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Orbital optimized unitary coupled cluster theory for quantum computer

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We propose an orbital optimized method for unitary coupled cluster theory (OO-UCC) within the variational quantum eigensolver (VQE) framework for quantum computers. OO-UCC variationally determines the coupled cluster amplitudes and also molecular orbital coefficients. Owing to its fully variational nature, first-order properties are readily available. This feature allows the optimization of molecular structures in VQE without solving any additional equations. Furthermore, the method requires smaller active space and shallower quantum circuits than UCC to achieve the same accuracy. We present numerical examples of OO-UCC using quantum simulators, which include the geometry optimization of water and ammonia molecules using analytical first derivatives of the VQE.

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I. INTRODUCTION

Coupled cluster theory (CC) is one of the most representative electron correlation methods in quantum chemistry [1–3]. It has some vital features to describe molecular electronic structures reliably. CC is size-extensive and can be improved systematically by increasing the excitation level. It converges to full configuration interactions (FCI) faster than truncated configuration interactions (CI) or Møller-Plesset perturbation theory. Furthermore, its energy is invariant to unitary transformations among the occupied/virtual orbitals. It is well known that for an electronic state where the mean-field approximation works well, the CC models considering up to triple excitations can provide chemical accuracy (e.g., 1 kcal/mol), if sufficiently large basis functions are employed. In particular, it has been established that CC singles and doubles with perturbative triples (i.e., CCSD (T)), which incorporates three-body interactions perturbatively, is a highly accurate method. It is often called the gold standard of molecular electronic structure theory [4].

In the framework of the traditional CC (TCC), the wave-function parameters are determined by solving projected amplitude equations and not variationally. Owing to its nonvariational properties, the validity of TCC is strongly dependent on the reference Hartree–Fock wave function. Indeed, CCSD and CCSD(T) often suffer from breakdowns in the systems where static electron correlations are strong, for example, multiple-chemical-bond breaking systems [1].

This issue can be solved if a CC wave function is parametrized variationally [5]. Some benchmark studies showed that the difference between the variational CC (VCC) and TCC is small for weakly correlated regions [5–7]. Nonetheless, VCC has a factorial scaling in the computational cost. Therefore it is only applicable to a tiny system where FCI can be performed. However, it has recently been shown that a variant of VCC—unitary coupled cluster (UCC) [8–15]—can be solved at a polynomial-scaling cost using a quantum computer [16]. A UCC wave function can be prepared on a quantum computer using the Trotter approximation with a polynomial number of quantum gates. Although the gate count for the accurate UCC can be much larger than what today's quantum devices are capable of [17], UCC can be a good starting point for analyzing the power of the quantum computer in the field of quantum chemistry.

The method enabling UCC on a quantum computer is called variational quantum eigensolver (VQE), which is a kind of quantum-classical hybrid algorithm [16]. In the VQE, a wave function is prepared through a parametrized quantum circuit corresponding to a wave function ansatz (e.g., UCC). Then, we measure its energy for given circuit parameters. The parameters of the circuit are iteratively tuned by a nonlinear optimizer running on a classical computer to minimize the energy. VQE calculations using actual quantum computers have already been performed for small molecules [16,18–23]. Recently, researchers have proposed

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electron-correlation methods based on UCC for quantum computers [24–33].

Although VQE allows the determination of UCC parameters based on the Rayleigh–Ritz variational procedure, the obtained UCC wave functions are not fully variational. UCC and its variants employ a Hartree–Fock determinant as a reference wave function; the orbitals are fixed and not altered during a UCC calculation. However, it is well known that the Hartree–Fock orbitals are not optimal orbitals for a correlated wave function. One method for obtaining such optimal orbitals is to optimize orbitals in such a way that the gradients of the energy with respect to orbital rotation parameters vanish. The combination of CC with orbital optimization (OO-CC) was first briefly mentioned in the paper of Purvis and Bartlett and then introduced by Sherrill *et al.* [34,35]. Since then, orbital optimized coupled cluster doubles (OO-CCD) and its variants have been developed by various researchers [35–52].

This paper concerns the orbital-optimization technique to UCC in the context of VQE. At this moment, the size of the orbital space that can be handled by a quantum computer is severely limited because of the number of available qubits. Therefore active space approximation is indispensable when we wish to use a quantum computer for quantum chemical problems. Improvement of the active space can be achieved by optimizing molecular orbitals with the VQE, which leads to a reduced number of qubits. Furthermore, the orbital-optimized VQE (OO-VQE) is a fully variational method, and the molecular gradients of OO-VQE (e.g., forces) can be calculated without solving response equations. The idea of using the orbital-optimization techniques for quantum computers has already been reported by Reiher *et al.* for the phase estimation algorithm (PEA) [53] and by Takeshita *et al.* for the VQE [54].

In this study, we implement OO-VQE using a quantum circuit simulator; we propose an orbital optimized unitary coupled cluster doubles (OO-UCCD) as a wave-function model for OO-VQE. It must be noted that after posting the initial manuscript of this work on the arXiv preprint server, an implementation of OO-UCCD by Sokolov *et al.* was uploaded on arXiv [55]. Their study carefully performed the cost and accuracy analysis of several variants of OO-UCCD methods, while our work focused on its fully variational nature and computed analytical derivatives for geometry optimizations which are a vital part of quantum chemical calculations. To the best of our knowledge, this is the first time that geometry optimizations have been performed for polyatomic molecules using analytic first derivatives of the VQE and *ab initio* Hamiltonian.

The remainder of this paper is organized as follows. First, Sec. II describes the theory of orbital optimized UCC (OO-UCC) based on VQE. Section III provides a brief description of the implementation of OO-UCC using a quantum circuit simulator. Section III also discusses simple numerical experiments to demonstrate its usefulness. Finally, Sec. IV concludes the paper.

II. THEORY

A. Unitary coupled cluster

The molecular electronic Hamiltonian in a spin-free form is expressed as

$$\hat{H} = \sum_{p,q} h_{pq}\hat{E}_{pq} + \sum_{p,q,r,s} h_{pqrs}\{\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\}, \tag{1}$$

where h_{pq} and h_{pqrs} are one- and two-electron integrals, respectively. $\hat{E}_{pq}$ is a singlet excitation operator and is defined as $\hat{E}_{pq} = \hat{c}^\dagger_{p,\alpha}\hat{c}_{q,\alpha} + \hat{c}^\dagger_{p,\beta}\hat{c}_{q,\beta}$, where $\hat{c}^\dagger_{p,\alpha}$ and $\hat{c}_{p,\beta}$ are creation and annihilation second quantized operators, respectively. p, q, r, s are the indices of general molecular spatial orbitals.

