A Jastrow-type decomposition in quantum chemistry for low-depth quantum circuits

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We propose an efficient $O(N^2)$-parameter ansatz that consists of a sequence of exponential operators, each of which is a unitary variant of Neuscamman’s cluster Jastrow operator. The ansatz can also be derived as a decomposition of $T_2$ amplitudes of the unitary coupled cluster with generalized singles and doubles, which gives a near full-CI energy, and reproduces it by extending the exponential operator sequence. Because the cluster Jastrow operators are expressed by a product of number operators and the derived Pauli operator products, namely the Jordan-Wigner strings, are all commutative, it does not require the Trotter approximation to implement to a quantum circuit and should be a good candidate for the variational quantum eigensolver algorithm by a near-term quantum computer. The accuracy of the ansatz was examined for dissociation of a nitrogen dimer, and compared with other existing $O(N^2)$-parameter ansatzes. Not only the original ansatz defined in the second-quantization form but also their Trotterized variants, in which the cluster amplitudes are optimized to minimize the energy obtained with a few, typically single, Trotter steps, were examined by quantum circuit simulators.

I. INTRODUCTION

Quantum chemistry is gaining more attention as a promising field of application of quantum computers because of its high affinity to the qubit representations and universal gate operations. An obvious advantage of quantum computers on quantum chemical calculations is that occupation-number vectors of the second quantization can be naturally mapped to the qubit representation by the Jordan-Wigner or Bravyi-Kitaev transformations, and arbitrary state in the vector space and unitary transformation are expressed by the qubits and quantum gates, while the space is usually truncated for the case of classical computers because the dimension of the vector space, namely the full-CI space, grows exponentially with the number of one-particle basis.

While quantum algorithms for numerical linear algebra is currently being developed, so far there are two main approaches for computing eigenvalues of the second-quantized electronic Hamiltonian. The first developed method is the phase estimation algorithm (PEA) in which an approximated eigenstate prepared on quantum registers is propagated with the Hamiltonian to encode the eigenvalue into the relative phases of binary states of ancilla qubits and the phase is decoded by a fractional binary expansion via the inverse quantum Fourier transformation (QFT). In theory, a desired precision $\epsilon$ can be achieved with a cost of $O(1/\epsilon)$, but in reality it largely increases the demand for coherence time, which is severe for near-term quantum computers without error corrections. There have been many attempts to mitigate the requirements, such as the iterative PEA which does not require the QFT. The second method is the variational quantum eigensolvers (VQE) in which a quantum computer is used only for evaluating energy expectation values of trial wavefunctions that are defined by a set of parameters, which are optimized by a classical computer. One of the advantages of the VQE over the PEA is that once a trial wavefunction is prepared, the measurements only require simple single qubit rotations, which should greatly reduce the coherence time requirements, ideally $O(1)$. In addition, the recent developments of the quantum algorithms for the evaluation of the derivatives with respect to the parameters in the exponents should greatly accelerate the variational optimization. The VQE is therefore a promising candidate algorithm in the noisy intermediate scale quantum computers (NISQ) era though the required times of measurements increases as $O(1/\epsilon^2)$ to achieve a desired precision $\epsilon$.

It is therefore important to develop an efficient wavefunction ansatz that requires only a small number of quantum gates to prepare on a quantum circuit. The widely-used unitary coupled cluster with singles and doubles (uCCSD) ansatz has $O(N^4)$ variational parameters and the depth should grow as $O(N^3)$ at least. A number of $O(N^2)$-parameter ansatz have been developed, such as the low-depth ansatz and low-rank approximation, and recently, k-fold products of unitary pair coupled cluster with generalized singles and doubles (UpCCGSD). Another obstacle to implement exponential operator ansatzs to quantum circuits is that all the Pauli operator products

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produced by the Jordan-Wigner or Bravyi-Kitaev transformations of the second quantized operators in an exponent
need to be split to a product of the exponential operators, each of which has only single Pauli product in the
exponent. It means many Trotter steps should be performed before the measurement if one wants to compute the
energy expectation value accurately as provided by the definition written in the second quantized operators. One
way to work around this problem is to adopt hardware oriented ansatizes, such as the hardware efficient ansa
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zar27 or an
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incremental adaptive scheme.
In this study, we present an efficient O(N²)-parameter ansatz for the VQE algorithm termed k-uCJ that consists
of repeated k-times multiplication of a unitary variant of the cluster Jastrow (CJ) exponential operator29,30
and can reproduce the generalized unitary coupled cluster (uCCGSD) ansatz26,31,32 by increasing k, which can give a
near full-CI energy.

II. THEORY

In this section, matrices can be real or complex. For clarification, they are denoted by italic and calligraphy letters,
e.g. K and \( \mathbb{K} \), respectively.

