals for MPS-based ansätze within the VQE paradigm [30, 40, 41]. Our method advances on these prior works in two important respects. First, the superposition of single-particle bases extends the reach of the TNQE ansatz beyond states obeying a one-dimensional area law of entanglement in a systematic manner. This has not been attempted previously and may now allow for circumvention of the simulability constraints of single MPS-based ansätze [14]. Second, our optimization routine is entirely gradient-free and can instead be considered as a natural generalization of the DMRG sweep algorithm to linear combinations of non-orthogonal matrix product states. This allows the algorithm to sidestep the barren plateau phenomenon [42], which may significantly reduce the overall measurement cost of ground-state energy estimation. The results presented in this first study are consistent with this prediction. We show that for ground states the energy can be

reliably converged via iterative quantum subspace diagonalizations, using  $O(NM^2\chi^4)$  calls to a QPU per sweep, with a gate count for each QPU call that scales at worst as  $O(N^2 + N\chi^2)$  and with circuit depths linear in  $N$ . We achieve chemical accuracy in numerical tests on two small chemical systems – a stretched water molecule and an octahedral arrangement of six hydrogen atoms – empirically demonstrating both significantly better converged energy estimates and a far lower sensitivity to shot noise than UCCSD, resulting in orders of magnitude reductions in the estimated quantum resources for the  $H_6$  cluster, with even greater reductions expected for larger systems.

## II. THEORY

Throughout this section we will assume basic familiarity with tensor network index and diagrammatic notations [3, 4], and we will make frequent use of the direct equivalence between tensors subject to unitary constraints and quantum gates. In the figures we will use circles and rounded shapes to denote classical tensors in tensor network diagrams, and we will use squares and rectangles to denote quantum gates in circuit diagrams. For an in-depth introduction to tensor network notation and the relation to quantum circuits, see e.g. [3, 4].

### A. Background

Expressed in a basis of  $N$  molecular orbitals, the second-quantized electronic structure Hamiltonian takes the form

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

where the one- and two-body coefficients  $h_{pq}$  and  $h_{pqrs}$  encode one- and two-electron integrals over the single-particle molecular orbital basis, and the creation and annihilation operators act on the Fock space of  $\eta$ -electron Slater determinants  $|\vec{k}\rangle = |k_1, \dots, k_N\rangle$  [43]. Each orbital occupancy index  $k_p$  has  $d$  possible values, where  $d = 2$  corresponding to occupancy values 0 or 1 when expressed in terms of spin-orbital sites, or  $d = 4$  corresponding to binary occupancy values 00 ( $\emptyset$ ), 01 ( $\uparrow$ ), 10 ( $\downarrow$ ), or 11 ( $\uparrow\downarrow$ ) for spatial orbital sites. The ground state problem consists in finding a superposition of Slater determinants  $|\Psi\rangle$  that minimizes the expectation value  $E_0 = \langle \Psi | \hat{H} | \Psi \rangle$ . The full configuration interaction (FCI) coefficient tensor  $\Psi^{k_1 \dots k_N}$  encodes the coefficients exactly describing the ground state of the system,

$$|\Psi_{\text{FCI}}\rangle = \sum_{\vec{k}} \Psi^{k_1 \dots k_N} |\vec{k}\rangle. \quad (2)$$

The FCI coefficient tensor can be decomposed via tensor-train factorization [44] – a sequence of index groupings, matricizations, and singular value decompositions

(SVDs) – into a tensor network format known as a matrix product state (MPS). A single matrix product state takes the form

$$|\phi_{\text{MPS}}\rangle = \sum_{\vec{k}} \left[ \sum_{l_1 \dots l_{N-1}}^{\chi} \Phi_{l_1}^{k_1} \Phi_{l_1 l_2}^{k_2} \dots \Phi_{l_{N-2} l_{N-1}}^{k_{N-1}} \Phi_{l_{N-1}}^{k_N} \right] |\vec{k}\rangle, \quad (3)$$

where the  $\Phi^{k_p}$  are the site tensors, each with  $\chi^2 d$  free parameters, so that the total number of tensor parameters is  $O(N\chi^2 d)$ . In the MPS format expectation values are extracted by efficient tensor network contraction with an analogous tensor-train factorization of the operator known as a matrix product operator (MPO) [8], so that the sum over  $d^N$  Slater determinants need not be explicitly computed. The generality of the SVD ensures that, before truncation of singular values, the MPS preserves all of the information in the FCI wavefunction and hence is an equivalent representation of the true ground state. The SVD is also known in this context as a Schmidt decomposition [45], and allows quantification of the entanglement between any left block  $A = \{1, \dots, p\}$  and right block  $B = \{p+1, \dots, N\}$  of the MPS,

$$|\phi_{\text{MPS}}\rangle = \sum_{l=1}^{\chi} \sigma_l |\phi_l^A\rangle \otimes |\phi_l^B\rangle, \quad (4)$$

where  $\sigma_1 \geq \dots \geq \sigma_{\chi}$  are the singular values, with Schmidt rank  $\chi \leq \min(d^{N_A}, d^{N_B}) = d^{N/2}$  at the central bond. Tracing over subsystem  $B$  yields the reduced density matrix of the  $A$  block,  $\rho^A = \sum_l \sigma_l^2 |\phi_l^A\rangle \langle \phi_l^A|$ . The von Neumann entropy across the partition is then given by

$$\mathcal{S}_{AB} = -\text{tr}(\rho^A \ln \rho^A) = -\sum_{l=1}^{\chi} \sigma_l^2 \ln \sigma_l^2. \quad (5)$$

The memory cost can be reduced at the expense of accuracy by truncating  $\chi$  at each bond, equivalent to projecting onto the first  $\chi$  left and right Schmidt vector pairs. This truncation necessarily enforces a notion of locality to the ansatz; an MPS with fixed bond dimension  $\chi \ll d^{N/2}$  obeys a one-dimensional area law of entanglement between the molecular orbitals, with maximal entropy between the left and right blocks equal to  $\ln(\chi)$ , seen by setting all singular values to be equal in Equations 4 and 5. In practical calculations the MPS is typically initialized with random parameters and optimized variationally by the one- or two-site DMRG sweep algorithm [8].

### B. TNQE Ansatz

The TNQE ansatz is a superposition of  $M$  non-orthogonal matrix product states  $\{|\phi_j\rangle\}$  expressed in different orbital bases,

$$|\psi\rangle = \sum_{j=1}^M c_j |\phi_j\rangle. \quad (6)$$

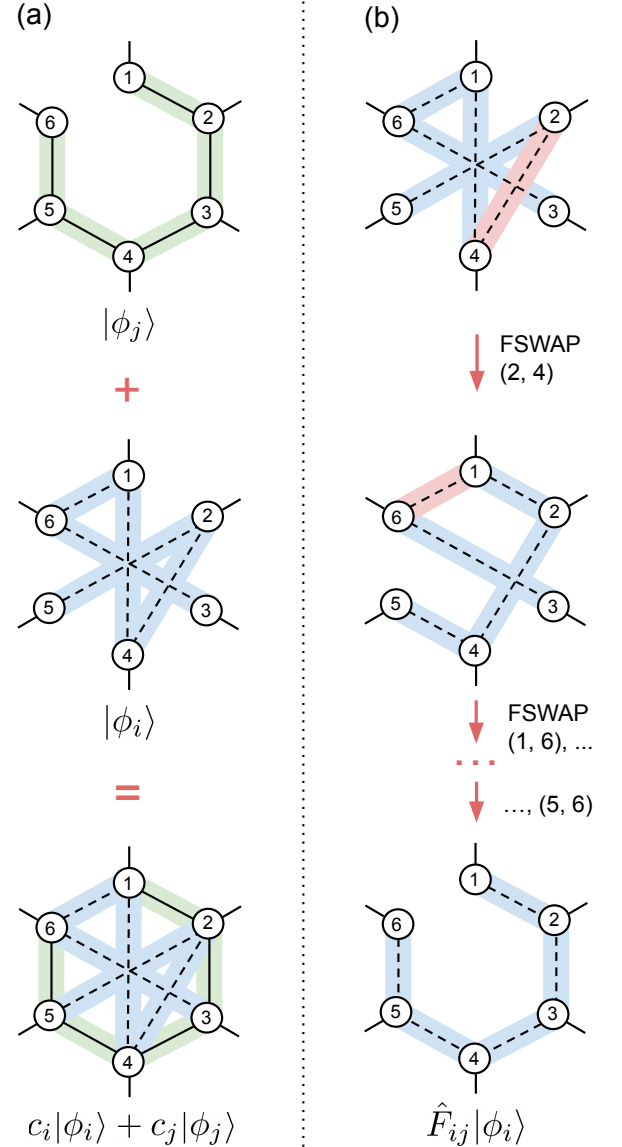


FIG. 1. (a) Graph representations of matrix product states  $|\phi_j\rangle$  and  $|\phi_i\rangle$  with different site orderings over the same set of  $N = 6$  molecular orbitals, and of the superposition state  $c_i |\phi_i\rangle + c_j |\phi_j\rangle$ . (b) A sequence of FSWAP operations  $\hat{F}_{ij}$  transforms the MPS  $|\phi_i\rangle$  into the orbital ordering of  $|\phi_j\rangle$ , giving rise to the tensor network in Figure 2 (a).

While each MPS obeys a one-dimensional area law within its own single-particle basis, their superposition allows for the efficient description of a broader class of wavefunctions. This additional flexibility is also the reason behind the exponential separation in complexity between the classical and quantum evaluations of expectation values in the hardest case, as we shall now demonstrate. To gain some intuition we shall first introduce the restricted subset of orbital permutations, i.e., the same set of orbitals but with different site orderings, before generalizing to arbitrary rotations of the single-particle basis.

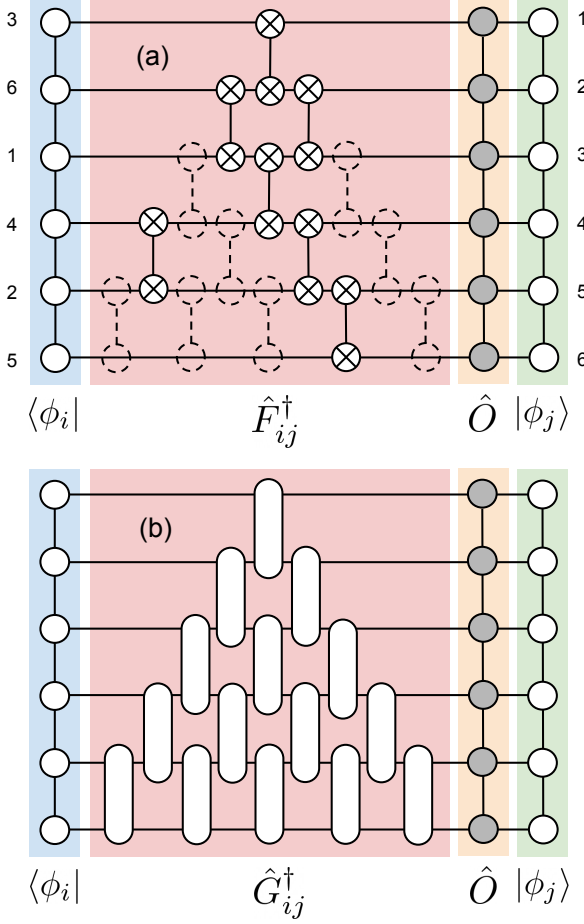


FIG. 2. (a) A tensor network to compute the off-diagonal matrix element  $\langle \phi_i | \hat{O} | \phi_j \rangle$  between matrix product states with permuted orbitals, given an efficient MPO representation of  $\hat{O}$ . The FSWAPs, denoted by pairs of crossed tensors, are selected by a bubble sort comparator network. Each comparator applies an FSWAP to rearrange neighboring orbitals if their order does not match the order in which they appear on the right. The dashed lines indicate the positions of non-swapping comparators. (b) A tensor network to compute  $\langle \phi_i | \hat{O} | \phi_j \rangle$  between matrix product states related by an arbitrary orbital rotation  $\hat{G}_{ij}^\dagger$ , which is decomposed into a pyramidal structure of Givens rotation tensors as defined in Equation 8.