A wave function in the traditional coupled cluster ansatz is given as

$$|\Psi\rangle = e^{\hat{T}}\,|0\rangle\,, \tag{2}$$

where $\hat{T}$ is an excitation operator $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$ and $|0\rangle$ is a reference wave function. In contrast, UCC uses an anti-Hermite operator $\hat{A}$ defined by the difference of the amplitude operator $\hat{T}$ of TCC and its Hermitian conjugate, i.e., $\hat{A} = \hat{T} - \hat{T}^\dagger$. Therefore a wave function of the UCC ansatz is expressed as

$$|\Psi\rangle = e^{\hat{A}}\,|0\rangle\,. \tag{3}$$

The Baker–Campbell–Hausdorff (BCH) expansion of the similarity transformed Hamiltonian of the traditional CC is terminated at the finite order, whereas that of UCC is not, owing to de-excitation operators $\hat{T}^\dagger$. The infinite BCH expansion makes the implementation of UCC on a classical computer unfeasible.

B. Orbital optimization

Optimizing orbitals is equivalent to minimizing a wave function with respect to orbital rotation parameters κ. The energy function of OO-UCC is given by

$$E(A,\kappa) = \langle\Psi|e^{-\hat{\kappa}}\hat{H}e^{\hat{\kappa}}|\Psi\rangle = \langle 0|e^{-\hat{A}}e^{-\hat{\kappa}}\hat{H}e^{\hat{\kappa}}e^{\hat{A}}|0\rangle\,, \tag{4}$$

where the orbital rotation operator is defined as $\hat{\kappa} = \sum_{pq}\kappa_{pq}(\hat{E}_{pq} - \hat{E}_{qp})$. When UCC parameters A are fixed, the second order expansion of the energy function becomes

$$\begin{aligned} E(A,\kappa) \approx{}& \langle\Psi|\hat{H}|\Psi\rangle + \sum_{pq}\kappa_{pq}\,\langle\Psi|[\hat{H},\hat{E}^-_{pq}]|\Psi\rangle \\ &+ \frac{1}{2}\sum_{pq,rs}\kappa_{pq}\,\langle\Psi|\,[[\hat{H},\hat{E}^-_{pq}],\hat{E}^-_{rs}] \\ &+ [[\hat{H},\hat{E}^-_{rs}],\hat{E}^-_{pq}]\,|\Psi\rangle\,\kappa_{rs}, \end{aligned} \tag{5}$$

where $\hat{E}^-_{pq} = \hat{E}_{pq} - \hat{E}_{qp}$. By taking the derivative with respect to κ, the following Newton–Raphson equation is obtained

$$\mathbf{H}\kappa = -\mathbf{g}, \tag{6}$$

whose elements are

$$H_{pq,rs} = \tfrac{1}{2}\,\langle\Psi|[[\hat{H},\hat{E}^-_{pq}],E^-_{rs}] + [[\hat{H},\hat{E}^-_{rs}],\hat{E}^-_{pq}]|\Psi\rangle \tag{7}$$

$$g_{pq} = \langle\Psi|[\hat{H},\hat{E}^-_{pq}]|\Psi\rangle\,. \tag{8}$$

H and g are often called electronic Hessian and gradients, respectively. One-particle and two-particle reduced density matrices (1RDM and 2RDM) are required to compute them in addition to the molecular Hamiltonian integrals h_{pq} and h_{pqrs}. They are readily available in VQE, because it measures 1RDM and 2RDM to compute electronic energy in a given quantum circuit.

C. Orbital optimized unitary coupled cluster doubles

The UCC singles and doubles (UCCSD) can be expressed as

$$|\Psi^{\mathrm{UCCSD}}\rangle = e^{\hat{A}_1+\hat{A}_2}\,|0\rangle\,, \tag{9}$$

where $\hat{A}_n = \hat{T}_n - \hat{T}_n^{\dagger}$ consists of n-excitation operators $\hat{T}_n$ and their conjugates. Starting from the UCCSD ansatz (9), we consider the following wave-function model by separating the singles and doubles parts:

$$|\Psi^{\mathrm{UCCSD}'}\rangle = e^{\hat{A}_2}e^{\hat{A}_1}\,|0\rangle\,. \tag{10}$$

The UCC operator $\hat{A}$ is not commutable unlike TCC, because of the existence of de-excitation operators $\hat{T}^{\dagger}$. Therefore the decomposed UCCSD ansatz is different from the original ansatz. The singles part $e^{\hat{A}_1}$ in this model is identical to the orbital rotation unitary operator $e^{\hat{\kappa}}$ that is present in Eq. (4). This implies that we can optimize its singles part $e^{\hat{A}_1}$ variationally using a classical computer via the well-established orbital-optimization technique. The singles only alter the Hartree–Fock determinant to another determinant $|\tilde{0}\rangle = e^{\hat{A}_1}|0\rangle$.

Considering the Slater determinant $|\tilde{0}\rangle$ as a reference wave function for UCC, we rewrite Eq. (10) and propose the orbital-optimized unitary coupled cluster doubles (OO-UCCD) model, given as

$$|\Psi^{\mathrm{OO-UCCD}}\rangle = e^{\hat{\tilde{A}}_2}\,|\tilde{0}\rangle\,. \tag{11}$$

The doubles part $e^{\hat{\tilde{A}}_2}$ in Eq. (11) is optimized by the VQE, while the reference determinant (i.e., the singles) is optimized by a classical computer using 1RDM and 2RDM from VQE. In the framework of VQE, these quantities need to be evaluated via measurements. Formally, measuring 2RDM scales to the fourth power with respect to the number of qubits, and it is a major bottleneck not only in VQE but also in OO-VQE. In addition, the measurement introduces statistical errors. In that sense, OO-UCCD (OO-VQE) is related to the multiconfigurational self-consistent field methods; these are based on stochastic electron correlation approaches such as full configuration interaction quantum Monte Carlo [56,57], the heat-bath CI [58], and variational Monte Carlo [59–64]. The costs and errors owing to the measurements can be reduced using simultaneous measurements and/or other techniques. Such techniques have been actively developed [65–75], and they can be used to alleviate the problems caused by measuring 1 and 2RDMs.