A. Unitarization of the CJ ansatz

An efficient parametrization for \( T_2 \) amplitudes of generalized CC, named as cluster Jastrow (CJ) ansatz
\[
T_{pσqσrτsτ} \simeq T_{pσqσrτsτ}^{CJ} = \sum_{jl} U_{pq} U_{qj} J_{jl}^{(στ)} U_{rl} U_{sl},
\]
was introduced by Neuscamman29,30 in his cluster Jastrow anti-symmetric geminal power (CJAGP) ansatz. Simultaneous optimization of the parameters \( U, J \) and the AGP reference function with a variational Monte Carlo
method provided an efficient and accurate description of both weak and strong electron correlation29,30,33,34. In the
CJ ansatz, the 4-index cluster operator \( \hat{T}_{CJ} \) is decomposed to two 2-index operators
\[
\hat{e}^{J_{CJ}} = \hat{e}^{K} \hat{e}^{J} e^{-\hat{K}}
\]
where
\[
\hat{T}_{CJ} = \sum_{pqrs,στ} T_{pqrs,στ}^{CJ} a_{pσ}^\dagger a_{qσ}^\dagger a_{rτ}^\dagger a_{sτ},
\]
\[
\hat{J} = \sum_{jl,στ} J_{jl}^{(στ)} a_{jσ}^\dagger a_{lτ}^\dagger a_{jσ} a_{lτ},
\]
\[
\hat{K} = \sum_{p<q,σ} K_{pq}(a_{pσ} a_{qσ} - a_{qσ}^\dagger a_{pσ}^\dagger)
\]
While \( e^{\hat{K}} \) is an orbital rotation operator and easy to map to quantum gates, \( \hat{J} \) is symmetric with respect to permutation
of the indices \( j \) and \( l \) and thus \( e^{\hat{J}} \) cannot be unitary if one restricts \( J \) to real matrices. The matrix \( J \) needs to be
replaced by pure imaginary matrices \( \mathcal{J} \) in order to make \( e^{\hat{J}} \) unitary operator, and we introduce a unitary variant of
the CJ ansatz, uCJ ansatz, by replacing \( \hat{K} \) and \( \hat{J} \) in Eq. (2) by
\[
\hat{K} = \sum_{pq,σ} K_{pq} a_{pσ}^\dagger a_{qσ},
\]
\[
\hat{J} = \sum_{jl,στ} \mathcal{J}_{jl}^{(στ)} a_{jσ}^\dagger a_{lτ}^\dagger a_{jσ} a_{lτ},
\]
where \( K \) is a complex anti-Hermite matrix and \( \mathcal{J}^{αα}(=\mathcal{J}^{ββ}), \mathcal{J}^{αβ}(=\mathcal{J}^{βα}) \) are pure imaginary symmetric matrices with
respect to the indices \( k \) and \( l \). Note that when we restricted \( K \) to real anti-symmetric matrices, energy expectation
values by the ansatz never fell below that of reference wavefunctions. The cluster amplitudes of uCJ are therefore generally complex numbers

$$T_{p,q,s,r,s'} \simeq T_{p,q,s,r,s'}^{\text{uCJ}} = \sum_{jl} U_{pj} U_{qj}^* \sigma_{jl} U_{rj} U_{sl}^*.$$  (8)

It is possible to restrict the amplitudes to real numbers by adding its complex conjugate $T_{p,q,s,r,s'} + T_{p,q,s,r,s'}^*$, but we found that the variational energy is not different from that with Eq. (8).

### B. Extension of uCJ ansatz

To recover the uCCGSD limit in Eq. (8), it is natural to extend the uCJ ansatz by introducing an extra index $x$ to $J$ and $K$ as

$$T_{p,q,s,r,s'} \simeq \sum_{x=1}^k \sum_{jl} U_{pj}^x U_{qj}^* \sigma_{jl}^x U_{rj} U_{sl}^x.$$  (9)

It is closely related to the low-rank approximation to the CCSD amplitudes recently introduced by Motta and co-workers, and originally by Peng and Kowalski to 4-index two-electron repulsion integrals as will be described in Appendix. The low-rank decomposition can be easily extended to uCCG cluster operator as

$$\hat{T}_{\text{CCG}} = \hat{T}_{\text{CCG}}^0 + \sum_{pqrs} \hat{a}_p^1 \hat{a}_q^1 \hat{a}_r^1 \hat{a}_s^1$$

thus

$$T_{p,q,s,r,s'}^{\text{uCCG}} = \sum_{pqrs} \sum_{x=1}^k \sum_{jl} \left\{ \sum_{pq} \left[ \left( \Sigma_{pq} L_{pq}^{x+} \hat{a}_p^1 \hat{a}_q^1 \right)^2 + \left( \Sigma_{pq} L_{pq}^{x-} \hat{a}_p^1 \hat{a}_q^1 \right)^2 \right] \right\}$$

$$= \frac{1}{2} \sum_{pqrs} \sum_{x=1}^k \sum_{jl} \left\{ \sum_{pq} \left[ \left( \Sigma_{pq} U_{pq}^{x+} \lambda_j^x \hat{a}_p^1 \hat{a}_q^1 \right)^2 + \left( \Sigma_{pq} U_{pq}^{x-} \lambda_j^x \hat{a}_p^1 \hat{a}_q^1 \right)^2 \right] \right\}$$

$$= \frac{1}{2} \sum_{pqrs} \sum_{x=1}^k \sum_{jl} \left\{ \sum_{pq} \left[ \left( \Sigma_{pq} U_{pq}^{x+} \lambda_j^x \hat{a}_p^1 \hat{a}_q^1 \right)^2 + \left( \Sigma_{pq} U_{pq}^{x-} \lambda_j^x \hat{a}_p^1 \hat{a}_q^1 \right)^2 \right] \right\}$$