A tensor network state can be thought of as a graph with  $N$  nodes representing the sites, in this case the molecular orbitals, and up to  $\binom{N}{2}$  edges representing the bonds. Then an MPS is described by a path visiting each node via  $N - 1$  unique edges (see Figure 1 (a)), a PEPS is a graph with  $2N - 2\sqrt{N}$  edges, and so on, up to a tensor network with full connectivity between all pairs of nodes. A fully connected tensor network is a classically inefficient description of a quantum state, requiring  $O(N\chi^{N-1})$  tensor parameters. Furthermore, the set of all fully connected states contains the set of all PEPS, the contraction of which is known to be #P-complete [46], and is thus believed to be exponentially hard even

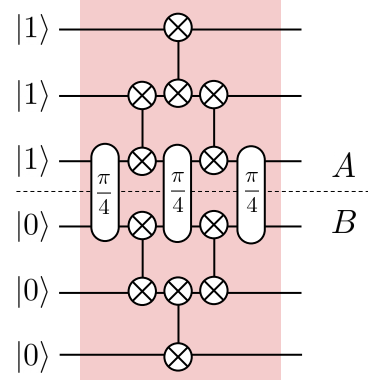


FIG. 3. A sequence of  $\pi/2$  and  $\pi/4$  orbital rotations to transform the unentangled state  $|1\rangle^{\otimes N_A} \otimes |0\rangle^{\otimes N_B}$  to a state with maximal von Neumann entropy across the A/B partition, where  $N_A = N_B = N/2$ , shown here for  $N = 6$ .

for a quantum computer. The superposition in Equation 6 requires only  $O(MN\chi^2)$  tensor parameters, and allows for the combination of matrix product states with different connectivity, as shown in Figure 1 (a). The set of all states that can be described by Equation 6 using both  $M$  and  $\chi$  of size polynomial in  $N$  may then be expected to lie somewhere in-between that of a single matrix product state and that of a fully connected tensor network.

The expectation value of an observable  $\hat{O}$  is given by

$$\langle \psi | \hat{O} | \psi \rangle = \sum_{ij} c_i^* c_j \langle \phi_i | \hat{O} | \phi_j \rangle, \quad (7)$$

which means that the off-diagonal matrix elements between non-orthogonal matrix product states must be computed. In the case that the site orderings are identical this is classically efficient by tensor network contraction, assuming an efficient MPO representation of  $\hat{O}$ . However when the site orderings differ additional tensors must be inserted to transform between the representations. Under an arbitrary permutation of the orbitals this is achieved with the correct treatment of fermionic antisymmetry via a nearest-neighbor fermionic-SWAP (FSWAP) network [47]. The sequence of FSWAP operations  $\hat{F}_{ij}$  to rearrange the orbital ordering of  $|\phi_i\rangle$  to that of  $|\phi_j\rangle$  is illustrated in Figure 1 (b). Representing these operations with classical tensors results in the tensor network in Figure 2 (a) to compute the matrix element  $\langle \phi_i | \hat{O} | \phi_j \rangle$ , which has a cost of contraction that rises steeply with the depth of the FSWAP network. Any pair of orderings can be connected by a path-restricted sorting network of depth lower bounded by  $O(N)$  [48, 49], e.g., a bubble sort [50]. The application of each FSWAP gate to the MPS on the left can grow the bond dimension by up to a factor of  $d$ , so  $\chi$  will rise exponentially with  $N$  unless severe truncations are applied. This implies that a large amount of entanglement can be generated in the ansatz through the site rearrangement, even though each matrix product state is individually of low bond dimension.



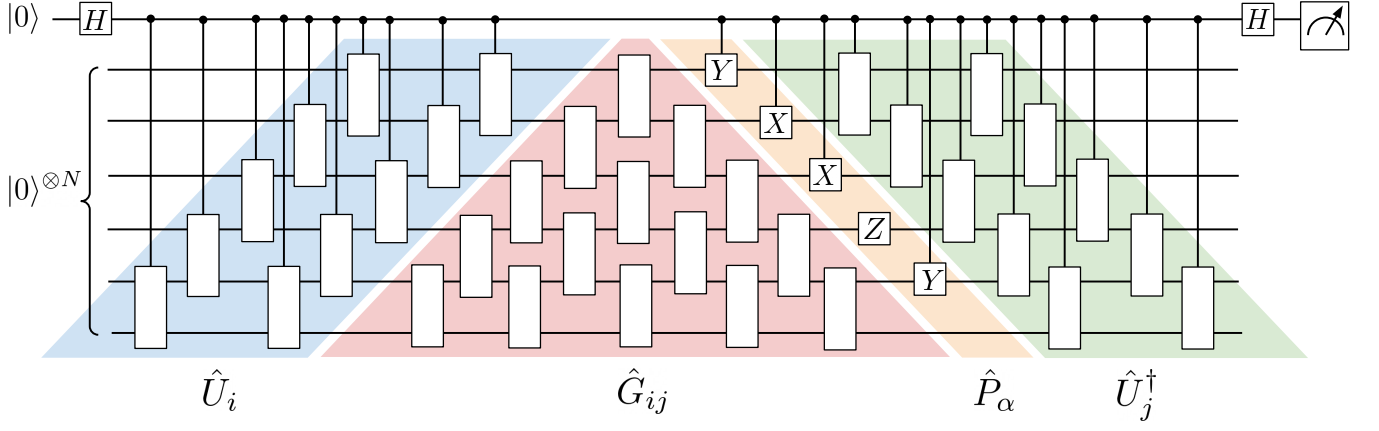


FIG. 4. A quantum circuit used to compute the matrix element  $\langle \phi_i | \hat{O} | \phi_j \rangle$  given controlled unitaries  $\hat{U}_i$  and  $\hat{U}_j$  to prepare  $|\phi_i\rangle$  and  $|\phi_j\rangle$  from the all-zero state in their respective orbital bases, an efficient Pauli string decomposition  $\hat{O} = \sum_{\alpha} o_{\alpha} \hat{P}_{\alpha}$ , and an orbital rotation  $\hat{G}_{ij}$  decomposed into Givens rotation gates as defined in Equation 8. The details of this circuit construction are explained in Section IID and Appendix B 1.

We note that while at first glance these tensor network contractions appear to be classically hard, the matrix elements can in principle be efficiently approximated by randomly sampling computational basis vectors from the matrix product state (see Appendix C). This suggests the potential for a powerful, although limited, new class of quantum-inspired classical tensor network methods via random sampling.

We now show that the restriction to orbital permutations can be lifted to create a far more expressive ansatz under arbitrary rotations of the single-particle basis. Kivlichan *et al.* [51] have shown how to decompose an arbitrary rotation of the molecular orbitals  $\hat{G}_{ij}$  into a sequence of nearest-neighbor Givens rotation gates of linear depth in  $N$ ,

$$\hat{G}_{ij} = \prod_{(p,\theta) \in \Theta_{ij}} \hat{g}_{p,p+1}(\theta), \quad (8)$$

where  $\Theta_{ij}$  is a set of  $\binom{N}{2}$  pairs  $(p, \theta)$  of site positions and rotation angles, and a Givens rotation between orbitals  $p$  and  $q$  with rotation angle  $\theta$  is written as

$$\hat{g}_{pq}(\theta) = \exp [\theta (\hat{a}_p^{\dagger} \hat{a}_q - \hat{a}_q^{\dagger} \hat{a}_p)]. \quad (9)$$

This decomposition follows from a QR factorization of the  $N \times N$  orbital rotation matrix, and is completely general as a consequence of the Thouless theorem [52]. As shown in Figure 2, there is an obvious resemblance between the sequence of Givens rotations to perform an arbitrary orbital rotation and the comparator network that implements an arbitrary orbital permutation. The connection becomes clear when one considers that the FSWAP gate is a special case of a Givens rotation gate with rotation angle  $\theta = \pi/2$ , up to a change of phase on one of the orbitals (see Appendix A 3). In some sense the transformation  $\hat{G}_{ij}$  can be thought of as a ‘quantum sorting network’, with potential implications for connecting

quantum chemistry with results in complexity theory. Although there is no longer an adequate orbital graph representation for the transformed state  $\hat{G}_{ij} |\phi_i\rangle$ , consider a cartoon picture in which a single path is mapped to a ‘superposition’ of exponentially many paths, with probability amplitudes determined by the rotation angles.

It follows from Equation 8 that any orbital rotation can be built up from pairwise orbital rotations, and in this work we shall explore this ‘bottom-up’ construction as a technique for manipulating the orbital entanglement during the MPS optimization. In quantum mechanics, the entanglement of a system is dependent on the basis in which it is measured; a system of low entanglement in one basis may have very high entanglement when expressed in a different basis. For instance, the tensor network in Figure 3 depicts a linear-depth sequence of orbital rotations that transforms a completely unentangled bitstring state, which corresponds to a  $d = 2$ ,  $\chi = 1$  MPS, to a state with maximal Schmidt rank at the central partition, i.e.  $\chi = 2^{N/2}$  (this transformation is explained in Appendix D). This appears to suggest that one may write down an MPS superposition ansatz with no classically efficient representation in any common orbital basis. It is argued in Appendix C that in contrast to the restricted case of orbital permutations, the matrix elements between matrix product states differing by arbitrary orbital rotations cannot be efficiently evaluated via random sampling, since there is no known classical algorithm to perform an orbital rotation on a computational basis vector with polynomial scaling of both time and memory requirements.

Figure 4 shows how to turn the tensor network in Figure 2 into a low-depth quantum circuit, given linear qubit connectivity on the system register and all-to-one connectivity to a single ancilla qubit, assuming an efficient Pauli string decomposition of the operator  $\hat{O}$  under the Jordan-Wigner transformation [53]. For a fixed bond dimension

$\chi$  the depth of the circuit grows only linearly in the number of qubits. Converging the expected energy of the TNQE ansatz requires an efficient optimization routine for both the tensor parameters and the rotation angles. In this work we show how the DMRG sweep algorithm can be naturally extended to the TNQE ansatz via quantum subspace diagonalization, resulting in a gradient-free optimization strategy that converges reliably even in the presence of relatively large noise perturbations to the matrix elements. Each sweep requires  $O(NM^2\chi^4)$  matrix element evaluations to optimize all the states simultaneously, which scales favorably provided that  $\chi$  is kept small and the resources of the ansatz are increased through  $M$ . The rotation angles are classically co-optimized – with no additional QPU calls – to reduce the bond entanglement during the parameter sweep, enacting a ‘transfer’ of entanglement between the bonds of the MPS and the orbital rotations. The TNQE ansatz inherits strict variationality and size consistency from its closest classical analogues, namely the non-orthogonal configuration interaction [54, 55] and orbital-optimized DMRG [56, 57].

### C. Optimization

Here we present a high-level overview of the generalized sweep algorithm, with further details provided in Appendix A.

#### 1. Parameter optimization

Matrix product states are commonly optimized to lower the expected energy by a two-site sweep algorithm, whereby the tensors of the MPS are orthogonalized to a pair of sites  $p, p+1$  which are then contracted, optimized, and decomposed back into site tensors. Here we explain how to generalize the conventional two-site algorithm to a linear combination of non-orthogonal matrix product states. Given a set of  $M$  arbitrary matrix product states  $\{|\phi_j\rangle\}$ , the optimal coefficients  $\{c_j\}$  to approximate the ground state of the Hamiltonian are obtained by solving the generalized eigenvalue problem

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}, \quad (10)$$

where the elements of the matrix pencil  $(\mathbf{H}, \mathbf{S})$  are given by

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle, \quad S_{ij} = \langle \phi_i | \phi_j \rangle. \quad (11)$$

The matrix  $\mathbf{E}$  is a diagonal matrix of generalized eigenvalues  $E_1, \dots, E_M$ . The optimal coefficients for the ground state estimate  $E_1$  are then given by the first column of  $\mathbf{C}$ , i.e.,  $c_j = C_{j1}$ . The MPS  $|\phi_j\rangle$  can be updated to reduce the ground state estimate  $E_1$  by decomposing the two-site tensor at sites  $p$  and  $p+1$  into a complete set of ‘one-hot’ tensors, which have the same indices and a

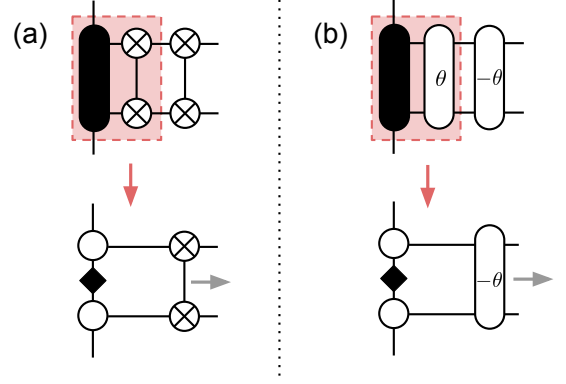


FIG. 5. (a) A schematic of the FSWAP insertion. The vertical arrow denotes the combined operations of contraction into the two-site tensor followed by SVD in tensor network diagrammatic notation [3, 4]. The horizontal arrow indicates merging into  $\hat{G}_{ij}$  if the update is accepted. (b) A schematic of the steps to compute the truncation error cost function  $\xi(\theta)$  in Equation 15 for the classical univariate optimization to determine  $\theta_{\text{opt}}$ . The adjoint rotation with angle  $-\theta_{\text{opt}}$  is then merged into  $\hat{G}_{ij}$ .

single non-zero element equal to 1. Since the MPS has orthogonality center at site  $p$ , the one-hot tensors represent a decomposition of  $|\phi_j\rangle$  into an orthonormal basis,

$$|\phi_j\rangle = \sum_{m=1}^{d^2\chi^2} t_m^{[j]} |\varphi_m^{[j]}\rangle, \quad \langle \varphi_m^{[j]} | \varphi_n^{[j]} \rangle = \delta_{mn}, \quad \sum_m |t_m^{[j]}|^2 = 1, \quad (12)$$

where  $\{t_m^{[j]}\}$  are the parameters of the two-site tensor. Each MPS can be expanded simultaneously from two-site tensors located at the same or different sites, resulting in a new matrix pencil  $(\mathbf{H}', \mathbf{S}')$  in the expanded subspace over the one-hot tensors with dimension  $Md^2\chi^2$ . The elements of the resulting expanded subspace matrices are given by

$$H'_{im,jn} = \langle \varphi_m^{[i]} | \hat{H} | \varphi_n^{[j]} \rangle, \quad S'_{im,jn} = \langle \varphi_m^{[i]} | \varphi_n^{[j]} \rangle. \quad (13)$$

After solving the generalized eigenvalue problem in the expanded subspace, the new optimal coefficients  $\{t_m^{[j]}\}$  for each two-site tensor are obtained by slicing and normalizing from the first column of the expanded solution matrix  $\mathbf{C}'$  (for further details see Appendix A1). Optimizing all states simultaneously requires  $O(M^2\chi^4)$  matrix element evaluations per site decomposition, so a full sweep over all sites requires  $O(NM^2\chi^4)$  matrix elements. We can also choose to optimize only a single MPS or any subset of MPSs. The effect of ill-conditioning of the generalized eigenvalue problem has been rigorously studied in [58]. In practice the condition number of  $\mathbf{S}'$  can be effectively regulated by discarding subspace vectors with a high degree of linear dependence (see Appendix A2).