In practice, OO-VQE repeatedly performs the VQE and the orbital optimization until convergence. The computational cost of OO-UCCD is, therefore, higher than that of UCCSD (or UCCD) by a factor of the number of iterations (typically several to several tens of times). Nonetheless, since the number of iterations is independent of the size of a molecule, OO-UCCD is applicable to the problems where UCCD (or UCCSD) is feasible in terms of computational time. In return for this increase in computational cost owing to self-consistency, Eq. (11) has the advantage that all the wave function parameters are fully variationally determined, and it requires a less complicated quantum circuit than Eq. (10). This property makes it easy to compute the first derivative and simplifies the higher-order derivative computations, as discussed in the next subsection. Furthermore, OO-UCCD can also incorporate correlations outside the active space. Similar to other existing orbital optimization methods, this feature is beneficial, especially for the system where the orbital relaxation effects play crucial roles, and the number of orbitals is larger than the number of available qubits (e.g., transition-metal complexes).

D. Analytical first derivatives of energy

An important advantage of OO-VQE including OO-UCCD is that all the wave-function parameters are variationally determined. This feature allows us to compute first analytical derivatives of the energy without solving any additional equation. They are vital quantities for quantum chemical calculations, because static molecular properties such as forces on nuclei are defined as the derivatives of the energy with respect to external parameters x (such as a position of atom or an external electric field). Here, the energy is considered as a function of external parameters x, the VQE circuit parameters θ and the orbital parameters κ, denoted as $E(x,\theta,\kappa)$ in this subsection. Then, the first derivatives of the VQE energy are given as

$$\begin{aligned}\frac{dE(x,\theta,\kappa)}{dx} &= \frac{\partial E(x,\theta,\kappa)}{\partial x} + \frac{\partial E(x,\theta,\kappa)}{\partial \theta}\frac{\partial \theta}{\partial x}\\ &\quad + \frac{\partial E(x,\theta,\kappa)}{\partial \kappa}\frac{\partial \kappa}{\partial x},\end{aligned} \tag{12}$$

where θ and κ indicate the quantum circuit parameters and molecular orbital parameters, respectively. The first term of the right-hand side of Eq. (12) is the Hellmann-Feynman term and is equivalent to the expectation value of the derivative of the Hamiltonian. The second term is zero since the VQE variationally determines θ. In the same way, the third term is also zero when the orbital is optimized. Thus the first-order OO-VQE energy derivatives can be determined by evaluating the expectation value of the derivative of the Hamiltonian.

This is not the case for the standard VQE without OO, which needs the third term to compute the first derivatives. To obtain the orbital response $\partial\kappa/\partial x$ in that term, we must solve the following first-order coupled-perturbed Hartree–Fock (CPHF) equation:

$$\frac{\partial^2 E_{\mathrm{HF}}(x,\kappa)}{\partial\kappa\partial\kappa}\frac{\partial\kappa}{\partial x} = \frac{\partial^2 E_{\mathrm{HF}}(x,\kappa)}{\partial x\partial\kappa}, \tag{13}$$

where $E_{\mathrm{HF}}(x,\kappa)$ is the Hartree–Fock energy. In practice, we use the Z-vector technique [76,77] so that we can avoid solving Eq. (13) for each of the external parameters (e.g. each Cartesian coordinate of a molecule) [78]. The second or higher-order derivatives require not only the orbital response but also the circuit parameter response. The latter can be computed analytically on a quantum computer using a method recently developed by a few of authors of this study [79].

E. Trotterization and Brueckner orbitals

Translating the UCC generator $e^{\hat{A}}$ into a quantum circuit needs Trotterization, which introduces an error owing to the finite Trotter number. Hereafter, we denote UCCSD and UCC doubles (UCCD) approximated by the n-step Trotter expansion as UCCSD$_n$ and UCCD$_n$, respectively. The wave-function ansatz, which we implement in this study, corresponds to OO-UCCD$_1$, where the Trotter expansion is truncated at the very first step. The OO-UCCD$_1$ ansatz can be written as

$$\begin{aligned} |\Psi\rangle &= \prod_{\mu}(e^{\hat{\hat{A}}_{2,\mu}})e^{\hat{A}_1}\,|0\rangle \\ &= \prod_{\mu}(e^{\hat{\hat{A}}_{2,\mu}})\,|\tilde{0}\rangle\,, \end{aligned} \tag{14}$$

where μ is an index for each double excitation (and de-excitation) operator and $\hat{A}_2 = \sum_{\mu}\hat{A}_{2,\mu}$. Although a single-Trotter-step UCC ansatz appears to be a crude approximation, Barkoutsos *et al.* have shown that it actually reproduces ground-state energy accurately [80]. O'Malley *et al.* have pointed out that the variational flexibility allows such an approximated wave function model to absorb the Trotterization error [18].

Note that the Trotter error depends on the ordering of the operators [81,82]. This order dependency makes UCCSD$_n$ inequivalent to OO-UCCD$_n$ even when $n = 1$. The orbital rotations of OO-UCCD$_1$ alter the doubles $\hat{A}_2$ in Hartree–Fock orbitals to $\hat{\hat{A}}_2$ in OO-UCCD$_1$'s optimized orbitals, which appear in Eqs. (11) and (14). Because of this change, the ordering of the doubles in OO-UCCD$_1$ is not matched to that in UCCSD$_1$. There is, thus, a difference between UCCSD$_1$ and OO-UCCD$_1$ caused by the dependency on the ordering of the doubles. Izmaylov *et al.* have recently proposed a way to reduce the order dependency based on the Lie algebra–Lie group connection [82].

A notable feature of the OO-UCCD ansatz is that the variational orbitals coincide with the commonly known Brueckner orbitals. Brueckner orbitals are optimal orbitals for a correlated wave function, where the singles' contribution (i.e., $\hat{T}_1$ or $\hat{A}_1$) vanishes. It is known that in the TCC framework, the variationally optimized orbitals are not the same as the Brueckner orbitals. This is because of the difference between $\hat{T}_1$ and the orbital rotation operators. Meanwhile, the singles of UCC $\hat{A}_1$ are identical to the orbital rotatioon operators. Nonetheless, the Brueckner orbitals of UCCSD are not identical to the OO-UCCSD optimzied orbitals because the anti-Hermitian operators $\hat{A}_1$ and $\hat{A}_2$ are not generally commutable with each other and the Trotterization makes a difference. The OO-UCCD ansatz is based on the separation of the singles and doubles *a posteriori* as shown in Eq. (10). Therefore the OO-UCCD naturally satisfies the Brueckner condition $e^{\hat{\hat{A}}_1} = 0$ and the variational condition $\frac{\partial E}{\partial \kappa} = 0$, simultaneously: variational orbitals are Brueckner orbitals in this ansatz.

