**Enhancement of Complete Active Space Self-Consistent Field (CASSCF) Calculation Accuracy on Noisy Quantum Device: Use of Spin-Restricted Ansatz and Constrained Optimizer for Photo-Excitation Calculations of Ethylene and Phenol Blue Dye**

Shigeki Gocho,¹,² Hajime Nakamura,³ Qi Gao,²,⁴ Takao Kobayashi,²,⁴ Taichi Inagaki,¹,² and Miho Hatanaka¹,²,*

¹School of Fundamental Science and Technology, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan.
²Quantum Computing Center, Keio University, Yokohama 223-8522, Japan.
³IBM Quantum – IBM Research Tokyo, Tokyo, 103-8510, Japan.
⁴Mitsubishi Chemical Corporation, Science & Innovation Center, Yokohama 227-8502, Japan.
*E-mail: hatanaka@chem.keio.ac.jp

**Abstract**

Quantum chemical calculations have contributed to a better understanding of the mechanisms of chemical phenomena and rational material design. However, the calculations are still difficult for materials such as polynuclear metal complexes and photofunctional molecules because of their quasi-degenerate wavefunctions. Quantum chemical calculations on quantum computers are expected to solve this problem. Because quantum computers currently have noisiness and a short decoherence time, algorithms that are applicable to noisy intermediate-scale quantum (NISQ) devices have attracted attention. This study examined a strategy that combined a chemistry-inspired spin-restricted ansatz and a new excited state calculation method called the variational quantum eigensolver under automatically-adjusted constraint (VQE/AC). Unlike the conventional excited state calculation method, called the variational quantum deflation (VQD), the VQE/AC does not require the predetermination of hyperparameters, i.e., the weights of constraint, which indicates that the VQE/AC could have a potential to describe the smooth potential energy surfaces and to achieve the geometry optimization. To validate this strategy, the singlet ground and excited states ($S_0$ and $S_1$) of ethylene and phenol blue were computed at the complete active space self-consistent field (CASSCF) level of theory using a simulator with a realistic device noise model and the ibm_kawasaki device. The errors for the $S_0$ and $S_1$ energies were limited to 2 kcal/mol for both the Franck–Condon (FC) and conical intersection (CI) geometries even on the ibm_kawasaki device.
Introduction

Computational chemistry has contributed significantly to a better understanding of the mechanisms of chemical phenomena and rational material design. In particular, with the development of the density functional theory (DFT)\textsuperscript{1,2} and time-dependent (TD) DFT methods,\textsuperscript{3} computational chemistry has become an indispensable technology in a wide range of fields dealing with catalytic, optical, optoelectronic, magnetic, and biomimetic materials. However, the DFT and TDDFT methods are not appropriate for computing quasi-degenerated systems, in which the static electronic correlation makes a large contribution. To take into account electronic correlations, the full-configuration interaction (FCI) method and multireference (MR) calculation methods\textsuperscript{4} such as the complete active space self-consistent field (CASSCF),\textsuperscript{5} MR configuration interaction,\textsuperscript{5} MR coupled-cluster,\textsuperscript{6} MR perturbation theory,\textsuperscript{7} and MR combined with DFT methods\textsuperscript{8} have been proposed. However, their applications to large molecules, in which large active spaces are required, are too demanding. For instance, polynuclear metal complexes such as the Fe\textsubscript{7}MoS\textsubscript{9} and Mn\textsubscript{3}CaO\textsubscript{4} complexes in nitrogenase and photosynthetic photosystem II, respectively, have quasi-degenerate characteristics due to the 3d orbitals of the metals, and their computational analyses by MR calculations are still awaited.\textsuperscript{9,10} The MR calculation methods are also indispensable for exploring the potential energy surfaces (PESs) of the excited states, especially near the conical intersection (CI) region, which induces the non-radiative deactivation of optical materials.\textsuperscript{11-13}

To solve this problem, quantum chemists have given attention to developing novel methods for performing FCI or MR calculations on quantum computers.\textsuperscript{10,14-19} This is because quantum computing can, in principle, reduce the computational time for the FCI in a polynomial compared to the classical devices, which require an exponential computation time.\textsuperscript{20-24} However, because the current quantum devices, the so-called noisy intermediate-scale quantum (NISQ) devices, are hamstrung by noisiness and short decoherence times, the focus has been on calculation methods that can run on short quantum circuits.\textsuperscript{25} One of the methods suitable for NISQ devices is variational quantum optimization (VQO) including the variational quantum eigensolver (VQE)\textsuperscript{26} and variational quantum deflation (VQD).\textsuperscript{27} These methods have been applied to PESs for small molecules,\textsuperscript{28-30} periodic systems\textsuperscript{31,32} energy profiles for lithium batteries,\textsuperscript{33,34} and the excitation energies of organic light-emitting diode (OLED) emitters.\textsuperscript{35}

Over the past few years, attention has also been given to methodologies for applying the CASSCF calculation, in which the molecular orbitals are optimized with respect to the wavefunction obtained by the VQO.\textsuperscript{36-38} CASSCF calculations using quantum devices have the advantage of handling larger active spaces than those using classical devices, thereby enhancing the interpretative and predictive power of the CASSCF calculations. Moreover, these methods were recently extended to perform state-average (SA) CASSCF calculations to provide a balanced description of all the states involved in a photo-excitation system.\textsuperscript{39,40} All these pioneering studies, however, have only
validated the theoretical accuracy of CASSCF calculations on an ideal quantum computer, which is far from practical enough to be useful for the current NISQ devices.