## 2. Orbital rotations

After each parameter update the optimized two-site tensors are decomposed into single-site tensors via SVD with a maximum Schmidt rank of  $d_\chi$ , which is then truncated to the  $\chi$  largest singular values. At this step some information is discarded by projecting onto the space of the first  $\chi$  left and right singular vector pairs of the Schmidt decomposition (see Equation 4). Given that entanglement is a basis-dependent quantity, it can be reduced before truncation by a local rotation of the orbitals  $p$  and  $p + 1$  without loss of information. The procedure is outlined with tensor network diagrams in Figure 5. To permute the orbitals, the double application of an FSWAP gate is equivalent to the identity and so does not alter the state. One of the FSWAPs is then contracted into the two-site tensor on the left prior to the SVD and the truncation error is computed as

$$\xi = 1 - \sum_{l=1}^{\chi} \sigma_l^2. \quad (14)$$

The orbital rearrangement is accepted if the truncation error at the bond is reduced by the FSWAP contraction, in which case the second FSWAP is then merged into  $\hat{G}_{ij}$  by updating the  $N \times N$  orbital rotation matrix and re-computing the rotation angles. Otherwise, the FSWAP insertion is rejected, and the two-site tensor parameters are reverted to their original values.

In the case of arbitrary orbital rotations, the unitary  $\hat{g}(\theta)$  is classically optimized to find the value of  $\theta_{\text{opt}}$  that minimizes the truncation error,

$$\theta_{\text{opt}} = \arg \min_{\theta} [\xi(\theta)]. \quad (15)$$

This is a purely classical co-optimization step with a cost  $O(\chi^3)$  that derives solely from performing the SVD on the contracted two-site tensor, thus requiring no additional QPU calls or energy gradient calculations. The adjoint rotation  $\hat{g}^\dagger(\theta_{\text{opt}}) = \hat{g}(-\theta_{\text{opt}})$  is then merged into  $\hat{G}_{ij}$ . In a sense this unitary ‘encodes’ a part of the information from the optimized two-site tensor, which is then merged into the basis rotation instead of being discarded.

In practice it is observed that interleaving orbital permutation sweeps with orbital rotation sweeps is highly effective at breaking the optimizer out of local minima. This corresponds to alternating between rearranging the orbitals to different site positions via nearest neighbor swapping, and mixing of the orbitals through nearest neighbor quantum superpositions. After the rotation step it is found to be beneficial to further mitigate the penalty in the expected energy incurred by singular value truncation using a sequence of single-site decompositions, with no additional matrix element computations required, as detailed in Appendix A 4.

## D. Matrix Element Circuit Compilation

Within the scope of this subsection we have used  $d = 2$  (spin-orbital sites) so that  $N$  is equal to the number of system qubits under the Jordan-Wigner transformation [53]. For the quantum evaluation of the matrix elements we first require a unitary circuit to prepare each  $|\phi_j\rangle$  from the vacuum state in their respective orbital bases,

$$|\phi_j\rangle = \hat{U}_j |0\rangle, \quad (16)$$

where  $|0\rangle$  is understood to refer to the multi-qubit state  $|0\rangle^{\otimes N}$ . We also require the Givens rotation circuits  $\hat{G}_{ij}$  to rotate each state  $|\phi_i\rangle$  into the orbital basis of another state  $|\phi_j\rangle$ . Finally we assume an efficient Pauli string decomposition for the observable  $\hat{O}$  in each orbital basis. For example, the electronic structure Hamiltonian in Equation 1 can be fully specified in any set of orbitals using  $O(N^4)$  unique two-body fermion operators, each of which decomposes into sixteen Pauli strings under the Jordan-Wigner transformation for a total of  $O(N^4)$  Pauli terms, written as

$$\hat{H} = \sum_{\alpha} h_{\alpha} \hat{P}_{\alpha}. \quad (17)$$

The matrix elements are expanded as a sum over expectation values of a set of unitary products with respect to the vacuum state,

$$\langle \phi_j | \hat{H} \hat{G}_{ij} | \phi_i \rangle = \sum_{\alpha} h_{\alpha} \langle 0 | \hat{U}_j^\dagger \hat{P}_{\alpha} \hat{G}_{ij} \hat{U}_i | 0 \rangle, \quad (18)$$

which can be evaluated in parallel via standard Hadamard test circuits as in Figure 4. This circuit makes a conditional application of  $\hat{U}_j^\dagger \hat{P}_{\alpha} \hat{G}_{ij} \hat{U}_i$  with control from a single ancilla qubit. The particle number conserving operator  $\hat{G}_{ij}$  acts trivially on the vacuum state, so does not require control. The ancilla qubit is measured in the  $z$ -basis at the end of the computation, and the real part of the expectation value is calculated from the probabilities

$$\text{Re} \langle \hat{U}_j^\dagger \hat{P}_{\alpha} \hat{G}_{ij} \hat{U}_i \rangle = P(0) - P(1). \quad (19)$$

The imaginary component can also be obtained via a change of phase of the ancilla qubit, however we note that the tensor elements in the TNQE ansatz can be restricted to real values without loss of generality, hence for real-valued observables there is no imaginary component of the expectation value. An overlap matrix element  $\langle \phi_j | \hat{G}_{ij} | \phi_i \rangle$  can be evaluated with a single Hadamard test circuit omitting the Pauli string. For a number of shots  $n_S$  the output of each Hadamard test circuit has variance  $\leq 1/n_S$  [59]. Consequently each overlap matrix element can be resolved to standard error  $\delta$  with  $n_S \approx \delta^{-2}$ , and, following a standard optimal measurement allocation over the Pauli strings [60], each Hamiltonian matrix element can be resolved up to standard error  $\delta$  with

$$n_S \approx \left( \frac{\sum_{\alpha} |h_{\alpha}|}{\delta} \right)^2. \quad (20)$$

There are several approaches in the literature for reducing the number of Pauli terms which will be important in the presence of gate noise [61, 62]. We leave the incorporation of these methods to future work.

The Hadamard test circuit requires a controlled version of the state preparation unitary. There are several proposals for MPS quantum circuit encodings [63–65], the simplest exact approach being direct synthesis of  $(\chi + d) \times (\chi + d)$  unitary encodings of each MPS tensor [63], with a total gate count that scales at worst as  $O(N\chi^2)$ , following standard asymptotic results for generic unitary synthesis [66]. For near-term hardware we present here a cost analysis based on the approximate disentangler technique pioneered by Ran [64] and developed by others [67, 68], but in principle any encoding scheme may be substituted. This technique is briefly explained in Appendix B 1, wherein we show how to cheaply add controls to the disentanglers, then decompose the entire circuit into CNOT gates and single-qubit rotations to derive an exact two-qubit gate count for each circuit in terms of the number of qubits  $N$  and the disentangler depth  $D$ , resulting in

$$n_{\text{CNOT}} = N^2 + (16D - 1)N - 16D. \quad (21)$$

We have omitted the cost of the controlled Pauli string, which will be constant in  $N$  for any  $k$ -local fermionic observable since the Pauli  $\hat{Z}$  strings of the Jordan-Wigner mapping act trivially on the vacuum state. The CNOT gate count of Eq. 21 presents an enormous advantage over existing ansätze such as the UCC-type ansätze that are characterized by a two-qubit gate cost that scales as  $O(N^4)$ .

With a single ancilla qubit, the layer depth in terms of CNOT gates and single-qubit rotations is given by

$$L = 28ND + 17. \quad (22)$$

This results from having to have to apply each controlled disentangler in sequence, introducing an unwanted scaling of  $O(ND)$ . However if the hardware is of sufficient fidelity to prepare and maintain an  $N/2$ -qubit GHZ state, then this limitation can be circumvented at the cost of using  $N/2$  ancillas. With this modification up to  $N/2$  controlled rotations can be applied in parallel with control from different ancilla qubits. The layer depth is then given by

$$L_{\text{GHZ}} = 28N + 56D - 13, \quad (23)$$

which may be worth the additional overhead of  $N/2$  ancillas and preparation of the GHZ state.

### III. RESULTS

Here are presented the results of numerical simulations using the ITensor Julia library [69] for the classical tensor network parts of the algorithm, with conversion to a

sparse matrix representation to evaluate the off-diagonal matrix elements. The code is available at [70]. For numerical convenience we have used spatial orbital sites with  $d = 4$ , which can be easily converted to the  $d = 2$  representation for quantum circuit encoding by use of SVDs. We have chosen to focus on spin-restricted rotations over the spatial orbitals, and we suggest experimentation with spin-symmetry breaking as a topic of future work. The parameter counts are reduced by enforcing particle number and  $z$ -spin symmetry using a standard block-sparse representation [71, 72]. An initial orbital basis is computed via restricted Hartree-Fock calculations in the PySCF Python package [73–75], and an initial orbital ordering is either chosen randomly or using mutual information heuristics common in DMRG calculations [76, 77].  $M$  is increased in stages, starting from a single MPS initialized with DMRG (see Appendix A 5). The effect of shot noise on the quantum processor is emulated by adding random Gaussian perturbations to the elements of  $\mathbf{H}'$  and  $\mathbf{S}'$  with standard error  $\delta$ .

We benchmark the TNQE method on a stretched water molecule and on an octahedral arrangement of six hydrogen atoms. All calculations are performed in the STO-3G minimal basis set, corresponding to seven spatial molecular orbitals for  $\text{H}_2\text{O}$  and to six spatial orbitals for octahedral  $\text{H}_6$ . This would be equivalent to running quantum circuits on system registers of 14 and 12 qubits respectively under the Jordan-Wigner mapping of spin-orbitals to qubits. We benchmark against classical DMRG calculations and against a simple sparse matrix implementation of UCCSD under a first-order Trotter decomposition. The UCCSD benchmark is optimized via the L-BFGS algorithm [78] with numerical gradients starting from zero amplitudes. While some reduction in the number of QPU calls for these benchmarking calculations may be possible by UCC parameter initialization with MP2 or projective coupled-cluster amplitudes [79], and by use of analytic gradient calculations [80], since our goal here is only to assess the feasibility and scalability of TNQE relative to a standard method, we leave a more detailed comparison against state-of-the-art VQE methods to future work.

#### A. Performance

In Figure 6 we demonstrate that TNQE can be reliably converged to chemical accuracy for the stretched water molecule with O-H bond length between  $2 - 3\text{\AA}$ , with bond dimension  $\chi = 3$  and subspace dimension  $M = 3$ . This dissociation region is known to be challenging for UCC-type ansätze [26]. The ease of convergence with low computational resources suggests that systems with weak to moderate amounts of electron correlation are not challenging for TNQE. In Figure 7 we show that TNQE also reliably attains chemical accuracy for the more strongly correlated octahedral  $\text{H}_6$  system with  $\chi = 4$  and  $M = 4$  across a wide range of internuclear



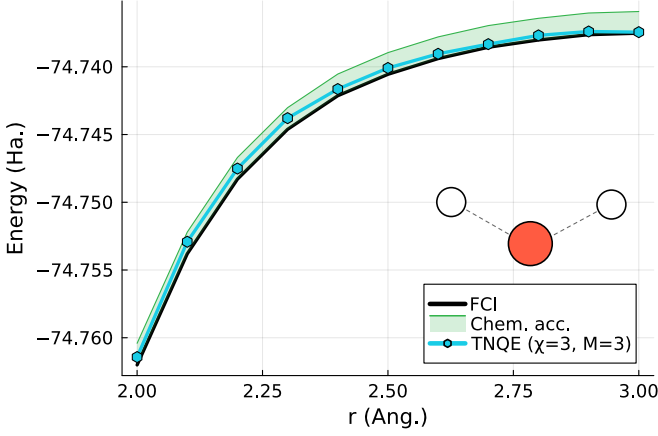


FIG. 6. TNQE ( $\chi = 3$ ,  $M = 3$ ) energies relative to chemical accuracy for a stretched  $\text{H}_2\text{O}$  molecule from  $r = 2\text{\AA}$  up to  $r = 3\text{\AA}$  in the STO-3G basis.