III. NUMERICAL EXAMPLES

In this section, we present some numerical results using the proposed method. Computational details are as follows. We have implemented OO-UCCD in Python using Qulacs, PySCF [83], and OpenFermion [84] program packages. Qulacs is used to simulate quantum circuits. PYSCF is used for orbital optimizations and for evaluating molecular Hamiltonian integrals [85]. OpenFermion is employed for mapping molecular Hamiltonian into a quantum circuit based on the Jordan–Wigner transformation. 1 and 2RDMs are computed not by sampling but by directly using a state vector. This implies that we have not considered (statistical) noise.

We employ the following ordering of the Trotterized operators on the quantum circuits for UCCSD$_1$ (UCCD$_1$): first, the doubles from two spatial occupied-virtual pairs; second, the doubles from the same spatial occupied-virtual pairs; finally, the singles. The double excitation operators $\hat{T}_n = t_{pq}^{rs}\hat{c}_p^{\dagger}\hat{c}_q^{\dagger}\hat{c}_r\hat{c}_s$ are generated so that the index strings *psqr* are in lexicographical order, where t_{pq}^{rs} is a doubles amplitude. Although Grimsley et al. have illustrated that the effect of the operator ordering could be significant, their results suggest that the impact of the ordering is not important in the systems used in this study [81].

A. Without the active space approximation

In this section, we show the results without the active space approximation. It means that all the orbitals were mapped into qubits. Then, the results with active space approximation will be presented in the next subsection. Hereafter, we denote the OO-UCCD and UCCSD using the active space approach as S-OO-UCCD and AS-UCCSD, respectively, to distinguish them from no-active-space calculations. In addition, the active space sizes are explicitly written after the name of an electron correlation method whenever the approximation is used. Let OO-UCCD and MP2 with the active space consisting of 6 spatial orbitals and 4 electrons be written as AS-OO-UCCD($6o$, $4e$) and MP2($6o$, $4e$), respectively.

We first investigate the potential energy curve (PEC) of LiH. Figure 1 shows the errors of our method with respect to the PECs computed by FCI and UCCSD$_1$ with the STO-3G basis sets. We did not employ the active space approximation. It can be seen that the energy difference between UCCSD$_1$ and OO-UCCD$_1$ is notably small in the entire range of the PEC. The energy deviation of OO-UCCD$_1$ from UCCSD$_1$ is 10^{-7} mhartree at 1.3 Å Li-H distance, whereas at 2.1 Å it is 3×10^{-5} mhatree. As mentioned above, the difference between UCCSD$_1$ and OO-UCCD$_1$ essentially comes from the order dependency of the doubles. Indeed, Grimsley *et al.* reported that the typical doubles-operator-order dependency results in an energy difference of an order of less than a microhartree for UCCSD$_1$ near the equilibrium geometry for LiH, whereas the magnitude of the order-dependency increases with an increase in the LiH bond length [81]. Our results are consistent with theirs.

In contrast, the deviation of UCCD$_1$ is at least five orders of magnitude larger than OO-UCCD$_1$. OO-UCCD is as accurate as UCCSD; likewise the standard OO-CCD calculations reproduce the CCSD results well. This indicates that UCCSD-level results can be obtained with a shallower quantum circuit using the orbital optimization technique at the cost of repeated VQE optimizations.

We next consider the double dissociation of the H_2O molecule using the STO-3G basis sets, where the two O-H bonds symmetrically stretch with a fixed HOH angle of 104.5°. Figure 2 illustrates that all the three unitary coupled cluster variants correctly describe the PEC of this reaction even in the bond-dissociation regime where four electrons are

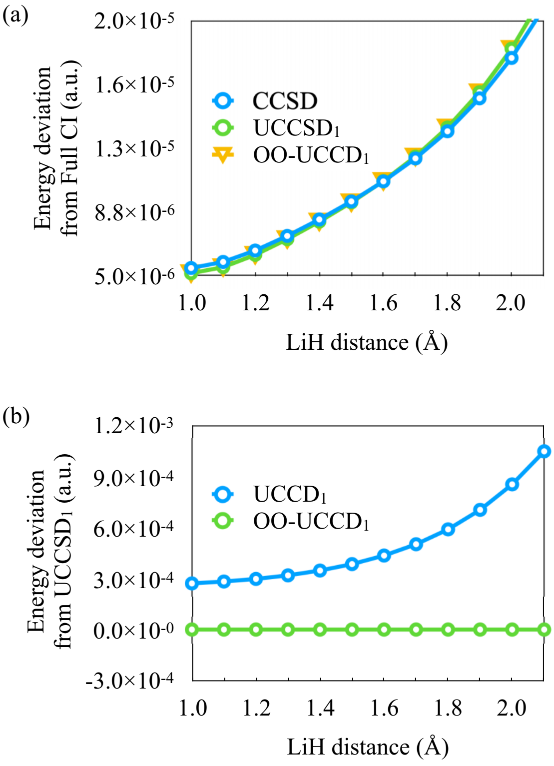

FIG. 1. Error of the OO-UCCD$_1$ method along with potential energy curves of the LiH molecule using the STO-3G basis sets. (a) Deviations from FCI energies compared with UCCSD$_1$ and the standard CCSD method. (b) Deviations from UCCSD$_1$ energies compared with UCCD$_1$.

strongly correlated. Meanwhile, as is well known, the error of CCSD with respect to FCI increases with the length of the O-H bonds, resulting in an artificial maximum at around 2.0 Å [5]. Though the PECs of UCCSD$_1$ and OO-UCCD$_1$ behaves similar to FCI, their errors also increase as the O-H distance increases. The deviations of UCCSD$_1$ and OO-UCCD$_1$ from the FCI are within 1 kcal/mol if the O-H bond length is less than 2 Å, while the error at 3 Å, where the PEC is almost flat, reaches 4 kcal/mol. This behavior of UCC is close to the results of the variational coupled cluster theory reported by Van Voorhis and Head-Gordon [5].