(10)

thus

$$T_{p,q,s,r,s'}^{\text{uCCG}} = \frac{1}{2} \sum_{pqrs} \sum_{x=1}^k \sum_{jl} \left\{ \sum_{pq} \left( \Sigma_{pq} U_{pq}^{x+} \lambda_j^x \hat{a}_p^1 \hat{a}_q^1 \right)^2 + \left( \Sigma_{pq} U_{pq}^{x-} \lambda_j^x \hat{a}_p^1 \hat{a}_q^1 \right)^2 \right\}$$

(11)

where $L^\pm$, $U^\pm$, and $\lambda^\pm$ are obtained by SVD

$$T_{pq,rs} = \sum_x V_{pq,x} \sigma_x V_{rs,x}$$

$$= \sum_x (\sqrt{\sigma_x} V_{pq,x})(\sqrt{\sigma_x} V_{rs,x})$$

$$= \sum_x \sigma_x L_{pq,x}^x L_{rs,x}^x$$

(12)
operators with different exponents. Note that the product form and the single exponential form are not equivalent because the unitary matrices are not restricted to rank-one matrices. The convergence to the exact amplitude should be much faster, i.e. more accurate with the same number of terms, $k$, for truncating the summation over $x$. Hereafter, they are denoted by the SVD($k$) and uCJ($k$) decompositions, respectively.

Instead of the single exponent form $e^{-iJx}$, we adopt a product form of the uCJ exponential operators

$$\hat{J}^x = \hat{J}_1^x + \hat{J}_2^x + \cdots$$

since the latter is more suitable for quantum computation. In this study, it is termed as $k$-uCJ ansatz since this splitting exponential operator form is analogous to $k$-fold products of ($k$)-UpCCGSD ansatz recently introduced by Lee and co-workers, in which a product of exponential operators of the pair coupled cluster double ($k$)-UpCCGSD with the generalized singles. Note that the product form and the single exponent form are not equivalent because the uCJ operators with different $x$ are not commutative, but we observed that these two forms gave very close variational energies if all the parameter are simultaneously optimized based on each ansatz.

C. Some considerations for implementation of the exponential ansatzs on quantum circuits

In principle, any unitary operation can be represented by quantum gates on universal quantum computer, but so far most of the quantum algorithms for quantum chemistry rely on the mapping of an exponential of a product of Pauli operators to a set of quantum gates consisting of CNOT and single qubit gates. Those Pauli operators are produced by the Jordan-Wigner or Bravyi-Kitaev transformations of the second-quantized operators of quantum chemistry.

For example, application of the elementary creation and annihilation operators are represented by the Pauli-X, Y, Z gates in the Jordan-Wigner transformation as

$$a_p^\dagger = \frac{1}{2}(\sigma_p^x \otimes \sigma_{p-1}^z - i \sigma_p^y \otimes \sigma_{p-1}^z)$$

$$a_p = \frac{1}{2}(\sigma_p^x \otimes \sigma_{p-1}^z + i \sigma_p^y \otimes \sigma_{p-1}^z)$$

where $\sigma_{-p}^z \equiv \sigma_p^z \otimes \sigma_{p-1}^z \otimes \cdots \sigma_1^z \otimes \sigma_0^z$, and thus an exponential operator $e^\tau$ is represented by an exponential of a summation of Pauli operator products, $e^{x} \sum_l \theta_l (\Pi_{\nu \in I} \sigma_{\nu})$. Note that the imaginary unit $i$ in the exponent reflects unitarity of the cluster operator $\hat{\tau}$. To compute an exponential operator $e^\tau$ on a quantum circuit accurately, one therefore needs to resort to the Trotter decomposition, e.g.

$$e^{x} \sum_l \theta_l (\Pi_{\nu \in I} \sigma_{\nu}) \approx \left( \prod_l e^{i\theta_l n^{-1} \Pi_{\nu \in I} \sigma_{\nu}} \right)^n,$$

because the Pauli operator products $\Pi_{\nu \in I} \sigma_{\nu}$ are usually not commutative. The many Trotter steps should increase the depth of the circuit. One way to avoid this problem is to simply adopt the single Trotter step form $\prod_l e^{i\theta_l \sigma_{\nu}}$, or $n$-step form, as an alternative ansatz. In fact, it was demonstrated that the single Trotter step ansatz of uCCSD gave nearly identical variational energies to the original uCCSD ansatz for a H$_2$ molecule. Hereafter, the Trotter $n$-step ansatz is denoted by a superscript ‘circ/n’ to the corresponding original ansatz, e.g. the energy of the $k$-CJF$^{\text{circ/n}}$ ansatzs are evaluated by performing the $n$-times symmetric Trotter steps with the $k$-CJF ansatz, respectively. In
fact, we found that not all exponential ansatz are compatible with their Trotter n-step ansatzs as will be shown in Sec. III B.