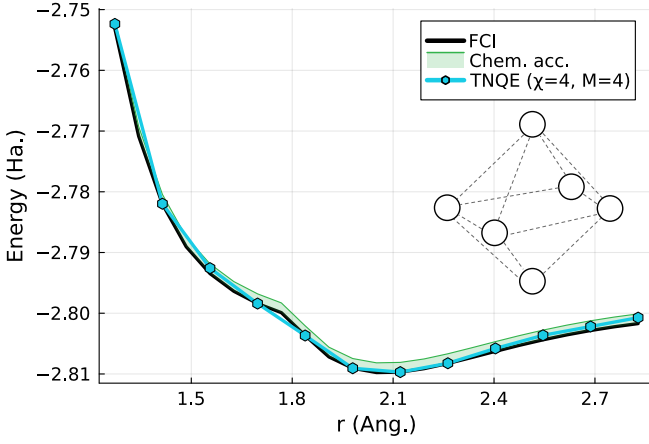


FIG. 7. TNQE ( $\chi = 4$ ,  $M = 4$ ) energies for octahedral  $\text{H}_6$  in the STO-3G basis compared against chemical accuracy from  $r = 1.13\text{\AA}$  up to  $r = 2.83\text{\AA}$ . The ‘kink’ in the FCI curve at  $\sim 1.75\text{\AA}$  is an artefact of the STO-3G basis set.

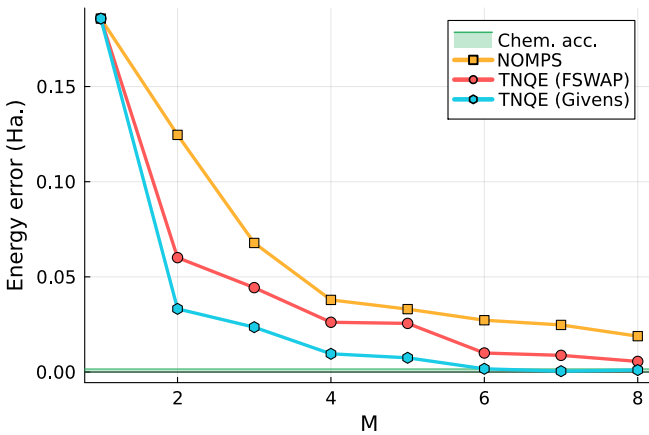


FIG. 8. Comparison of NOMPS, TNQE-F (FSWAP), and TNQE-G (Givens) energies at  $\chi = 3$  with increasing  $M$  for octahedral  $\text{H}_6$  at  $r = 1.70\text{\AA}$  in the STO-3G basis.

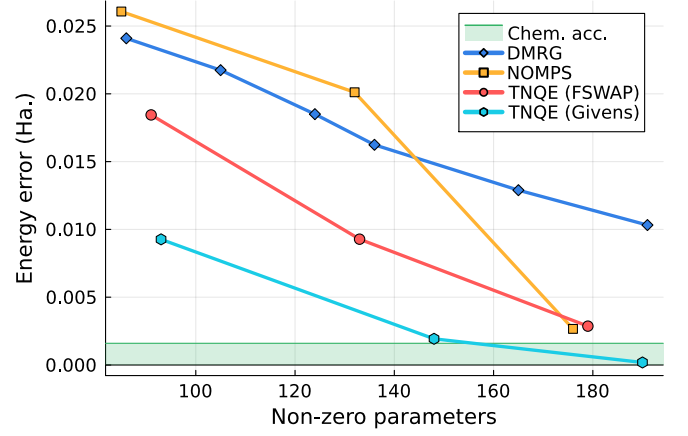


FIG. 9. Comparison of DMRG, NOMPS, TNQE-F (FSWAP), and TNQE-G (Givens) energies with increasing non-zero parameter count for octahedral  $\text{H}_6$  at  $r = 1.70\text{\AA}$  in the STO-3G basis. The DMRG bond dimension is increased from  $\chi = 8$  to  $\chi = 13$ , while the TNQE bond dimension is fixed at  $\chi = 4$  and  $M$  is increased from 2 to 4.

separations, demonstrating that TNQE can also handle cases of much stronger electron correlation with a very manageable increase in the computational resources. Figure 10 shows that the TNQE energy is drastically more accurate than the UCCSD energy estimate for this system across all bond lengths.

To assess the prospects for quantum advantage, the convergence of TNQE with increasing subspace dimension  $M$  is compared against two classically tractable variants of the method, the first of which removes all of the orbital rotations and permutations. We refer to this variant, which is tractable by classical tensor network contraction, as non-orthogonal matrix product states (NOMPS). The second variant restricts the orbital rotations to orbital permutations with FSWAP networks. As explained in Appendix C, this variant is in principle dequantizable by classical random sampling. We will refer to this variant in the text as TNQE-F. The TNQE ansatz using Givens rotations with arbitrary angles is not tractable using any known classical algorithm, and we refer to this as TNQE-G. Figure 8 shows a clear advantage for TNQE-G over both NOMPS and TNQE-F in the octahedral  $\text{H}_6$  system at  $1.70\text{\AA}$  with  $\chi = 3$ . While TNQE-G touches the threshold for chemical accuracy at  $M = 6$ , the dequantizable TNQE-F and classical NOMPS sit at  $\sim 10$  mHa and  $\sim 30$  mHa respectively for  $M = 6$ , and have still not converged to chemical accuracy at  $M = 8$ .

In Figure 9 TNQE is benchmarked against classical DMRG by directly comparing the total number of tensor parameters in the non-zero blocks: this number scales as  $O(N\chi^2)$  for DMRG and as  $O(MN\chi^2)$  for TNQE. For this example, we scale up the parameters in the TNQE variants at a fixed value of  $\chi = 4$  by increasing  $M$  from 2 to 4. For the DMRG curve we have  $M = 1$  by definition and we increase  $\chi$  from 8 up to 13. For the octahedral  $\text{H}_6$

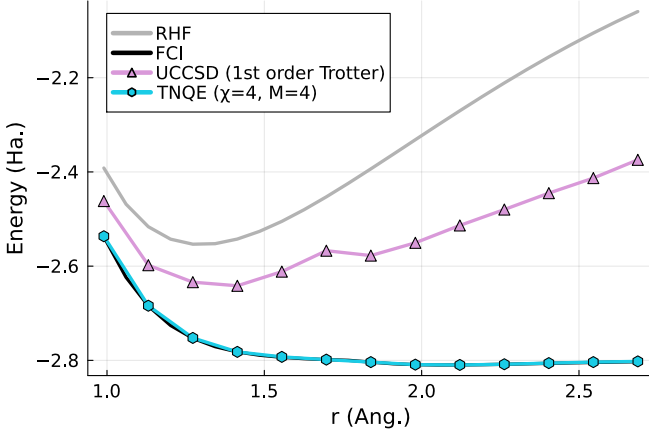


FIG. 10. TNQE ( $\chi = 4$ ,  $M = 4$ ) energies for octahedral  $H_6$  in the STO-3G basis compared against RHF and UCCSD from  $r = 0.99\text{\AA}$  up to  $r = 2.69\text{\AA}$ . The FCI curve appears underneath the TNQE curve at this energy scale. The ‘kink’ in the UCCSD curve at  $\sim 1.75\text{\AA}$  is an artefact arising from the minimal basis set.

system at  $r = 1.70\text{\AA}$  we observe that TNQE achieves far better energies at low parameter counts. However we are careful not to claim this as proof that TNQE outperforms DMRG for this small system, and we mention several caveats to this comparison. First, at larger bond dimensions ( $\chi \geq 15$ ) the DMRG curve converges almost exactly to the FCI energy, with a slightly decreased parameter count of  $\sim 180$ , roughly on par with the number of parameters for TNQE at  $\chi = 4$ ,  $M = 4$ . This may be due to a rearrangement of the internal block-sparse structure at larger bond dimensions. It may also be possible to improve the convergence of the DMRG curve with localized orbitals or other classical techniques. There is also some ambiguity regarding the inclusion of the Givens rotation angles in the total parameter count of TNQE. These are not ‘free’ parameters in the TNQE ansatz and are mutually interdependent, so it is not clear how or whether they should be counted. Nonetheless, the results at low parameter counts are encouraging for the prospect of observing a more decisive advantage in larger strongly correlated systems. Furthermore, these results have all been obtained with superpositions over spin-restricted orbital bases. This restriction can easily be lifted to include orbital bases of broken spin symmetry, which may reveal a yet stronger improvement in the energy compared to the standard spin-restricted variants of DMRG [81].

### B. Cost estimates

In Appendix B 2 we produce detailed estimates of the exact CNOT gate count and circuit depth for TNQE (with both the one-ancilla and the GHZ-ancilla circuit variants) and UCCSD Trotterized to first order, using a CNOT-efficient circuit encoding of the UCC fermion

Cost metric	UCCSD	TNQE
CNOTs per circuit	3.0e3	1.2e3
Qubits (GHZ)	12	13 (18)
Layer depth (GHZ)	3.9e3	2.0e3 (6.6e2)
QPU calls (batched)	2.5e4 (1.6e4)	5.6e5 (2.4e2)
Noise tol. (overlap)	1.0e-8	1.0e-4 (1.0e-5)
Total shots	5.4e23	6.4e16
Total CNOTs	1.6e27	7.7e19
Correlation energy	33.2%	99.7%

TABLE I. Quantum resource estimates for the UCCSD (first order Trotter) and TNQE ( $\chi = 4$ ,  $M = 4$ ) calculations for the octahedral  $H_6$  system in the STO-3G basis set. The number of qubits and the layer depth of the TNQE circuits are given for both a single ancilla qubit and a GHZ ancilla register. Each QPU call corresponds to one VQE energy expectation value, or to one TNQE Hamiltonian or overlap matrix element. The ‘batched’ QPU calls refers to the number of batches of parallelizable QPU calls. The total shots refers to the estimated sum total of circuit repetitions to resolve all of the QPU calls to within the noise tolerance. The total CNOT count is given by the total shots multiplied by the CNOT gate executions per circuit repetition.

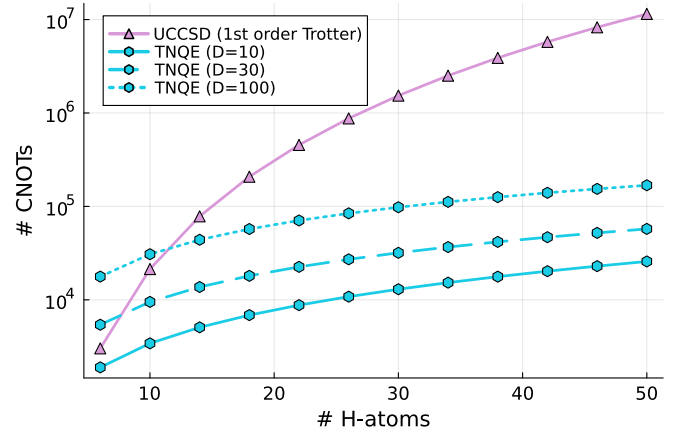


FIG. 11. Comparison of UCCSD and TNQE CNOT counts per circuit for systems with increasing numbers of hydrogen atoms, with arbitrary geometric structure, in the minimal basis set. The UCCSD gate counts are estimated using a CNOT-efficient encoding scheme [82], and the TNQE gate counts are obtained from Equation 21 with disentangler depths  $D$  of 10, 30, and 100 (see also Appendix B 1).

operators [82]. We also estimate the total number of QPU calls to converge the energy estimate, where each QPU call corresponds to a single Hamiltonian or overlap evaluation, noting that the QPU calls in TNQE are highly parallelizable. We simulate shot noise in the matrix elements and expectation values with standard error  $\delta$ , and we find that while UCCSD fails to converge with noise levels of  $\delta = 10^{-7}$  and requires  $\delta = 10^{-8}$  to match the noiseless result to within 3 mHa after 100 iterations, TNQE reliably converges to within chemical accuracy after 48 sweeps with  $\delta = 10^{-4}$  in the Hamil-

tonian matrix elements and  $\delta = 10^{-5}$  in the overlaps. We hypothesize that this may be due in part to effective regulation of the subspace condition number, as detailed in Appendix A 2. From this we derive estimates for the number of shots to resolve each QPU call to these levels of precision, and hence the total number of CNOT gate executions required for the computation. We summarize these findings in Table I for the octahedral  $\text{H}_6$  system at  $r = 1.70\text{\AA}$  in the STO-3G basis. We comment on the high prefactors in the number of shots for both methods in Section IV. While the primary driver behind our cost reductions in the octahedral  $\text{H}_6$  system is the high noise tolerance of the TNQE optimizer, we show in Figure 11 that the CNOT gate count per circuit also scales much more favorably for TNQE with increasing system size, observing a reduction in the CNOT count of nearly two orders of magnitude for 50 hydrogen atoms with disentangler depths (see Appendix B 1) as high as  $D = 100$ .