Third, we report the geometry optimization of the water and ammonia molecules with STO-3G basis sets using the analytical derivatives of UCCD$_1$, UCCSD$_1$, and OO-UCCD$_1$. For comparison, we carried out Hartree–Fock, MP2, CCSD, CCSD(T), and FCI calculations. The CCSD and CCSD(T) geometries were obtained by the ORCA program package using numerical gradients [86,87]. All electrons were correlated in these calculations.

Table I shows the error of the total energy from FCI for each optimized geometry and the root mean square deviation (RMSD) error of each optimized structure. The RMSD error is a commonly used measure of the structural difference of two molecules. It was computed using the deviations of Cartesian coordinates of atoms from the reference FCI values, where the molecular structure was superimposed on the reference structure. It shows that OO-UCCD$_1$ is close to FCI in terms of both structure (i.e., 3×10^{-4} Å) and energy (i.e., 0.2 mhartree). One can see that OO-UCCD$_1$ and UCCSD$_1$ provided virtually the same geometries and energies for these two systems, though they are not exactly same to each other

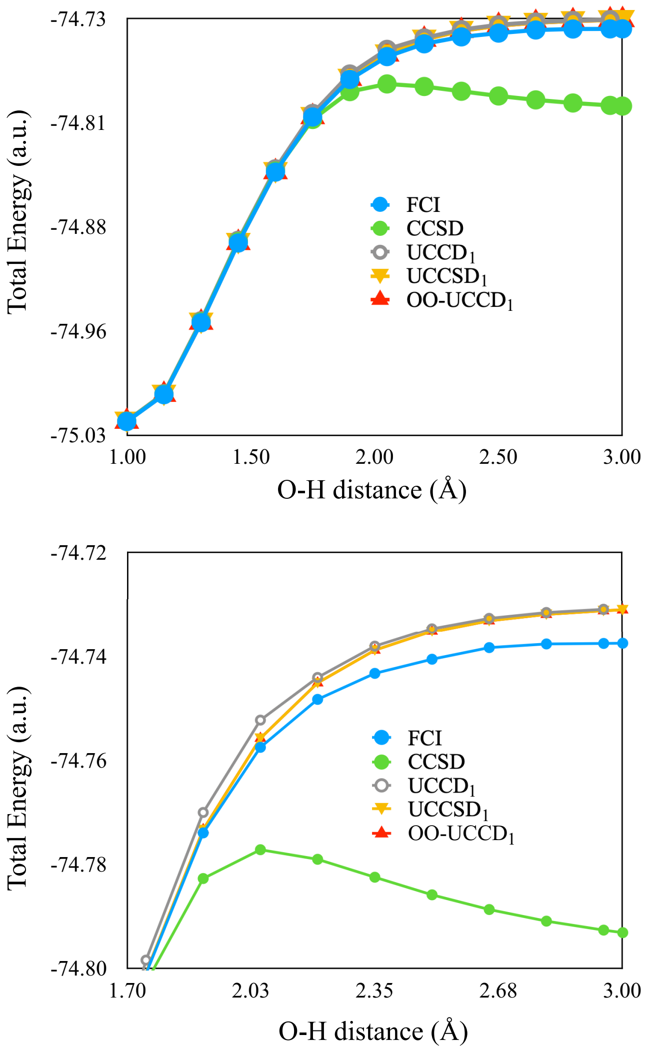

FIG. 2. Potential energy curves of the double dissociation of the water molecule's OH bonds computed at OO-UCCD$_1$, UCCD$_1$, UCCSD$_1$, CCSD, and FCI using the STO-3G basis sets.

TABLE I. RMSD errors (in angstrom) for geometries optimized by OO-UCCD$_1$/STO-3G and standard wave-function models HF, MP2, CCSD, and CCSD(T) relative to FCI. The parentheses show deviations of energies at optimized geometries from FCI.

	NH_3	H_2O
HF	3.2×10^{-2} (7.3×10^{-2})	2.4×10^{-2} (5.7×10^{-2})
MP2	9.0×10^{-3} (2.1×10^{-2})	9.3×10^{-3} (1.7×10^{-2})
CCSD	2.9×10^{-4} (2.5×10^{-4})	1.7×10^{-4} (1.5×10^{-4})
UCCD$_1$	5.1×10^{-4} (3.7×10^{-4})	5.1×10^{-4} (4.1×10^{-4})
UCCSD$_1$	3.3×10^{-4} (1.8×10^{-4})	7.1×10^{-5} (1.0×10^{-4})
OO-UCCD$_1$	3.3×10^{-4} (1.8×10^{-4})	6.7×10^{-5} (1.0×10^{-4})
CCSD(T)	8.1×10^{-5} (1.3×10^{-4})	1.7×10^{-4} (7.8×10^{-5})

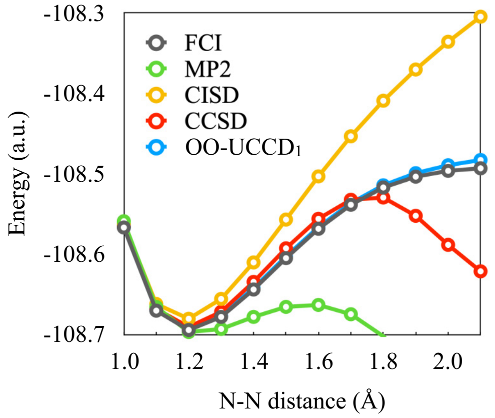

FIG. 3. Potential energy curves of the N_2 molecule computed at AS-OO-UCCD$_1$(6*o*, 6*e*), MP2(6*o*, 6*e*), CISD(6*o*, 6*e*), CCSD(6*o*, 6*e*), and FCI(6*o*, 6*e*) using the STO-3G basis sets, where six orbitals and six electrons were correlated. Other orbitals were kept fixed and not used during all the post-Hartree–Fock calculations; here, the external orbital rotation was omitted for AS-OO-UCCD$_1$(6*o*, 6*e*).

owing to the order dependency of the doubles as explained above (e.g., 4 μÅ in the RMSD error of H_2O).