Interestingly, the \( k \)-uCJ ansatz defined by Eq. (9) can be implemented without the Trotter approximation by nature. Because the operator \( \hat{J} \) only have the number operators

\[
a^\dagger_p a_p a^\dagger_q a_q = \frac{1}{4} (1 - \sigma^z_p)(1 - \sigma^z_q),
\]

which are written by \( \sigma^z \) matrices, they are all commutative. If the orbital rotations \( e^{\hat{K}} \) is implemented by using the Givens rotations \( 44,45 \), one can implement the \( k \)-uCJ to a quantum circuit without use of Trotter approximation.

III. RESULTS AND DISCUSSION

An important field of applications of quantum computation in quantum chemistry is the multireference problem where rigorous algorithms with polynomial cost are not well established though a lot of effort has been devoted, such as \textit{ab initio} density-matrix renormalization group theory.\textsuperscript{46,47} We examined the performance of various exponential ansatzs on the description of triple bonds dissociation of \( \text{N}_2 \) molecule with the STO-6G basis sets. The six Hartree-Fock canonical orbitals, HOMO—2 to LUMO+2, were used to construct the Fock space represented by a quantum register on a circuit simulator, i.e. the \( \alpha \) and \( \beta \) spin-orbital were assigned to twelve qubits. The ordering and character of the six canonical orbitals remain unchanged between \( r = 1.0 - 2.4 \text{ \AA} \) bond length.

A. Variational minimization without the Trotter approximation

First, we examined the accuracy of the \( k \)-uCJ ansatz and various existing exponential ansatzs with the HF reference function. At this point, the energy expectation values were evaluated not by using a quantum circuit simulator but by the standard matrix exponentiations, and thus the Trotterization was absent. Figure 1a (top panel) shows the potential energy curves of the full-CI and \( k \)-uCJ (\( k=1,2,3 \)) ansatzs and the SVD low-rank approximation by Eq.(11). The result of the conventional CCSD calculations is also shown for comparison.

The 1-uCJ works well at around the equilibrium bond length, e.g. the energy deviates from the full-CI by 6 mE\(_h\) at \( r=1.2 \text{ \AA} \), where the multireference effect is not so significant, but it cannot describe the dissociation correctly. The error is rapidly decreased by increasing \( k \), e.g. less than 1 mE\(_h\) at around the equilibrium bond length and at the dissociation. It was also observed that the convergence to the full-CI energy is relatively slow at the intermediate region and the maximum error is 7 mE\(_h\) with \( k=2 \), and 3 mE\(_h\) with \( k=3 \) at \( r=2.0 \text{ \AA} \).

The SVD low-rank approximation by Eq. (11) was found to be problematic for this system. Not only the convergence to the reference full-CI energy is slower than the \( k \)-uCJ even at the equilibrium bond length region, but we also found that it becomes pathologically slow when the multireference effect is important. In the first place, to describe the dissociation correctly by the low-rank approximation, we needed to optimize the reference \( T_2 \) amplitude by more expensive ansatz, e.g. the uCCGD, that can correctly describe the dissociation. The SVD low-rank approximation is not suited for this kind of purpose.

The \( k \)-uCJ ansatz has similarity to the \( k \)-UpCCGSD ansatz since both ansatzs take a product of the single exponential operators uCJ or UpCCGSD, and the number of parameters grows only quadratically \( O(N^2) \) with the number of orbitals \( N \) if \( k \) is constant, and thus is expected to be expressed by a quantum circuit with linear \( O(N) \) depth. Figure 1b (bottom panel) shows the potential energy curves obtained with 1-uCJ and \( k \)-UpCCGSD ansatzs. The result of 1-uCJ with AGP ansatz, in which the exponential operator of 1-uCJ was applied to the AGP reference wavefunction and all the parameters including the AGP itself were simultaneously optimize, is also shown for comparison.

The CJ exponential operator was originally combined with the anti-symmetric geminal power (AGP) reference wavefunction in the original CJ-AGP ansatz,\textsuperscript{29} which are expected to serve complementary roles to describe the electron correlation and can give better description than that with the HF reference. In fact, its unitary variant, 1-uCJ-AGP ansatz, well reproduced the full-CI results both at equilibrium bond length region and at dissociation region with less than 5 mE\(_h\) error. It should be noted that relatively large error was observed at the intermediate region, e.g. \( \sim 25 \text{ mE}_h \) error at \( r=1.7 \text{ \AA} \), though the CJ-AGP ansatz almost perfectly reproduced the full-CI result for
whole the bond stretching ($r=1.01.8$) in the original work by Neuscamman. The unitarization could slightly weaken the flexibility of the CJ ansatz.