#### IV. DISCUSSION

We have presented a new class of hybrid quantum-classical algorithm, which we call a tensor network quantum eigensolver, to evaluate chemical ground state energies on near-term quantum computers. We have combined techniques from classical tensor networks, variational quantum algorithms, and quantum subspace diagonalization to eliminate the reliance on costly and unreliable gradient-based optimizers. We have demonstrated reliable convergence to chemical accuracy in small chemical systems, with low parameter counts that suggest a possible regime of practical quantum advantage over classical DMRG. Additionally we report a high tolerance to shot noise and efficient use of quantum resources, with per-circuit gate counts of  $O(N^2)$  and circuit depths of  $O(N)$ , signalling the potential of the method to scale well to larger systems in the NISQ era. While constructed from matrix product states of low bond dimension, the TNQE ansatz uses orbital rotations to mimic the entanglement structure of systems without a one dimensional area law of entanglement, as is likely to be the case in many real-world instances of strong electron correlation such as cuprates [83] or the oxygen-evolving complex of photosystem II [84].

The argument for realizing an exponential quantum advantage with TNQE rests on the degree to which these orbital rotations are of practical utility in the energy calculations. This should now be rigorously tested on larger and more complex chemical problems. We note that the orbital rotation heuristics we have developed appear to be improvable from both a quantum information and a quantum chemistry perspective, for example using the quantum mutual information [76], or initializing the orbitals from unrestricted Hartree-Fock calculations with broken spin symmetry [55]. Achieving practical results at scale will require further research into a number of open questions. First, the gate count, the number of

measurements, and the classical cost of solving the generalized eigenvalue problem scale cheaply with the number of matrix product states, as  $O(1)$ ,  $O(M^2)$ , and  $O(M^3)$  respectively, but somewhat less favorably with the bond dimension, at worst as  $O(\chi^2)$ ,  $O(\chi^4)$ , and  $O(\chi^6)$ . Establishing the optimal tradeoff between  $M$  and  $\chi$  will be necessary to fully characterize the scalability of the algorithm. The method also requires the efficient quantum circuit encoding of a large number of matrix product states to high fidelity. It is not known how this cost will scale using the disentangler method [64], in terms of both the classical overhead and the circuit depth, and the optimal encoding of matrix product states is currently an ongoing topic of research. It is also unknown how the number of sweeps required for convergence will scale with the system size. A deeper understanding of the noise resilience and the identification of possible regimes where this breaks down will be important for implementations on real quantum hardware with both stochastic and coherent gate errors.

While the estimate of  $\sim 10^{16}$  shots for a TNQE calculation on 12 system qubits is orders of magnitude cheaper than the estimate of  $\sim 10^{23}$  for UCCSD, the measurement prefactor will need to be addressed in future work. Although the circuit repetitions are highly parallelizable, running calculations on  $\sim 10^{14}$  QPUs in parallel is prohibitive with current hardware availability. The shot noise limit,  $n_S \propto \delta^{-2}$ , is a generic problem facing near-term algorithms, and has been frequently discussed in the context of VQE [23, 60]. Improvements in hardware fidelity may enable amplitude amplification techniques [85] to provide a quadratic reduction in the measurement scaling, to  $n_S \propto \delta^{-1}$ , for a tradeoff in the circuit depth.

Tensor networks have played a central role in the ‘dequantization’ of quantum algorithms and simulations [86, 87], providing a richer understanding of the arguments for and against both near-term and fault-tolerant quantum advantage [88]. Here we have taken a complementary approach, identifying tensor network contractions that are thought to be classically hard and exploiting their efficient quantum evaluation as algorithmic components. This design philosophy yields quantum algorithms that are not limited by classical contraction constraints, and are by construction difficult to spoof with tensor networks. In the domain of quantum chemical simulation this provides new tools to extend tensor network descriptions of chemical systems to higher connective geometries and to study highly entangled states of chemical interest with low-depth quantum circuits. We argue that far from being antithetical to quantum computing, the tensor network paradigm is compatible with and actively beneficial for emerging quantum algorithms, enabling a virtuous cycle between the development of both quantum-inspired classical methods and classical-inspired quantum methods. We anticipate the techniques developed in this work finding applications beyond quantum chemistry, in fields such as condensed matter physics and quantum machine learning.

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## Appendix A: Details of the generalized sweep algorithm

In the following subsections we explain the steps of the generalized sweep algorithm, as well as a procedure for iterative construction of the MPS subspace, which are then summarized with pseudocode in Algorithms A.1 and A.2.

### 1. Parameter optimization

In classical *ab initio* quantum chemistry, matrix product states are commonly optimized variationally using the two-site DMRG algorithm. Summarized at a high level, the MPS is orthogonalized to site  $p$ , the site tensors between sites  $p$  and  $p+1$  are contracted, optimized, and decomposed by SVD into new site tensors. The procedure is repeated over all the bonds of the MPS in sequence from left to right. In practical calculations the right blocks of the MPS are pre-cached while the left block is iteratively updated. In equation form, we write the orthogonalization to site  $p$  as

$$\begin{aligned} |\phi\rangle &= \sum_{\vec{k}} \left[ \sum_{l_1 \dots l_{N-1}} \Phi_{l_1}^{k_1} \Phi_{l_1 l_2}^{k_2} \dots \Phi_{l_{N-1}}^{k_N} \right] |\vec{k}\rangle \\ &= \sum_{\vec{k}} \left[ \sum_{l_1 \dots l_{N-1}} U_{l_1}^{k_1} U_{l_1 l_2}^{k_2} \dots T_{l_{p-1} l_{p+1}}^{k_p k_{p+1}} \dots V_{l_{N-1}}^{k_N} \right] |\vec{k}\rangle, \end{aligned} \quad (\text{A1})$$

$$(\text{A2})$$

where  $T_{l_{p-1} l_{p+1}}^{k_p k_{p+1}}$  is the two-site tensor formed from contracting the tensors at sites  $p$  and  $p+1$ . In this form the tensors in the left and right blocks have the property that, for any sites  $q < p$  and  $r > p+1$ ,

$$\sum_{k_1 \dots k_q} \sum_{l_1 \dots l_{q-1}} (U_{l_1}^{k_1} U_{l_1 l_2}^{k_2} \dots U_{l_{q-1} l_q}^{k_q} U_{l_q}^{k_{q+1}}) = \mathbb{1}_{l_q l'_q}, \quad (\text{A3})$$

$$\sum_{k_r \dots k_N} \sum_{l_{r-1} \dots l_{N-1}} (V_{l_{r-1}}^{k_r} V_{l_{r-1} l_r}^{k_{r+1}} \dots V_{l_{N-1}}^{k_N} V_{l_{N-1}}^{k_{N+1}}) = \mathbb{1}_{l_{r-1} l'_{r-1}}. \quad (\text{A4})$$

The two-site tensor  $T$  is optimized to lower the expectation value  $\langle \phi | \hat{H} | \phi \rangle$  and then decomposed back into site

tensors by SVD with truncation from  $d\chi$  to  $\chi$  singular values,

$$T_{l_{p-1} l_{p+1}}^{k_p k_{p+1}} \approx \sum_{l_p, l'_p}^{\chi} U_{l_{p-1} l_p}^{k_p} \Sigma_{l_p l'_p} V_{l'_p l_{p+1}}^{k_{p+1}} = \sum_{l_p}^{\chi} U_{l_{p-1} l_p}^{k_p} T_{l_p l_{p+1}}^{k_p k_{p+1}}, \quad (\text{A5})$$

where the tensor  $\Sigma$  is the diagonal matrix of singular values, which is contracted into  $V$  in order to move the orthogonality center to site  $p+1$ . Note that we must renormalize the state since we have thrown away some information.

We now demonstrate that finding the optimal coefficients for the two-site tensor is equivalent to diagonalizing in an expanded subspace spanned by an orthonormal set of states. We can decompose the tensor  $T$  as a sum over “one-hot” tensors, which are tensors with the same indices as  $T$  and a single nonzero element equal to one,

$$T_{l_{p-1} l_{p+1}}^{k_p k_{p+1}} = \sum_{m=1}^{d^2 \chi^2} t_m [\varphi_m]_{l_{p-1} l_{p+1}}^{k_p k_{p+1}}, \quad (\text{A6})$$

where  $m$  indexes the one-hot tensors  $\varphi_m$  and we use square braces to separate the sum index  $m$  from the tensor indices. Replacing the two-site tensor  $T$  with one of the one-hot tensors  $\varphi_m$  results in a new matrix product state which we call a “one-hot” state, denoted  $|\varphi_m\rangle$ . Since  $|\phi\rangle$  is in orthogonal form centred at  $p$ , we can use the orthogonality relations (Equations A3, A4) to trivially compute the overlap between two one-hot states as

$$\langle \varphi_m | \varphi_n \rangle = \sum_{\substack{k_p k_{p+1} \\ l_{p-1} l_{p+1}}} [\varphi_m]_{l_{p-1} l_{p+1}}^{k_p k_{p+1}} [\varphi_n^\dagger]_{l_{p-1} l_{p+1}}^{k_p k_{p+1}} = \delta_{mn}. \quad (\text{A7})$$

Furthermore, by the same orthogonality relations, we have that

$$\langle \varphi_m | \phi \rangle = t_m, \quad \langle \phi | \phi \rangle = \sum_m |t_m|^2 = 1. \quad (\text{A8})$$

Therefore the one-hot states must form a complete and orthonormal basis for all of the states that can be obtained by optimizing the two-site tensor,

$$|\phi\rangle = \sum_{m=1}^{d^2 \chi^2} t_m |\varphi_m\rangle, \quad \langle \varphi_m | \varphi_n \rangle = \delta_{mn}, \quad \sum_{m=1}^{d^2 \chi^2} |t_m|^2 = 1. \quad (\text{A9})$$

Then by computing the  $O(d^4 \chi^4)$  matrix elements  $H_{mn} = \langle \varphi_m | \hat{H} | \varphi_n \rangle$  and diagonalizing

$$\mathbf{H} = \mathbf{C} \mathbf{E} \mathbf{C}^\dagger \quad (\text{A10})$$

we find the optimal coefficients from the first column of the solution matrix, i.e.  $t_m = C_{m1}$ . Exact diagonalization has an asymptotic cost of  $O(\chi^6)$ , which is a factor of  $\chi^3$  more expensive than standard variants of the two-site algorithm using iterative solvers [89, 90]. Provided

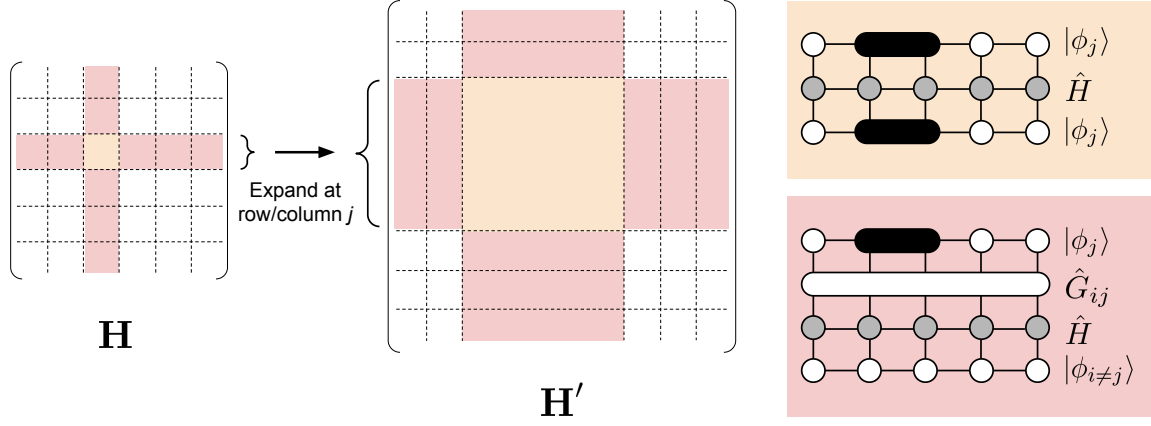


FIG. A.1. An illustration of the expansion of the Hamiltonian subspace matrix  $\mathbf{H}$  at row/column  $j$  via the one-hot tensor decomposition of the two-site tensor of state  $|\phi_j\rangle$  over sites  $p, p+1$ . The tensor networks on the right are used to evaluate the diagonal and off-diagonal blocks of the expanded subspace matrix  $\mathbf{H}'$ . We can find the elements of the expanded overlap matrix  $\mathbf{S}'$  by removing the Hamiltonian MPO from the tensor networks. Each matrix element can be efficiently obtained using a quantum circuit encoding of the tensor network as in Figure 4.

that the bond dimension is kept small this remains only a modest additional cost.