On the other hand, UCCD$_1$ is less accurate than CCSD and the other two UCC models because of the lack of the singles contributions, though UCCD$_1$ is more precise than MP2. The number of the VQE parameters θ and the depth of the quantum circuits of OO-UCCD$_1$ and UCCD$_1$ were 120 and 2720, respectively, for NH_3, while those of UCCSD$_1$ were 135 and 2780, respectively. These results demonstrate that the orbital-optimization allows us to slightly reduce the circuit depth while retaining the accuracy.

Furthermore, a comparison with CCSD and CCSD(T) suggests that OO-UCCD$_1$'s energy is more accurate than that of CCSD and less accurate than that of CCSD(T) when electron correlation is weak. This tendency is consistent with the findings of Kühn *et al.* for the total energy and reaction energy [17]; in terms of geometry, OO-UCCD$_1$ is slightly better than both CCSD and CCSD(T) for H_2O, while for NH_3 it is close to CCSD and worse than CCSD(T).

B. With the active space approximation

Next, we examine the potential energy curve (PEC) of N_2 using the active space approximation. This system, involving triple bond breaking, is a well-known benchmark for electron correlation methods, where the standard methods of many body perturbation theory such as MP2, CCSD, and CCSD(T) breakdown. We have computed the PEC at the AS-OO-UCCD$_1$(6*o*, 6*e*)/STO-3G level of theory by fixing the lowest four occupied orbitals and eight electrons. Figure 3 shows the PEC along with those computed by MP2(6*o*, 6*e*), CISD(6*o*, 6*e*), CCSD(6*o*, 6*e*), and FCI(6*o*, 6*e*). It shows that AS-OO-UCCD can treat a multiple-bond-breaking system appropriately where electrons of the breaking chemical bond are strongly correlated. In this system, the differences among AS-UCCD, AS-OO-UCCD, and AS-UCCSD were small. They are at most 0.2 kcal/mol owing to the little orbital relaxation effect in the small basis sets. The root mean square deviations (RMSD) of AS-UCCD$_1$(6*o*, 6*e*) and AS-OO-UCCD$_1$(6*o*, 6*e*) with respect to AS-UCCSD$_1$(6*o*, 6*e*) PEC is 0.02 kcal/mol in the range of 1.0–2.1 Å.

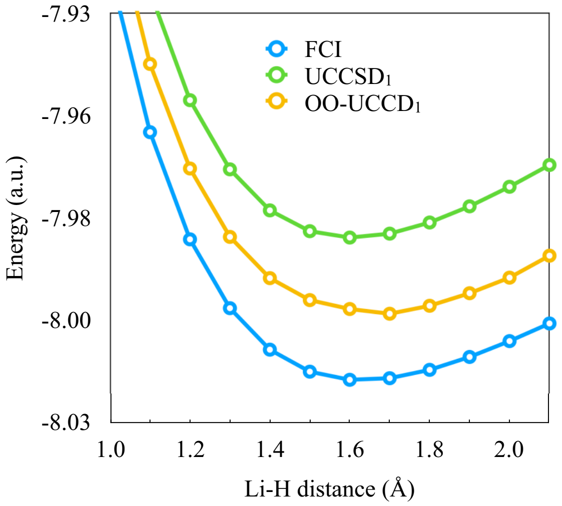

FIG. 4. Potential energy curves of the LiH molecule computed at AS-*OO*-UCCD$_1$(4*o*, 2*e*), AS-*UCCSD*$_1$(4*o*, 2*e*), and FCI using the 6-311G basis sets. AS-OO-UCCD$_1$ and AS-UCCSD$_1$ calculations employed active space consisting of four orbitals and two electrons [i.e., (4*o*, 2*e*)], while all the orbitals and electrons were correlated for FCI.

The PEC of LiH with 6-311G basis sets, given in Fig. 4, is another example. For comparison, we computed the PEC by AS-OO-UCCD$_1$(4*o*, 2*e*) and also by AS-UCCSD$_1$(4*o*, 2*e*) and FCI. Only four orbitals and two electrons were correlated in these VQE calculations, and the orbital optimization was performed for all the orbitals and electrons. This example shows how the orbital optimization effectively considers the electron correlations outside the active space. Figure 4 illustrates that AS-OO-UCCD$_1$(4*o*, 2*e*) has lower energy and is closer to FCI without active space than AS-UCCSD(4*o*, 2*e*), indicating that AS-OO-UCCD$_1$ captures more electron correlation effects.

IV. SUMMARY

In this work, we have developed OO-UCCD. OO-UCCD treats singles contributions not on quantum computers but on classical computers. All the wave function parameters are fully variationally determined in OO-UCC. This property makes the time-independent first-order properties readily available. Therefore geometry optimization or *ab initio* molecular dynamics can be performed using VQE without solving orbital response equations. Moreover, OO-UCCD incorporates the electron correlation effects outside the active space effectively. These aspects seem useful, especially in the age of noisy intermediate-scale quantum computers (NISQ) [88,89], where the number of qubits and the coherence time are severely limited. Such an OO-VQE method may be useful for solving quantum chemical problems once quantum computers become commonplace.

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[1] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).

[2] I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory*, Cambridge Molecular Science (Cambridge University Press, Cambridge, 2009).

[3] R. J. Bartlett, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 126 (2012).

[4] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[5] T. Van Voorhis and M. Head-Gordon, J. Chem. Phys. **113**, 8873 (2000).

[6] B. Cooper and P. J. Knowles, J. Chem. Phys. **133**, 234102 (2010).

[7] F. A. Evangelista, J. Chem. Phys. **134**, 224102 (2011).

[8] W. Kutzelnigg, J. Chem. Phys. **77**, 3081 (1982).

[9] W. Kutzelnigg and S. Koch, J. Chem. Phys. **79**, 4315 (1983).

[10] W. Kutzelnigg, J. Chem. Phys. **82**, 4166 (1985).

[11] R. J. Bartlett, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **155**, 133 (1989).

[12] A. G. Taube and R. J. Bartlett, Int. J. Quantum Chem. **106**, 3393 (2006).

[13] T. Yanai, Y. Kurashige, D. Ghosh, and G. K.-L. Chan, Int. J. Quantum Chem. **109**, 2178 (2009).

[14] T. Yanai and G. K.-L. Chan, J. Chem. Phys. **124**, 194106 (2006).

[15] G. Harsha, T. Shiozaki, and G. E. Scuseria, J. Chem. Phys. **148**, 044107 (2018).