The k-UpCCGSD ansatz with $k = 1$ is not adequate for describing the PEC, and the error is rapidly decreased by increasing $k$, while the convergence to the full-CI energy is bit slower than the $k$-CJ in particular at around the equilibrium bond length and at the dissociation. Again, the energies were computed based on the original definitions written in the second quantized operator, and there is no guarantee that those can also be reproduced efficiently by the quantum gates on quantum circuits if the cluster operators are not commutative. This point will be examined in the next subsection.

B. Variational energies with the Trotter splitting ansatzs

In the previous subsection, all the energies were evaluated by using matrix exponentiation as provided by the definitions written in the second quantization. As noted above, however, most of the exponential ansatzs, except for the $k$-uCJ, require the Trotter decomposition to be accurately computed on quantum circuits. Here, instead of performing the time consuming many Trotter steps to reproduce the original ansatzs, we adopted the alternative ansatzs that are defined by the single or $n$-times Trotter steps for the summation over the Pauli operator products.
produced by the Jordan-Wigner transformation of the original ansatzs.

Figure 2 shows the potential energy curves obtained with the 1-UpCCGSD$^{\text{circ} / n}$ and $k$-uCJ$^{\text{circ} / n}$ ansatzs. As expected, the $k$-uCJ$^{\text{circ} / 1}$ reproduced the results of the original $k$-uCJ ansatz. However, it is somewhat surprising that the potential energy curve of the 1-UpCCGSD$^{\text{circ} / 1}$ was much different from that of the original 1-UpCCGSD ansatz, in fact the 1-UpCCGSD$^{\text{circ} / 1}$ is less powerful than the 1-UpCCGSD ansatz. To find a clue to these discrepancies, we performed another variant of the 1-UpCCGSD in which the singles and doubles operators were split as $e^{T_1 - T_1^\dagger} e^{T_2 - T_2^\dagger}$ instead of $e^{(T_1 + T_2) - (T_1 + T_2)^\dagger}$, hereafter denoted by 1-UpCCGSD$^{\text{split} - (T_1, T_2)}$. Interestingly, the potential energy curve of the UpCCGSD$^{\text{split} - (T_1, T_2)}$ is nearly identical to that of the 1-UpCCGSD$^{\text{circ} / 1}$. It clearly suggests that the large discrepancies between the 1-UpCCGSD and 1-UpCCGSD$^{\text{circ} / 1}$ is mainly caused by splitting the singles and doubles cluster operators, which should be caused accompanying the splitting of the products of the Pauli operators in the single Trotter step approximation. As shown, the 1-UpCCGSD$^{\text{circ} / n}$ is converged to the result of the original 1-UpCCGSD by increasing the number of the Trotter steps as $n=1,3,5$.

IV. SUMMARY

In this study, we present an efficient $O(N^2)$-parameter ansatz for the VQE algorithm, named $k$-uCJ ansatz, which is related to a tensor decomposition of the coupled cluster amplitudes specifically generalized CC, and should be converged to the uCCGD accuracy by increasing the number of terms, $k$. Each term of the expansion is identical to the unitary variant of the cluster Jastrow (CJ) ansatz introduced by Neuscamman, though the Jastrow parameters are restricted to pure imaginary by the unitarization and the physics captured by the ansatz can be different from the CJ ansatz. It was confirmed that the $k$-CJ ansatz rapidly converged to the full-CI energy with increasing the $k$, and the chemical accuracy can be obtained with $k=3$ for the triple bond dissociation of the N$_2$ molecule.

The accuracy of the exponential ansatzs were examined not only with their original definition but also with their ‘hardware-friendly’ variants, in which all the Pauli products generated by the Jordan-Wigner transformation are split by a few, typically single, Trotter steps. Interestingly, the single Trotter step variants gave nearly identical potential energy curves to the original single exponential ansatz except for the $k$-UpCCGSD$^{\text{circ} / 1}$, which is considerably less accurate than the original $k$-UpCCGSD.

One of the advantages of the $k$-uCJ ansatz for quantum computation is that it does not need the Trotterization to implement on a quantum circuit because the cluster operators in each exponent are all commutative. The $k$-uCJ ansatz is therefore a good candidate for an efficient quantum computation with the near-term quantum computers. It should be noted that one drawback of the use of a product of exponential operator ansatz is that the parameter optimization is often trapped by the local minimum, as has been already reported by Lee. We also found that the use of the anti-symmetrized geminal power (AGP) reference function can improve the description of the $k$-uCJ, as
the CJAGP ansatz does, thus to improve the reference function should be another issue to be explored.