Now we shall see how to generalize the two-site optimization algorithm to the multi-reference case. Given a set of MPS basis states  $\{|\phi_j\rangle\}$ , we may calculate the optimal coefficients  $\{c_j\}$  to approximate the ground state of the Hamiltonian by solving the generalized eigenvalue problem

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}, \quad (\text{A11})$$

where the matrix elements of  $\mathbf{H}$  and  $\mathbf{S}$  are given by

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle, \quad (\text{A12})$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle. \quad (\text{A13})$$

The matrix  $\mathbf{E}$  is a diagonal matrix of eigenvalues  $E_1, \dots, E_M$ . The optimal coefficients for the ground state estimate  $E_1$  are then given by the first column of  $\mathbf{C}$ , that is,  $c_j = C_{j1}$ . We can immediately see the connection to the two-site decomposition. By expanding a chosen reference state  $|\phi_j\rangle = \sum_m t_m^{[j]} |\varphi_m^{[j]}\rangle$  and computing the additional matrix elements

$$H'_{jm,jn} = \langle \varphi_m^{[j]} | \hat{H} | \varphi_n^{[j]} \rangle, \quad S'_{jm,jn} = \delta_{mn}, \quad (\text{A14})$$

$$H'_{jm,i} = \langle \varphi_m^{[j]} | \hat{H} | \phi_i \rangle, \quad S'_{jm,i} = \langle \varphi_m^{[j]} | \phi_i \rangle, \quad (\text{A15})$$

we can lower the ground state estimate  $E'_1$  by solving the generalized eigenvalue problem on the expanded subspace matrices  $\mathbf{H}'$  and  $\mathbf{S}'$  (see Figure A.1). This can be extended in a straightforward manner to simultaneously expand any subset of the matrix product states at the same or different sites. To optimize all states simultaneously we compute the matrix elements between all of the expanded one-hot states,

$$H'_{im,jn} = \langle \varphi_m^{[i]} | \hat{H} | \varphi_n^{[j]} \rangle, \quad S'_{im,jn} = \langle \varphi_m^{[i]} | \varphi_n^{[j]} \rangle. \quad (\text{A16})$$

Having solved the generalized eigenvalue problem, we find the optimal coefficients for each two-site tensor from slicing and normalizing the first column of  $\mathbf{C}'$ ,

$$t_m^{[j]} = \frac{C'_{jm,1}}{\sqrt{\sum_n |C'_{jn,1}|^2}}. \quad (\text{A17})$$

To optimize a single MPS this procedure requires  $O(Md^2\chi^2)$  matrix element evaluations in the off-diagonal ( $i \neq j$ ) blocks per site decomposition, while to optimize all states simultaneously requires  $O(M^2d^4\chi^4)$  off-diagonal matrix elements. Note that we need the QPU only for the  $i < j$  blocks, since the  $i = j$  blocks are classically tractable by tensor network contraction, and we may copy matrix elements into the adjoint blocks since  $\mathbf{H}' = \mathbf{H}'^\dagger$  and  $\mathbf{S}' = \mathbf{S}'^\dagger$ . In practical calculations the  $z$ -spin and particle number symmetry are typically enforced by way of an internal block-sparse tensor structure [71, 72], so the scalings in the number of matrix elements will have some prefactor less than one. To complete a full sweep over all  $N-1$  bonds requires  $O(NM^2d^4\chi^4)$  matrix elements per sweep. There is no requirement to decompose each MPS at the same bond, although we find this to be an effective strategy in small-scale calculations.

## 2. Numerical stability

The quantity of principal concern regarding numerical stability is the condition number of the expanded matrix  $\mathbf{S}'$ . We can directly control this quantity by discarding one-hot states that have a high degree of linear dependence. Intuitively this representational flexibility is already present within the rest of the states in the subspace, so the discarded states are in some sense redundant. In fact the discarding step appears to be beneficial



for convergence of the optimizer, possibly because it encourages each matrix product state to capture different features of the ground state. We formalize the linear dependence condition by measuring the squared norm of the projection of each of the one-hot states onto the subspace of the previous states. Let  $\mathbf{S}^\dagger$  denote the reduced overlap matrix consisting of the upper-left block of  $\mathbf{S}'$  over the rows and columns  $im = 1, \dots, jn-1$ , and let  $\vec{\varphi}$  be the vector of overlaps of the one-hot tensor  $|\varphi_n^{[j]}\rangle$  with the states in the upper-left subspace, i.e.  $\varphi_{im} \equiv \langle \varphi_m^{[i]} | \varphi_n^{[j]} \rangle$ . Then the squared norm of the projected state  $\vec{\varphi}^\dagger$  is given by

$$\|\vec{\varphi}^\dagger\|^2 = \vec{\varphi}^\dagger [\mathbf{S}^\dagger]^{-1} \vec{\varphi}. \quad (\text{A18})$$

We discard the state  $|\varphi_n^{[j]}\rangle$  if  $1 - \|\vec{\varphi}^\dagger\|^2$  is less than some set tolerance, e.g.  $10^{-3}$ . As a secondary check we also discard the state if the condition number of the new reduced overlap matrix including  $|\varphi_n^{[j]}\rangle$  is above a certain threshold. Since we have discarded the linearly dependent states in the upper left block the matrix inverse should remain well-behaved (in practice we use the Moore-Penrose pseudoinverse with singular value tolerance  $\sqrt{\varepsilon} \|\mathbf{S}^\dagger\|$  where  $\varepsilon$  is the machine epsilon and  $\|\cdot\|$  is the operator 2-norm).

We can further control the solution of the generalized eigenvalue problem by thresholding the singular values of  $\mathbf{S}'$  [58]. We have implemented two common thresholding strategies known as projection and inversion. For both methods, we begin by computing

$$\mathbf{S}' = \mathbf{U} \mathbf{\Lambda} \mathbf{U}^\dagger. \quad (\text{A19})$$

We filter the eigenvalues to keep only those greater than a chosen singular value tolerance, i.e.  $\lambda > \epsilon$ . Then by the projection method, we take the rectangular matrix of the remaining eigenvectors  $\mathbf{U}_\epsilon$  and solve

$$[\mathbf{U}_\epsilon^\dagger \mathbf{H}' \mathbf{U}_\epsilon] \mathbf{C}' = [\mathbf{U}_\epsilon^\dagger \mathbf{S}' \mathbf{U}_\epsilon] \mathbf{C}' \mathbf{E}'. \quad (\text{A20})$$

Then the columns of  $\mathbf{U}_\epsilon^\dagger \mathbf{C}'$  provide the approximate desired coefficients. By the inversion method, we remove the eigenvalues  $\lambda \leq \epsilon$  from  $\mathbf{\Lambda}$ , and then solve

$$\mathbf{U} \mathbf{\Lambda}_\epsilon^{-1} \mathbf{U}^\dagger \mathbf{H}' = \mathbf{C}' \mathbf{E}' \mathbf{C}'^\dagger. \quad (\text{A21})$$

The coefficients are provided by the renormalized columns  $\tilde{c}_i / \sqrt{\tilde{c}_i^\dagger \mathbf{S}' \tilde{c}_i}$ . Following [58] we can calculate the eigenvalue condition number of the ground state by

$$\kappa_1 = \frac{\|\tilde{c}_1\|^2}{\sqrt{E_1^2 + 1}}. \quad (\text{A22})$$

Provided this number is not too large, then the ground state may still be relatively insensitive to small perturbations even when  $\epsilon \ll 1$ , although this does not address the issue of the ordering of the subspace eigenstates. Using the measures outlined above we find that in practice

the optimizer explores the space surrounding the ground state in a highly restricted manner, such that the more ill-conditioned regions of the non-orthogonal state space are largely avoided. This is backed up empirically by our finding that we can reliably converge the energy estimate with Gaussian noise in the overlap matrix elements on the order of  $10^{-5}$ .

### 3. Orbital permutations and rotations

As in the two-site DMRG algorithm, the optimized two-site tensor is decomposed back into single-site tensors by SVD and the bond dimension is truncated from  $d\chi$  to  $\chi$  singular values. Prior to the SVD we apply a local orbital permutation or rotation to the two-site tensor in order to reduce the truncation error. In the case of spin-orbital sites  $d = 2$ , the FSWAP gate acting on neighboring orbitals has the form

$$\hat{f} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \quad (\text{A23})$$

Note that this differs from a generic SWAP gate only in the phase on the last element, which encodes fermionic antisymmetry under the exchange of two electrons, i.e.,  $\hat{f}|11\rangle = -|11\rangle$ . A Givens rotation with angle  $\theta$  has the form

$$\hat{g}(\theta) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(\theta) & -\sin(\theta) & 0 \\ 0 & \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (\text{A24})$$

We can also use a phased version of the FSWAP gate which corresponds exactly to a  $\theta = \pi/2$  Givens rotation,

$$(\hat{1} \otimes \hat{Z}) \hat{f} = \hat{g}(\frac{\pi}{2}). \quad (\text{A25})$$

In the case of either  $\hat{f}$  or  $\hat{g}(\theta)$  this matrix is reshaped to a  $2 \times 2 \times 2 \times 2$  tensor, which we denote here as  $F$  or  $G_\theta$ . In the case of orbital permutations, we contract

$$\tilde{T}_{l_{p-1}l_{p+1}}^{k_p k_{p+1}} = \sum_{k'_p k'_{p+1}} T_{l_{p-1}l_{p+1}}^{k'_p k'_{p+1}} F_{k'_p k'_{p+1}}^{k_p k_{p+1}}, \quad (\text{A26})$$

and perform SVDs on both the original and swapped two-site tensors

$$T = U \Sigma V, \quad \tilde{T} = \tilde{U} \tilde{\Sigma} \tilde{V}. \quad (\text{A27})$$

We accept the FSWAP insertion if

$$\sum_{l=1}^{\chi} \tilde{\sigma}_l^2 > \sum_{l=1}^{\chi} \sigma_l^2. \quad (\text{A28})$$

For orbital rotations we contract

$$[T_\theta]_{l_{p-1}l_{p+1}}^{k_p k_{p+1}} = \sum_{k'_p k'_{p+1}} T_{l_{p-1}l_{p+1}}^{k'_p k'_{p+1}} [G_\theta]_{k'_p k'_{p+1}}^{k_p k_{p+1}} \quad (\text{A29})$$

and perform the SVD

$$T_\theta = U_\theta \Sigma_\theta V_\theta. \quad (\text{A30})$$

We then carry out a univariate black-box optimization on the angle  $\theta$  to obtain

$$\theta_{\text{opt}} = \arg \min_{\theta} \left[ 1 - \sum_{l=1}^{\chi} [\sigma_\theta]_l^2 \right]. \quad (\text{A31})$$

The numerical bottleneck for this optimization will be the multiple SVD calls with cost  $O(\chi^3)$ . Provided that  $\chi$  is kept small then this remains a low-cost classical co-processing step. We can extend to permutations and rotations over spatial orbital sites (without spin-mixing) by defining FSWAP and Givens operations on the  $d = 4$  sites in terms of the above operations for  $d = 2$  to which we add the subscripts  $\hat{f}_2$  and  $\hat{g}_2(\theta)$ :

$$\hat{f}_4 = (\hat{\mathbf{1}}_2 \otimes \hat{f}_2 \otimes \hat{\mathbf{1}}_2)(\hat{f}_2 \otimes \hat{f}_2)(\hat{\mathbf{1}}_2 \otimes \hat{f}_2 \otimes \hat{\mathbf{1}}_2), \quad (\text{A32})$$

$$\hat{g}_4(\theta) = (\hat{\mathbf{1}}_2 \otimes \hat{s}_2 \otimes \hat{\mathbf{1}}_2)(\hat{g}_2(\theta) \otimes \hat{g}_2(\theta))(\hat{\mathbf{1}}_2 \otimes \hat{s}_2 \otimes \hat{\mathbf{1}}_2), \quad (\text{A33})$$

where  $\hat{\mathbf{1}}_2$  is the single-qubit identity and  $\hat{s}_2$  denotes the generic two-qubit SWAP gate. Then we reshape to a  $4 \times 4 \times 4 \times 4$  tensor and apply the same steps as before. In practical calculations we find that interleaving orbital permutation sweeps with orbital rotation sweeps is highly effective at breaking the optimizer out of local minima. This corresponds to alternating between rearranging the orbitals to different site positions via nearest neighbor swapping, and mixing of the orbitals through nearest neighbor quantum superpositions.