[16] A. Peruzzo, J. McClean, P. Shadbolt, M.-H. Yung, X.-Q. Zhou, P. J. Love, A. Aspuru-Guzik, and J. L. O'Brien, Nat. Commun. **5**, 4213 (2014).

[17] M. Kühn, S. Zanker, P. Deglmann, M. Marthaler, and H. Weiß, J. Chem. Theory Comput. **15**, 4764 (2019).

[18] P. J. J. O'Malley, R. Babbush, I. D. Kivlichan, J. Romero, J. R. McClean, R. Barends, J. Kelly, P. Roushan, A. Tranter, N. Ding, B. Campbell, Y. Chen, Z. Chen, B. Chiaro, A. Dunsworth, A. G. Fowler, E. Jeffrey, E. Lucero, A. Megrant, J. Y. Mutus, M. Neeley, C. Neill, C. Quintana, D. Sank, A. Vainsencher, J. Wenner, T. C. White, P. V. Coveney, P. J. Love, H. Neven, A. Aspuru-Guzik, and J. M. Martinis, Phys. Rev. X **6**, 031007 (2016).

[19] A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. M. Chow, and J. M. Gambetta, Nature (London) **549**, 242 (2017).

[20] C. Hempel, C. Maier, J. Romero, J. McClean, T. Monz, H. Shen, P. Jurcevic, B. P. Lanyon, P. Love, R. Babbush, A. Aspuru-Guzik, R. Blatt, and C. F. Roos, Phys. Rev. X **8**, 031022 (2018).

[21] I. G. Ryabinkin, S. N. Genin, and A. F. Izmaylov, J. Chem. Theory Comput. **15**, 249 (2018).

[22] A. J. McCaskey, Z. P. Parks, J. Jakowski, S. V. Moore, T. D. Morris, T. S. Humble, and R. C. Pooser, npj Quantum Inf. **5**, 99 (2019).

[23] Q. Gao, H. Nakamura, T. P. Gujarati, G. O. Jones, J. E. Rice, S. P. Wood, M. Pistoia, J. M. Garcia, and N. Yamamoto, arXiv:1906.10675.

[24] I. G. Ryabinkin, T.-C. Yen, S. N. Genin, and A. F. Izmaylov, J. Chem. Theory Comput. **14**, 6317 (2018).

[25] J. Lee, W. J. Huggins, M. Head-Gordon, and K. B. Whaley, J. Chem. Theory Comput. **15**, 311 (2018).

[26] H. R. Grimsley, S. E. Economou, E. Barnes, and N. J. Mayhall, Nat. Commun. **10**, 3007 (2019).

[27] W. J. Huggins, J. Lee, U. Baek, B. O'Gorman, and K. B. Whaley, New J. Phys **22**, 073009 (2020).

[28] N. P. Bauman, E. J. Bylaska, S. Krishnamoorthy, G. H. Low, N. Wiebe, C. E. Granade, M. Roetteler, M. Troyer, and K. Kowalski, J. Chem. Phys. **151**, 014107 (2019).

[29] N. P. Bauman, G. H. Low, and K. Kowalski, J. Chem. Phys. **151**, 234114 (2019).

[30] I. G. Ryabinkin, R. A. Lang, S. N. Genin, and A. F. Izmaylov, J. Chem. Theory Comput. **16**, 1055 (2020).

[31] Y. Matsuzawa and Y. Kurashige, J. Chem. Theory Comput. **16**, 944 (2020).

[32] G. Greene-Diniz and D. M. Ramo, arXiv:1910.05168.

[33] F. A. Evangelista, G. K.-L. Chan, and G. E. Scuseria, J. Chem. Phys. **151**, 244112 (2019).

[34] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[35] C. D. Sherrill, A. I. Krylov, E. F. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 4171 (1998).

[36] A. Köhn and J. Olsen, J. Chem. Phys. **122**, 084116 (2005).

[37] R. C. Lochan and M. Head-Gordon, J. Chem. Phys. **126**, 164101 (2007).

[38] F. Neese, T. Schwabe, S. Kossmann, B. Schirmer, and S. Grimme, J. Chem. Theory Comput. **5**, 3060 (2009).

[39] C. Kollmar and A. Heßelmann, Theor. Chem. Acc. **127**, 311 (2010).

[40] U. Bozkaya, J. M. Turney, Y. Yamaguchi, H. F. Schaefer III, and C. D. Sherrill, J. Chem. Phys. **135**, 104103 (2011).

[41] U. Bozkaya and H. F. Schaefer III, J. Chem. Phys. **136**, 204114 (2012).

[42] J. B. Robinson and P. J. Knowles, J. Chem. Phys. **136**, 054114 (2012).

[43] J. B. Robinson and P. J. Knowles, J. Chem. Phys. **138**, 074104 (2013).

[44] T. N. Lan and T. Yanai, J. Chem. Phys. **138**, 224108 (2013).

[45] U. Bozkaya and C. D. Sherrill, J. Chem. Phys. **139**, 054104 (2013).

[46] K. Boguslawski, P. Tecmer, P. A. Limacher, P. A. Johnson, P. W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, J. Chem. Phys. **140**, 214114 (2014).

[47] U. Bozkaya, Phys. Chem. Chem. Phys. **18**, 11362 (2016).