In the NISQ era, quantum computers can treat a few hundred orbitals at most, which is not quite large enough for describing the dynamical correlation in most cases. A straightforward approach to this problem is to adopt the active space model and use the VQE as an alternative to the full-CI in the active space, as done in the DMRG-CASSCF and subsequent dynamical correlation theories. In that case, the cumulant approximation to the high-order reduced density matrices should be necessary to reduce the required times of the measurements. Another approach is to cast the dynamical correlation into the active space Hamiltonian by similarity transformations in the first or second quantization, e.g. Ref [59,60] and Ref [61–64], respectively, and many others though it is not possible to list them all here. The \( k \)-uCJ ansatz is particularly suitable for this approach because the similarity transformed Hamiltonians usually possess more than two-body interactions and it is straightforward to extend the \( k \)-uCJ ansatz to more than two-body Jastrow factor forms.

V. COMPUTATIONAL DETAILS

An in-house code written in Python 3 was used to perform all the calculations. The HF canonical orbitals and molecular integrals were generated by the PySCF library and the fermionic algebra for the exponential ansatz in the Fock space and the mapping to a qubit representation by the Jordan-Wigner transformation were handled by using the OpenFermion library. The quantum circuit simulations were performed by the Qulacs library.

1. Lanyon, B. P.; Whitfield, J. D.; Gillett, G. G.; Goggin, M. E.; Almeida, M. P.; Kassal, I.; Biamonte, J. D.; Mohseni, M.; Powell, B. J.; Barbieri, M.; Aspuru-Guzik, A.; White, A. G. Towards Quantum Chemistry on a Quantum Computer. Nature Chem 2010, 2, 106–111.
2. Wecker, D.; Bauer, B.; Clark, B. K.; Hastings, M. B.; Troyer, M. Gate-Count Estimates for Performing Quantum Chemistry on Small Quantum Computers. Phys. Rev. A 2014, 90, 022305.
3. McArdle, S.; Endo, S.; Aspuru-Guzik, A.; Benjamin, S.; Yuan, X. Quantum Computational Chemistry. 2018, arXiv: 1808.10402.
4. Cao, Y.; Romero, J.; Olson, J. P.; Degroote, M.; Johnson, P. D.; Kieferová, M.; Kivlichan, I. D.; Menke, T.; Peropadre, B.; Sawaya, N. P. D.; Sim, S.; Veis, L.; Aspuru-Guzik, A. Quantum Chemistry in the Age of Quantum Computing. 2018, arXiv: 1812.09976.
5. Berry, D. W.; Gimblett, C.; Motta, M.; McClean, J. R.; Babbush, R. Qubitization of Arbitrary Basis Quantum Chemistry Leveraging Sparsity and Low Rank Factorization. 2019, arXiv: 1902.02134.
6. Motta, M.; Sun, C.; Tan, A. T. K.; Rourke, M. J. O.; Ye, E.; Minnich, A. J.; Brandao, F. G. S. L.; Chan, G. K.-L. Quantum Imaginary Time Evolution, Quantum Lanczos, and Quantum Thermal Averaging. 2019, arXiv: 1901.07653.
7. Huggins, W. J.; Lee, J.; Baek, U.; O’Gorman, B.; Whaley, K. B. A Non-Orthogonal Variational Quantum Eigensolver. arXiv:1909.09114 [physics, physics:quant-ph] 2019.
8. Parrish, R. M.; McMahon, P. L. Quantum Filter Diagonalization: Quantum Eigendecomposition without Full Quantum Phase Estimation. arXiv:1909.08925 [quant-ph] 2019.
9. Kitaev, A. Y. Quantum Measurements and the Abelian Stabilizer Problem. 1995, arXiv: quant–ph/9511026.
10. Aspuru-Guzik, A. Simulated Quantum Computation of Molecular Energies. Science 2005, 309, 1704–1707.
11. Dobciˇcek, M.; Johansson, G.; Shumeiko, V.; Wendin, G. Arbitrary Accuracy Iterative Quantum Phase Estimation Algorithm Using a Single Ancillary Qubit: A Two-Qubit Benchmark. Phys. Rev. A 2007, 76, 030306.
12. O’Malley, P. J. J. et al. Scalable Quantum Simulation of Molecular Energies. Phys. Rev. X 2016, 6, 031007.
13. Peruzzo, A.; McClean, J.; Shadbolt, P.; Yung, M.-H.; Zhou, X.-Q.; Love, P. J.; Aspuru-Guzik, A.; O’Brien, J. L. A Variational Eigenvalue Solver on a Photonic Quantum Processor. Nat Commun 2014, 5, 4213.
14. McClean, J. R.; Romero, J.; Babbush, R.; Aspuru-Guzik, A. The Theory of Variational Hybrid Quantum-Classical Algorithms. New J. Phys. 2016, 18, 023023.
15. McClean, J. R.; Babbush, R.; Love, P. J.; Aspuru-Guzik, A. Exploiting Locality in Quantum Computation for Quantum Chemistry. J. Phys. Chem. Lett. 2014, 5, 4368–4380.
16. McArdle, S.; Jones, T.; Endo, S.; Li, Y.; Benjamin, S.; Yuan, X. Variational Quantum Simulation of Imaginary Time Evolution. 2018, arXiv: 1804.03023.
17. Endo, S.; Jones, T.; McArdle, S.; Yuan, X.; Benjamin, S. Variational Quantum Algorithms for Discovering Hamiltonian Spectra. Phys. Rev. A 2019, 99, arXiv: 1806.05707.
Bartlett, R. J.; Kucharski, S. A.; Noga, J. Alternative Coupled-Cluster Ansätze II. The Unitary Coupled-Cluster Method. Chem. Phys. Lett. 1989, 155, 133–140.