#### 4. Mitigation of the energy penalty

Even after the orbital rotations the truncation error can significantly and nontrivially affect the energy estimate of the ansatz. We mitigate this truncation effect without growing the bond dimension by performing a sequence of alternating single-site decompositions at sites  $p$  and  $p+1$  following each two-site decomposition. We can do this with no additional QPU calls by contracting the single-site one-hot states with the two-site one-hot states obtaining isometries that can be applied to the blocks of  $\mathbf{H}'$  and  $\mathbf{S}'$ . More precisely, following SVD of the two-site tensor  $T = U\Sigma V$  we form  $T^{(1)} = U\Sigma$  and decompose this single-site tensor into  $d\chi^2$  one-hot tensors  $\{\varphi_m^{(1)}\}$ , defining a new one-hot decomposition

$$T = \sum_m t_m^{(1)} \varphi_m^{(1)} V. \quad (\text{A34})$$

---

#### Algorithm A.1 Generalized sweep algorithm

---

```

1:  $p \leftarrow 1$ 
2: while  $p < N$  do
3:    $E_{\text{old}} \leftarrow E_1$ 

4:   for  $j$  in jset do
5:     orthogonalize  $|\phi_j\rangle$  to site  $p$ 
6:     contract two-site tensor  $T^{[j]}$  over sites  $p, p+1$ 
7:     decompose  $T^{[j]}$  to obtain  $\{|\varphi_m^{[j]}\rangle\}$ 
8:     classically contract  $\langle \varphi_m^{[j]} | \hat{H} | \varphi_n^{[j]} \rangle$ 
9:     for  $i < j$  do
10:      if  $i$  in jset then
11:        call QPU for  $\langle \varphi_m^{[i]} | \hat{H} | \varphi_n^{[j]} \rangle, \langle \varphi_m^{[i]} | \varphi_n^{[j]} \rangle$ 
12:      else
13:        call QPU for  $\langle \phi_i | \hat{H} | \varphi_n^{[j]} \rangle, \langle \phi_i | \varphi_n^{[j]} \rangle$ 
14:      end if
15:    end for
16:  end for

17:  discard linearly dependent columns of  $(\mathbf{H}', \mathbf{S}')$ 
18:  solve  $\mathbf{H}'\mathbf{C}' = \mathbf{S}'\mathbf{C}'\mathbf{E}'$ 

19:  for  $j$  in jset do
20:    update  $T^{[j]}$  parameters from  $\mathbf{C}'$ 
21:    if rotation type 'FSWAP' then
22:      compute  $\xi$  and  $\tilde{\xi}$ 
23:      if  $\tilde{\xi} < \xi$  then
24:         $T^{[j]} \leftarrow T^{[j]} F$ 
25:         $\hat{G}_{ij} \leftarrow \hat{f}_{p,p+1} \hat{G}_{ij}$ 
26:      end if
27:    else if rotation type 'Givens' then
28:      compute  $\theta_{\text{opt}} = \arg \min_{\theta} [\xi(\theta)]$ 
29:       $T^{[j]} \leftarrow T^{[j]} G_{\theta_{\text{opt}}}$ 
30:       $\hat{G}_{ij} \leftarrow \hat{g}_{p,p+1}(-\theta_{\text{opt}}) \hat{G}_{ij}$ 
31:    end if
32:    truncate  $T^{[j]} = U^{[j]} \Sigma^{[j]} V^{[j]}$  to  $\chi$  singular values
33:  end for

34:   $\text{rep} \leftarrow 1$ 
35:  while  $\text{rep} \leq \text{nreps}$  do
36:    for  $q \in \{p, p+1\}$  do
37:      apply single-site  $q$  isometries to  $(\mathbf{H}', \mathbf{S}')$ 
38:      discard linearly dependent columns of  $(\mathbf{H}', \mathbf{S}')$ 
39:      solve  $\mathbf{H}'\mathbf{C}' = \mathbf{S}'\mathbf{C}'\mathbf{E}'$ 
40:      for  $j$  in jset do
41:        update  $T^{[j]}$  parameters from  $\mathbf{C}'$ 
42:      end for
43:    end for
44:     $\text{rep} \leftarrow \text{rep} + 1$ 
45:  end while

46:   $E_{\text{new}} \leftarrow E'_1$ 
47:  if  $E_{\text{new}} < E_{\text{old}} + E_{\text{tol}}$  then
48:    accept updates to  $T^{[j]}, \hat{G}_{ij}$ 
49:    apply new rotations to Hamiltonian coefficients
50:  else
51:    revert  $T^{[j]}, \hat{G}_{ij}$  to original values
52:  end if

53:   $p \leftarrow p + 1$ 
54: end while

```

---

Contracting all of the single-site one-hot tensors  $\varphi_m^{(1)}V$  with each the two-site one-hot tensors  $\varphi_n^{(2)}$  results in a rectangular  $d\chi^2 \times d^2\chi^2$  transformation matrix. Multiplying the appropriate blocks of  $\mathbf{H}'$  and  $\mathbf{S}'$  yields the  $Md\chi^2 \times Md\chi^2$  matrices of the single-site decomposition over all the states. After the single-site decompositions we impose a further condition that the parameter update is rejected if the new ground state energy estimate is higher than the previous estimate by a fixed tolerance on the order of  $\sim 1$  mHa. We find that in combination these measures can effectively mitigate any remaining convergence issues due to truncation. This final step completes the generalized sweep algorithm, summarized with high-level pseudocode in Algorithm A.1.

---

**Algorithm A.2** Iterative subspace construction

---

```

1:  $M \leftarrow 1$ 
2: compute RHF molecular orbitals
3: choose initial orbital ordering (random or heuristic)
4: initialize  $|\phi_1\rangle$  with random parameters
5: optimize  $|\phi_1\rangle$  with classical DMRG

6: while  $M < M_{\max}$  do
7:    $M \leftarrow M + 1$ 
8:   initialize  $|\phi_M\rangle$  with random parameters
9:   for  $i < M$  do
10:     $\hat{G}_{iM} \leftarrow \hat{G}_{i,M-1}$ 
11:   end for

12:    $s \leftarrow 1$ 
13:   while  $s \leq \text{ns1}$  do
14:     Algorithm A.1 with ‘FSWAP’ and jset= $\{M\}$ 
15:      $s \leftarrow s + 1$ 
16:   end while

17:    $s \leftarrow 1$ 
18:   while  $s \leq \text{ns2}$  do
19:     Algorithm A.1 with ‘FSWAP’ and jset= $\{1, \dots, M\}$ 
20:     Algorithm A.1 with ‘Givens’ and jset= $\{1, \dots, M\}$ 
21:      $s \leftarrow s + 1$ 
22:   end while

23: end while

```

---

## 5. Iterative subspace construction

In practical calculations it is found to be an effective strategy to increase  $M$  in stages, starting with a single matrix product state optimized with classical DMRG. At each stage a new MPS is added to the subspace, in the same orbital basis as the last MPS and with random parameters, and optimized individually for a number of sweeps with FSWAPs applied. Following this all the MPSs are optimized simultaneously with sweeps alternating between FSWAPs and Givens rotations. These steps are summarized in Algorithm A.2. We do not claim this iterative subspace construction to be optimal, although, as we have demonstrated, this procedure reliably

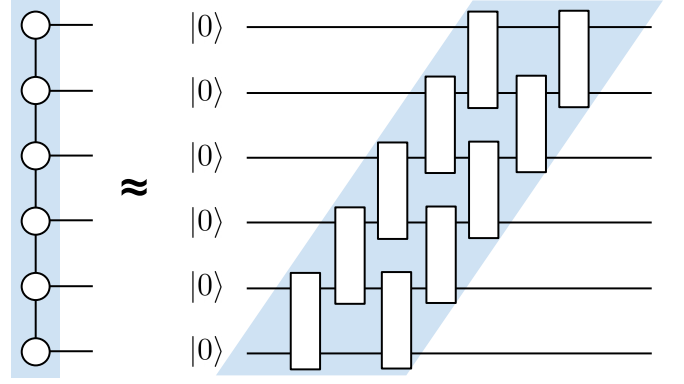


FIG. B.1. A circuit diagram illustrating the approximate preparation of a matrix product state via  $D$  layers of disentanglers, shown here with  $D = 2$ .

converges to chemical accuracy in numerical experiments on small systems.

## Appendix B: Detailed cost estimates

### 1. TNQE circuit synthesis

Here we break down the gate cost and layer depth for the disentangler-based implementation of the matrix element quantum circuits. The disentangler method first introduced by Ran [64] works by truncating the target MPS to  $\chi = 2$  and then computing a staircase-like circuit of one- and two-qubit unitaries that map the truncated MPS to the all-zero state (the one-qubit gate can then be then merged into the last two-qubit gate). Applying these gates to the untruncated MPS results in a new MPS that is closer in fidelity to the all-zero state. Repeating this procedure  $D$  times results in a sequence of  $D$  disentangler layers that, when applied in reverse to the all-zero state, approximately prepares the original MPS up to some desired fidelity, as shown in Figure B.1.

We reduce the prefactors in the gate count by exploiting the fact that the matrix product states used in the TNQE ansatz are entirely real-valued without loss of generality, from which it follows that the disentangling gates  $U$  are also real-valued orthogonal transformations. An orthogonal unitary  $U$  satisfies  $\det(U) = \pm 1$ . For any orthogonal matrix with determinant  $+1$  one can compute a real matrix  $\sqrt{U}$  such that  $(\sqrt{U})^2 = U$  and  $\sqrt{U}\sqrt{U}^T = \sqrt{U}^T\sqrt{U} = I$ . Then we may apply controlled- $U$  by a standard technique [91], with one application each of  $\sqrt{U}$  and  $\sqrt{U}^T$  and four additional CNOTs, as shown in Figure B.2. Thus adding control to an arbitrary two-qubit orthogonal gate introduces a factor of two to the synthesis cost plus an additional four CNOT gates. Note in the case that  $\det(U) = -1$ , we may instead compute  $\sqrt{-U}$ , and after application of controlled- $(-U)$  flip the phase of the ancilla  $|1\rangle$  state by

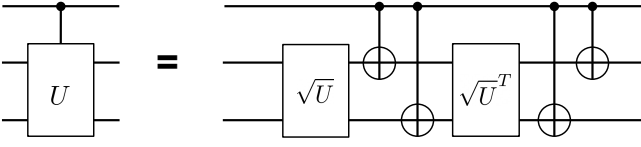


FIG. B.2. Adding control to an arbitrary orthogonal two-qubit gate  $U$  with two two-qubit rotations and four additional CNOT gates.

applying a  $Z$  gate to the ancilla qubit. To complete the cost estimate we decompose each  $\sqrt{U}$  into six single-qubit  $R_y$  gates and two CNOT gates via the Cartan decomposition [92]. We can do this regardless of the determinant of  $\sqrt{U}$  because the global phase will cancel with that of  $\sqrt{U}^T$ . Therefore each controlled two-qubit rotation requires a total of eight CNOT gates with a layer depth of 14. It is easily verified that the Givens rotations have determinant equal to +1 and therefore can be implemented with two CNOT gates and five gate layers.

Assuming a fully-connected architecture, we can evaluate a matrix element with two controlled MPS preparation unitaries, each of which require  $(N-1)D$  controlled two-qubit rotations. In addition we must add in the  $\binom{N}{2}$  Givens rotation unitaries. Only three of the rotation unitaries contribute to the layer depth since the rest can be performed fully in parallel with the controlled disentangles. We thus arrive at the Equations 21, 22, and 23 in the main text.

## 2. Cost estimates for ground state energy estimation of octahedral $H_6$ in the STO-3G basis

### a. TNQE

We optimize the ansatz via the procedure detailed in the main text and in Algorithm A.2, performing four sweeps over the new state followed by 12 sweeps over all states alternating between FSWAPs and Givens rotations (i.e. six of each). The TNQE algorithm requires the evaluation of  $O(Md^2\chi^2)$  matrix elements per site decomposition when optimizing a single state, or  $O(M^2d^4\chi^4)$  matrix elements when optimizing all states at once. As noted in the main text we have some reduction in the number of one-hot basis states for each site decomposition due to the block-sparse structure of the quantum number conserving MPS. We count up the number of matrix elements in the off-diagonal blocks giving a total number of QPU calls  $n_Q = 5.6 \times 10^5$ .

We may perform all the matrix element computations at each site decomposition in parallel, so the number of parallel sets of QPU calls is simply the number of sweeps multiplied by the number of bonds per sweep for a total of 240.

We include a small Gaussian noise term drawn from  $\mathcal{N}(0, \delta^2)$  to simulate shot noise in the matrix elements.

Empirically we find that we can reliably converge to chemical accuracy with noise levels less than or equal to  $\delta = 10^{-4}$  in the Hamiltonian matrix elements and  $\delta = 10^{-5}$  in the overlap matrix elements. We therefore require  $n_S \approx 10^{10}$  shots per overlap matrix element to resolve the matrix elements to this level of precision, and, following Equation 20 in the main text,  $n_S \approx 2.2 \times 10^{11}$  shots per Hamiltonian matrix element. We have made the approximation  $\sum_\alpha |h_\alpha| \approx \sum_{pq} |h_{pq}| + \sum_{pqrs} |h_{pqrs}| = 46.95$  Hartree, with integral coefficients expressed in the initial RHF orbital basis. The total number of overlap and Hamiltonian matrix elements are each  $n_Q/2$ , which gives a total number of shots  $6.44 \times 10^{16}$ .