[48] D. Kats and D. P. Tew, J. Chem. Theory Comput. **15**, 13 (2018).
[49] J. Lee and M. Head-Gordon, J. Chem. Theory Comput. **14**, 5203 (2018).
[50] R. H. Myhre, J. Chem. Phys. **148**, 094110 (2018).
[51] D. P. Tew and D. Kats, J. Chem. Theory Comput. **14**, 5435 (2018).
[52] T. Sato, H. Pathak, Y. Orimo, and K. L. Ishikawa, J. Chem. Phys. **148**, 051101 (2018).
[53] M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, and M. Troyer, Proc. Natl. Acad. Sci. **114**, 7555 (2017).
[54] T. Takeshita, N. C. Rubin, Z. Jiang, E. Lee, R. Babbush, and J. R. McClean, Phys. Rev. X **10**, 011004 (2020).
[55] I. Sokolov, P. K. Barkoutsos, P. J. Ollitrault, D. Greenberg, J. Rice, M. Pistoia, and I. Tavernelli, J. Chem. Phys. **152**, 124107 (2020).
[56] R. E. Thomas, Q. Sun, A. Alavi, and G. H. Booth, J. Chem. Theory Comput. **11**, 5316 (2015).
[57] G. Li Manni, S. D. Smart, and A. Alavi, J. Chem. Theory Comput. **12**, 1245 (2016).
[58] J. E. Smith, B. Mussard, A. A. Holmes, and S. Sharma, J. Chem. Theory Comput. **13**, 5468 (2017).
[59] F. Schautz and C. Filippi, J. Chem. Phys. **120**, 10931 (2004).
[60] J. Toulouse and C. J. Umrigar, J. Chem. Phys. **126**, 084102 (2007).
[61] C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, Phys. Rev. Lett. **98**, 110201 (2007).
[62] H. Luo, J. Chem. Phys. **135**, 024109 (2011).
[63] K. Haghighi Mood and A. Lüchow, J. Phys. Chem. A **121**, 6165 (2017).
[64] J. Ludovicy, K. H. Mood, and A. Lüchow, J. Chem. Theory Comput. **15**, 5221 (2019).
[65] N. C. Rubin, R. Babbush, and J. McClean, New J. Phys. **20**, 053020 (2018).
[66] A. F. Izmaylov, T.-C. Yen, R. A. Lang, and V. Verteletskyi, J. Chem. Theory Comput. **16**, 190 (2019).
[67] V. Verteletskyi, T.-C. Yen, and A. F. Izmaylov, J. Chem. Phys. **152**, 124114 (2020).
[68] T.-C. Yen, V. Verteletskyi, and A. F. Izmaylov, J. Chem. Theory Comput. **16**, 2400 (2020).
[69] A. F. Izmaylov, T.-C. Yen, and I. G. Ryabinkin, Chem. Sci. **10**, 3746 (2019).
[70] A. Jena, S. Genin, and M. Mosca, arXiv:1907.07859.
[71] P. Gokhale, O. Angiuli, Y. Ding, K. Gui, T. Tomesh, M. Suchara, M. Martonosi, and F. T. Chong, arXiv:1907.13623.
[72] W. J. Huggins, J. McClean, N. Rubin, Z. Jiang, N. Wiebe, K. B. Whaley, and R. Babbush, arXiv:1907.13117.
[73] G. Torlai, G. Mazzola, G. Carleo, and A. Mezzacapo, Phys. Rev. Res. **2**, 022060 (2020).
[74] A. Zhao, A. Tranter, W. M. Kirby, S. F. Ung, A. Miyake, and P. J. Love, Phys. Rev. A **101**, 062322 (2020).
[75] I. Hamamura and T. Imamichi, npj Quantum Inf. **6**, 56 (2020).
[76] N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984).
[77] T. Helgaker and P. Jørgensen, Theor. Chim. Acta **75**, 111 (1989).
[78] R. M. Parrish, E. G. Hohenstein, P. L. McMahon, and T. J. Martinez, arXiv:1906.08728.
[79] K. Mitarai, Y. O. Nakagawa, and W. Mizukami, Phys. Rev. Res. **2**, 013129 (2020).
[80] P. K. Barkoutsos, J. F. Gonthier, I. Sokolov, N. Moll, G. Salis, A. Fuhrer, M. Ganzhorn, D. J. Egger, M. Troyer, A. Mezzacapo, S. Filipp, and I. Tavernelli, Phys. Rev. A **98**, 022322 (2018).
[81] H. R. Grimsley, D. Claudino, S. E. Economou, E. Barnes, and N. J. Mayhall, J. Chem. Theory Comput. **16**, 1 (2019).
[82] A. F. Izmaylov, M. Díaz-Tinoco, and R. A. Lang, Phys. Chem. Chem. Phys. **22**, 12980 (2020).
[83] Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. D. McClain, E. R. Sayfutyarova, S. Sharma, S. Wouters, and G. K. Chan, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **8**, e1340 (2017).
[84] J. R. McClean, K. J. Sung, I. D. Kivlichan, Y. Cao, C. Dai, E. S. Fried, C. Gidney, B. Gimby, P. Gokhale, T. Häner, T. Hardikar, V. Havlíçek, O. Higgott, C. Huang, J. Izaac, Z. Jiang, X. Liu, S. McArdle, M. Neeley, T. O'Brien, B. O'Gorman, I. Ozfidan, M. D. Radin, J. Romero, N. Rubin, N. P. D. Sawaya, K. Setia, S. Sim, D. S. Steiger, M. Steudtner, Q. Sun, W. Sun, D. Wang, F. Zhang, and R. Babbush, Quantum Science and Technology **5**, 034014 (2020).
[85] Q. Sun, J. Yang, and G. K.-L. Chan, Chem. Phys. Lett. **683**, 291 (2017).
[86] F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 73 (2012).
[87] F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **8**, e1327 (2018).
[88] J. Preskill, Quantum **2**, 79 (2018).
[89] F. Arute, K. Arya, R. Babbush, D. Bacon, J. C. Bardin, R. Barends, R. Biswas, S. Boixo, F. G. S. L. Brandao, D. A. Buell, B. Burkett, Y. Chen, Z. Chen, B. Chiaro, R. Collins, W. Courtney, A. Dunsworth, E. Farhi, B. Foxen, A. Fowler, C. Gidney, M. Giustina, R. Graff, K. Guerin, S. Habegger, M. P. Harrigan, M. J. Hartmann, A. Ho, M. Hoffmann, T. Huang, T. S. Humble, S. V. Isakov, E. Jeffrey, Z. Jiang, D. Kafri, K. Kechedzhi, J. Kelly, P. V. Klimov, S. Knysh, A. Korotkov, F. Kostritsa, D. Landhuis, M. Lindmark, E. Lucero, D. Lyakh, S. Mandrà, J. R. McClean, M. McEwen, A. Megrant, X. Mi, K. Michielsen, M. Mohseni, J. Mutus, O. Naaman, M. Neeley, C. Neill, M. Y. Niu, E. Ostby, A. Petukhov, J. C. Platt, C. Quintana, E. G. Rieffel, P. Roushan, N. C. Rubin, D. Sank, K. J. Satzinger, V. Smelyanskiy, K. J. Sung, M. D. Trevithick, A. Vainsencher, B. Villalonga, T. White, Z. J. Yao, P. Yeh, A. Zalcman, H. Neven, and J. M. Martinis, Nature (London) **574**, 505 (2019).