Preskill, J. Quantum Computing in the NISQ Era and Beyond. Quantum 2018, 2, arXiv: 1801.00862.

Mitarai, K.; Nakagawa, Y. O.; Mizukami, W. Theory of Analytical Energy Derivatives for the Variational Quantum Eigensolver. 2019, arXiv: 1905.04054.

Motta, M.; Ye, E.; McClean, J. R.; Li, Z.; Minnich, A. J.; Babbush, R.; Chan, G. K.-L. Low Rank Representations for Quantum Simulation of Electronic Structure. 2018, arXiv: 1808.02625.

Lee, J.; Huggins, W. J.; Head-Gordon, M.; Whaley, K. B. Generalized Unitary Coupled Cluster Wavefunctions for Quantum Computation. J. Chem. Theory Comput. 2019, 15, arXiv: 1810.02327.

Kundala, A.; Mezzacapo, A.; Temme, K.; Takita, M.; Brink, M.; Chow, J. M.; Gambetta, J. M. Hardware-Efficient Variational Quantum Eigensolver for Small Molecules and Quantum Magnets. Nature 2017, 549, 242–246.

Grimsley, H. R.; Economou, S. E.; Barnes, E.; Mayhall, N. J. An Adaptive Variational Algorithm for Exact Molecular Simulations on a Quantum Computer. Nat Commun 2019, 10, 3007.

Neuscamman, E. Communication: A Jastrow Factor Coupled Cluster Theory for Weak and Strong Electron Correlation. J. Chem. Phys. 2013, 139, 181101.

Neuscamman, E. Improved Optimization for the Cluster Jastrow Antisymmetric Geminal Power and Tests on Triple-Bond Dissociations. J. Chem. Theory Comput. 2016, 12, 3149–3159.

Nakatsuji, H. Structure of the Exact Wave Function. J. Chem. Phys. 2000, 113, 2949–2956.

Nooijen, M. Can the Eigenstates of a Many-Body Hamiltonian Be Represented Exactly Using a General Two-Body Cluster Expansion? Phys. Rev. Lett. 2000, 84, 4.

Neuscamman, E. Size Consistency Error in the Antisymmetric Geminal Power Wave Function Can Be Completely Removed. Phys. Rev. Lett. 2012, 109, 203001.

Neuscamman, E. The Jastrow Antisymmetric Geminal Power in Hilbert Space: Theory, Benchmarking, and Application to a Novel Transition State. J. Chem. Phys. 2013, 139, 194105.

Peng, B.; Kowalski, K. Highly Efficient and Scalable Compound Decomposition of Two-Electron Integral Tensor and Its Application in Coupled Cluster Calculations. J. Chem. Theory Comput. 2017, 13, 4179–4192.

Stein, T.; Henderson, T. M.; Scuseria, G. E. Seniority Zero Pair Coupled Cluster Doubles Theory. J. Chem. Phys. 2014, 140, 214113.

Limacher, P. A.; Ayers, P. W.; Johnson, P. A.; De Baerdemacker, S.; Van Neck, D.; Bultinck, P. A New Mean-Field Method Suitable for Strongly Correlated Electrons: Computationally Facile Antisymmetric Products of Nonorthogonal Geminals. J. Chem. Theory Comput. 2013, 9, 1394–1410.

Boguslawski, K.; Tecmer, P.; Ayers, P. W.; Bultinck, P.; De Baerdemacker, S.; Van Neck, D. Efficient Description of Strongly Correlated Electrons with Mean-Field Cost. Phys. Rev. B 2014, 89, 201106.

Boguslawski, K.; Ayers, P. W. Linearized Coupled Cluster Correction on the Antisymmetric Product of 1-Reference Orbital Geminals. J. Chem. Theory Comput. 2015, 11, 5252–5261.

Henderson, T. M.; Bulik, I. W.; Scuseria, G. E. Pair Extended Coupled Cluster Doubles. J. Chem. Phys. 2015, 142, 214116.

Nielsen, M. A.; Chuang, I. L. Quantum Computation and Quantum Information, 10th ed.; Cambridge University Press: Cambridge; New York, 2010.

Seeley, J. T.; Richard, M. J.; Love, P. J. The Bravyi-Kitaev Transformation for Quantum Computation of Electronic Structure. J. Chem. Phys. 2012, 137, 224109.