We count the number of CNOT gates using the formula 21 with number of qubits  $N = 12$ . We find that we can prepare all of the one-hot matrix product states with very high fidelities (errors in the seventh decimal place) with disentangler depth  $D = 6$ , for a total of  $1.2 \times 10^3$  CNOT gates per quantum circuit. In some cases we need to apply a small number of re-optimization loops over the disentanglers using a QR factorization of a black-box optimized matrix, somewhat similar to the strategies advocated in [67, 68]. We use the layer depth formulae of Equations 22 and 23 to compute a layer depth of  $3.1 \times 10^3$ , which as explained in the main text could be significantly reduced at the expense of six additional qubits and ten additional CNOT gates to  $6.6 \times 10^2$ . We note that it is substantially more expensive in terms of disentangler depth  $D$  to prepare the full MPS  $|\phi_i\rangle$  than its basis vectors under the one-hot decomposition, which have reduced entanglement across many of the bonds. In practice we never need to prepare the full MPS as we can always compute the matrix elements using a one-hot decomposition with appropriate one-hot basis vector coefficients. Further research is needed to obtain a more detailed understanding of how the layer depth  $D$  depends on the bond dimension  $\chi$  in practice.

### b. UCCSD

The UCCSD ansatz has the form

$$|\psi_{\text{UCCSD}}\rangle = \exp(\hat{T} - \hat{T}^\dagger) |\psi_{\text{HF}}\rangle, \quad (\text{B1})$$

where  $|\psi_{\text{HF}}\rangle$  is the Hartree-Fock Slater determinant and  $\hat{T} = \hat{T}_1 + \hat{T}_2$  is the sum of singles and doubles cluster operators,

$$\hat{T}_1 = \sum_{\substack{p \in \text{vir} \\ q \in \text{occ}}} \theta_{pq} \hat{a}_p^\dagger \hat{a}_q, \quad (\text{B2})$$

$$\hat{T}_2 = \sum_{\substack{p > q \in \text{vir} \\ r > s \in \text{occ}}} \theta_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s. \quad (\text{B3})$$

Since the Hamiltonian does not connect sectors of different  $\hat{S}_z$  symmetry we use the same parameter for all of the different spin terms, and we find that this restriction has



a negligible effect on the energy estimate. For the octahedral  $H_6$  system, with  $N = 6$  spatial orbitals and  $\eta/2 = 3$  occupied orbitals, we have a total of 9 singles parameters and 36 doubles parameters for 45 total parameters. We optimize the ansatz using the L-BFGS algorithm which calculates numerical gradients at each step, followed by a line search requiring additional QPU calls. We terminate the optimizer after 100 iterations, counting a total of  $n_Q = 2.5 \times 10^4$  QPU calls. We may parallelize the energy evaluations for the numerical gradients, but not those for the line search. For 45 parameters this implies 90 energy evaluations per step to compute the gradients which can be done simultaneously, so subtracting from the total evaluations we arrive at  $1.6 \times 10^4$  sequential QPU calls with parallelization.

We add a small Gaussian noise term drawn from  $\mathcal{N}(0, \delta^2)$  to simulate shot noise in the energy evaluations. Empirically we find that the optimizer fails to converge to the noiseless result at noise levels of  $\delta = 10^{-7}$ , with energy errors above 10 mHa, and we must go to noise levels of  $\delta = 10^{-8}$  to achieve agreement with the noiseless result to within 3 mHa after 100 iterations. By Equation 20 we require a number of shots  $n_S \approx 2.2 \times 10^{19}$  to resolve each energy evaluation to this level of precision. This gives a total number of shots for the computation of  $n_Q \cdot n_S \approx 5.4 \times 10^{23}$ .

We use a CNOT-efficient encoding scheme for the fermionic excitation operators [82]. We count a total of  $3.0 \times 10^3$  CNOT gates for our system of  $N = 6$  spatial orbitals and  $\eta = 6$  electrons, with a layer depth (counting both CNOT gates and single-qubit rotations, using the equations and figures provided in [82]) of  $3.9 \times 10^3$  layers.

### Appendix C: Discussion of exponential quantum advantage and dequantization

Here we discuss attempts at efficient classical computation, or ‘dequantization’, of the off-diagonal matrix element contractions. We argue that while dequantization is possible in the restricted case of orbital permutations, there is no known classical algorithm enabling dequantization in the case of arbitrary orbital rotations. In the following analysis we choose  $d = 2$  corresponding to qubit sites for simplicity.

Consider first the restricted case of orbital permutations. The application of an FSWAP gate between neighboring sites of an MPS can grow the bond dimension by up to a factor of 2. There are provable lower bounds of  $O(N)$  for the depth of a sorting network on a one-dimensional graph [48, 49], which means that the bond dimensions will in general grow to  $O(2^N)$  under arbitrary permutations of the orbitals. However, since the FSWAP gate is contained within the Clifford subgroup, we know that we can simulate the FSWAP network circuit in polynomial time on a classical computer by the Gottesman-Knill theorem [93, 94]. If the input state is

a computational basis vector (or ‘bitstring state’) then it is obvious how to compute the output from the FSWAP network in linear time by simply rearranging the bits and updating the phase after each FSWAP. Since there exists an efficient perfect sampling algorithm for bitstring distributions defined by matrix product states [95, 96], we can in principle compute the overlap between two matrix product states by the random sampling algorithm suggested in Section D3 of the supplementary material of [97], which we summarize here. Suppose that we have two matrix product states  $|\phi_i\rangle$  and  $|\phi_j\rangle$ , and an efficient sampling algorithm for bitstring states  $|x\rangle$  drawn with probabilities equal to  $|\langle x|\phi_i\rangle|^2$ . We may insert a resolution of the identity by summing over all bitstring states,

$$\langle \phi_i | \phi_j \rangle = \sum_x \langle \phi_i | x \rangle \langle x | \phi_j \rangle \quad (C1)$$

$$= \sum_x \frac{|\langle \phi_i | x \rangle|^2 \langle x | \phi_j \rangle}{\langle x | \phi_i \rangle}. \quad (C2)$$

It has been shown in [98] that the quantity  $\frac{\langle x | \phi_j \rangle}{\langle x | \phi_i \rangle}$  for randomly sampled states  $|x\rangle$  drawn with probability  $|\langle x | \phi_i \rangle|^2$  has mean equal to  $\langle \phi_i | \phi_j \rangle$  and constant variance, and hence we may compute the overlap in polynomial time up to an additive error by randomly sampling bitstrings to reconstruct the sum in Equation C2, provided that we can efficiently compute the overlap  $\langle x | \phi_j \rangle$ . Since we can efficiently evaluate the transformation of a bitstring acted on by the FSWAP network, we can efficiently compute this overlap in the restricted case of orbital permutations.

In the case of more general orbital rotations, for which the corresponding quantum circuits include non-Clifford gates, there is no way to efficiently transform a bitstring from one representation into the other without an exponentially large memory/time cost. This is because the action of a Givens rotation between two qubits maps the output to a superposition of bitstrings with probabilities determined by the rotation angle  $\theta$ . For instance, the two-qubit bitstring  $|10\rangle$  maps to

$$\hat{g}(\theta) |10\rangle = \cos(\theta) |10\rangle + \sin(\theta) |01\rangle. \quad (C3)$$

Hence the sequence of Givens rotations described in [51] to implement an arbitrary basis rotation on a bitstring with  $\eta$  ones and  $N - \eta$  zeros in the first basis will result in a superposition over  $\binom{N}{\eta}$  bitstring states in the second basis. This prevents us from efficiently evaluating the overlaps  $\langle x | \phi_j \rangle$ .

One might consider instead sampling from both matrix product states in their respective bases, and then computing the overlaps between the sampled bitstrings using techniques from classical quantum chemistry to evaluate overlaps between Slater determinants in rotated single-particle bases [54, 55, 99]. Putting aside the fact that this involves performing a classical factorization of an arbitrarily ill-conditioned matrix, it is easy to show that this approach cannot work. Consider the insertion of a

double resolution of the identity into the overlap  $\langle \phi_i | \phi_j \rangle$  over bitstrings  $|x\rangle$  in the basis of  $|\phi_i\rangle$  and bitstrings  $|y\rangle$  in the basis of  $|\phi_j\rangle$ :

$$\langle \phi_i | \phi_j \rangle = \sum_{x,y} \langle \phi_i | x \rangle \langle x | y \rangle \langle y | \phi_j \rangle \quad (\text{C4})$$

$$= \sum_{x,y} \frac{|\langle \phi_i | x \rangle|^2 \langle x | y \rangle |\langle y | \phi_j \rangle|^2}{\langle x | \phi_i \rangle \langle \phi_j | y \rangle}. \quad (\text{C5})$$

Let us take the limiting case of identical states  $|\phi_i\rangle = |\phi_j\rangle$  expressed in the same single-particle basis. Since the states are identical then their overlap should evaluate to 1. It is easy to write down an MPS of bond dimension 2 that is an equally weighted superposition over all bitstring states by setting all the tensor elements equal to 1 and normalizing. Then  $|x\rangle$  and  $|y\rangle$  will be independently sampled from the uniform distribution over all bitstring states. It is clear that for any polynomially large number of samples the probability of obtaining a nonzero overlap of  $|\phi_i\rangle$  with itself will be  $O(\frac{\text{poly}(N)}{\exp(N)})$ . It appears then that dequantization attempts relying on independently sampling from both matrix product states cannot be successful.

#### Appendix D: Generation of maximal entanglement via orbital rotations

Here our objective is to find an orbital rotation that maps an unentangled bitstring state to a state with maximal Schmidt rank across the central partition. Since orbital rotations are particle number conserving, an input bistring with  $\eta$  particles (ones) will be mapped to a superposition over the  $\eta$ -particle bitstrings. We will accomplish the stated goal using the starting state  $|\vec{k}_0\rangle = |1\rangle^{\otimes N_A} \otimes |0\rangle^{\otimes N_B}$ , where  $N_A = N_B = N/2$ , by rotating into an equally weighted superposition of states

$$\hat{G} |\vec{k}_0\rangle = \frac{1}{2^{N/4}} \sum_{l=1}^{2^{N/2}} \sigma_l |\vec{k}_l^A\rangle \otimes |\vec{k}_l^B\rangle, \quad (\text{D1})$$

where  $\sigma_l \in \{\pm 1\}$ , and the set of states  $\{|\vec{k}_l^A\rangle\}$  run over all the  $2^{N/2}$  unique bitstring states defined on subsystem  $A$ , with each state  $|\vec{k}_l^B\rangle$  obtained as the bit-flipped mirror image of  $|\vec{k}_l^A\rangle$ . For instance,

$$|\vec{k}_l^A\rangle = |10110111\rangle \implies |\vec{k}_l^B\rangle = |00010010\rangle. \quad (\text{D2})$$

Thus the superposition is entirely contained within the  $N/2$ -particle subspace, and each left-right pair is a unique

pair of left- and right- bistrings, so we have that

$$\langle \vec{k}_l^A | \vec{k}_{l'}^A \rangle = \langle \vec{k}_l^B | \vec{k}_{l'}^B \rangle = \delta_{ll'}. \quad (\text{D3})$$

Consequently, Equation D1 denotes a Schmidt decomposition of  $\hat{G} |\vec{k}_0\rangle$  over the  $A/B$  partition, with Schmidt rank equal to  $2^{N/2}$  and maximal von Neumann entropy across the partition. We construct the transformation  $\hat{G}$  using a sequence of  $\pi/2$  and  $\pi/4$  pairwise orbital rotations, where the  $\pi/4$  rotation gate is given by

$$\hat{g}(\frac{\pi}{4}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (\text{D4})$$

and we choose a phase convention for the  $\pi/2$  gate so that it is equal to the FSWAP gate given in Equation A23. The  $\pi/2$  gate acts ‘deterministically’ on a bitstring state, in that each input bitstring is mapped to a single output bitstring, and this gate will be used to move particles between neighboring positions. The  $\pi/4$  gate acts ‘non-deterministically’, mapping a unique bitstring to a superposition of ‘swapped’ and ‘non-swapped’ bitstrings, and will be used to generate entanglement across the  $A/B$  partition. The procedure is as follows: starting from the bitstring  $|\vec{k}_0\rangle$ , the application of a  $\pi/4$  gate on the qubits on either side of the partition boundary results in the state

$$\frac{1}{\sqrt{2}} \left( |1 \dots 11\rangle \otimes |00 \dots 0\rangle \right. \quad (\text{D5})$$

$$\left. + |1 \dots 10\rangle \otimes |10 \dots 0\rangle \right). \quad (\text{D6})$$

A sequence of FSWAPs is then applied within the bulk of each partition to deterministically move the particle in the right partition to site  $N$ , and the ‘hole’ in the left partition to site 1, resulting in the state

$$\frac{1}{\sqrt{2}} \left( (-1)^{N/2-1} |11 \dots 1\rangle \otimes |0 \dots 00\rangle \right. \quad (\text{D7})$$

$$\left. + |01 \dots 1\rangle \otimes |0 \dots 01\rangle \right). \quad (\text{D8})$$

Another  $\pi/4$  gate is then applied at the boundary, resulting in a superposition over four unique bitstring state pairs, and the newly transferred particle and ‘hole’ are moved to the ‘next available’ sites, i.e. sites  $N-1$  and 2 respectively. Repeating this procedure  $N/2$  times yields the desired superposition in Equation D1, and parallelizing these operations results in the ‘diamond-shaped’ tensor network to construct  $\hat{G}$  as depicted in Figure 3.