Barkoutsos, P. K.; Gontier, J. F.; Sokolov, I.; Moll, N.; Salis, G.; Fuhrer, A.; Ganzhorn, M.; Egger, D. J.; Troyer, M.; Mezzacapo, A.; Filipp, S.; Tavernelli, I. Quantum Algorithms for Electronic Structure Calculations: Particle/Hole Hamiltonian and Optimized Wavefunction Expansions. Phys. Rev. A 2018, 98, arXiv: 1805.04340.

Wecker, D.; Hastings, M. B.; Wiebe, N.; Clark, B. K.; Nayak, C.; Troyer, M. Solving Strongly Correlated Electron Models on a Quantum Computer. Phys. Rev. A 2015, 92, 062318.

Kivlichan, I. D.; McClean, J.; Wiebe, N.; Gidney, C.; Aspuru-Guzik, A.; Chan, G. K.-L.; Babbush, R. Quantum Simulation of Electronic Structure with Linear Depth and Connectivity. Phys. Rev. Lett. 2018, 120, 110501.

White, S. R.; Martin, R. L. *Ab Initio* Quantum Chemistry Using the Density Matrix Renormalization Group. J. Chem. Phys. 1999, 110, 4127–4130.

Chan, G. K.-L.; Head-Gordon, M. Highly Correlated Calculations with a Polynomial Cost Algorithm: A Study of the Density Matrix Renormalization Group. J. Chem. Phys. 2002, 116, 4462–4476.
Appendix: Jastrow-type decomposition of the Hamiltonian

The four-index two-electron repulsion integrals (ERI) in \( \textit{ab initio} \) Hamiltonian \( \hat{H} = \sum_{pq,\sigma} f_{pq} a^\dagger_{pq} a_{q\sigma} + \sum_{pqr,s,\tau} h_{pqr,s} a^\dagger_{pq} a_{q\sigma} a^\dagger_{rs} a_{s\tau} \), can also be decomposed by the Jastrow-type parametrization, which is rather simpler.
be compared with the low-rank approximation to Hamiltonian introduced by Peng and Kowalski

\[ J \]

While full-rank matrices are more flexible than the low-rank approximation with the same number of terms, the cost of the atomic-orbital integral transformation in classical algorithms, but the Jastrow-type parametrization is again more flexible than the low-rank approximation with the same number of terms, \( k \), as shown in Figure 3. The parameters were determined by minimizing the error \( \Delta = |h - h^{\text{svd}}| \). This should be advantageous when it is used for real-time propagation by \( e^{-iHt} \) or the evaluation of the energy expectation values for VQE on quantum computers, e.g. Ref. 68 and references therein.

\[ \sum_{x=1}^{k} \sum_{j,l,\sigma} J_{j,l}^{x} A_{j,l}^{x} \t A_{j,l}^{x} = \sum_{x=1}^{k} f_{pq} a_{pq}^{a} a_{qs}^{a} + \sum_{x=1}^{k} e^{-K_{x}^{x} J_{x}^{x}} \]

where \( \t A_{j,l}^{x} = \sum_{p} a_{pq}^{t} U_{pq}^{x} \) and \( K^{x} \) and \( J^{x} \) are real matrices as in Eq. (4), (5). This Jastrow-type parametrization should be advantageous when it is used for the evaluation of the energy expectation values for VQE on quantum computers, e.g. Ref. 68 and references therein.

\[ h_{pq,s} \simeq h_{pq,s}^{\text{svd}} = \sum_{x=1}^{k} \left( \sum_{i} U_{pq}^{x} \lambda_{i}^{x} U_{iq}^{x} \right) \left( \sum_{j} U_{rl}^{x} \lambda_{i}^{x} U_{s}^{x} \right) = \sum_{x=1}^{k} \sum_{kl} U_{pq}^{x} U_{r}^{x} \lambda_{i}^{x} \lambda_{i}^{x} U_{s}^{x} U_{s}^{x}, \]

(20)

While full-rank matrices \( J^{x} \) are not separable for the indices \( j \) and \( l \) and thus may not be suitable for reducing the cost of the atomic-orbital integral transformation in classical algorithms, but the Jastrow-type parametrization is again more flexible than the low-rank approximation with the same number of terms, \( k \), as shown in Figure 3. The parameters were determined by minimizing the error \( \Delta = |h - h^{\text{svd}}| \). This should be advantageous when it is used for real-time propagation by \( e^{-iHt} \) or the evaluation of the energy expectation values for VQE on quantum computers, e.g. Ref. 68 and references therein.

(a) \( k = 2 \)

(b) \( k = 4 \)

(c) \( k = 8 \)

(d) \( k = 16 \)

FIG. 3: Potential energy curves for the low-lying singlet states of the \( N_{2} \) molecule using the STO-6G basis set where the four lowest orbitals are frozen, i.e. 6 electrons are distributed to the other 6 orbitals. \( E^{\text{JF}} \) and \( E^{\text{svd}} \) were obtained by diagonalizing the approximated Hamiltonian given by Eq. (20) and Eq. (22), respectively.