To obtain sufficient energy accuracy for CASSCF calculations using NISQ devices, promising error mitigation approaches have been proposed. However, these techniques still do not provide sufficient accuracy for investigating the PES using the CASSCF method. For example, in the case of the ground state calculations for Li complexes, a deviation of several mHa (3-5 kcal/mol) as well as a large spin contamination were observed even with the error mitigation approach. The situation becomes much more pronounced for the excitation energy calculation of OLED emitter molecules because of the “cost function” for the excited state calculation (see Descriptions of the VQE and VQD in Results and Discussion). Thus, further improvements in the computational techniques are needed to achieve an accuracy that is approximately one order of magnitude higher than those of the current approaches.

To deal with this issue, in this work, we propose a new excited state calculation method, named VQE under automatically-adjusted constraint (VQE/AC), and combined it with an appropriate ansatz that restricts the spin multiplicity. The VQE/AC is based on a classical constrained optimization algorithm and does not require the cost function, which could cause an error in the VQD calculation. The spin-restricted ansatz can span the subspace of the target spin state, which could avoid the undesired spin contamination. The advantages of this ansatz are as follows: (1) minimum number of variational parameters to fully span the appropriate symmetry subspace and (2) shorter circuit depth than those of other conventional ansätze. To validate our strategy, we perform the CASSCF calculations for ethylene and phenol blue (4-[4-(dimethylamino)phenyl]iminoo]-2,5-cyclohexadien-1-one, shown in Scheme 1). The phenol blue is a nonfluorescent dye, which shows an ultrafast internal conversion from the excited state to the ground state after photoexcitation, and its optical properties have been investigated by both spectroscopic experiments and a theoretical simulation. From the viewpoint of an industrial application, the phenol blue is a primary skeletal structure part of indoaniline dyes, which have been applied to cyan-colored materials in photography and dye diffusion thermal transfer printings. To develop a robust dye, it is very important to locate its CI where the nonradiative decay occurs efficiently. In this paper, we first describe the basic idea of VQE, VQD, VQE/AC, and the spin-restricted ansatz. We then apply our approach to the ground and excited states of ethylene at the Frank–Condon (FC) and CI geometries, and compare it with other methods. We also demonstrate the feasibility of our approach by the excited state calculation of the phenol blue dye using the simulators and the real device called ibm_kawasaki.
Results and Discussion

Descriptions of the VQE and VQD

The VQE\textsuperscript{26} is a ground-state calculation method that uses quantum circuits. The basic idea of the VQE comes from the variational principle: the energy expectation value calculated by any trial wavefunction $\Psi(\theta)$ with parameter $\theta$ satisfies the following:

$$\langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle \geq E_0,$$

where $\hat{H}$ is a given Hamiltonian, and $E_0$ is the minimum eigenvalue. Because this equality is valid only when the trial function is the exact eigenstate of the Hamiltonian (i.e., the wavefunction of the ground state), the energy and wavefunction of the ground state can be obtained by finding the parameters $\theta$ that minimize the energy expectation value. The trial wavefunction in the VQE is constructed using a quantum circuit called \textit{ansatz}, and the energy expectation value is computed via quantum measurement. The measurement outcome and parameters are handed over to a classical optimizer, and the parameters are updated so that the energy decreases. The ground state can be obtained by repeating this process until the energy converges.

The excited states can be calculated in a manner similar to the method used by the VQE by minimizing a “cost function” instead of the energy. This method is called VQD.\textsuperscript{27} The definition of the cost function depends on the target state, as well as the target system. For instance, the cost function, $C_1(\theta)$, for the first excited state can be defined as follows:

$$C_1(\theta) = \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle + \beta | \langle \Psi(\theta) | \Psi_0 \rangle |^2,$$

where $\Psi_0$ is the ground state wavefunction that was previously obtained by the VQE, and $\beta$ is a hyperparameter that must be given before the VQD calculation. The second term of Eq. (2) implies the constraint of searching the subspace orthogonal to the ground state. The parameter $\beta$ needs to be sufficiently large (roughly speaking, greater than the energy difference between the ground state and the excited state).\textsuperscript{27} However, too large $\beta$ could lead to an undesired higher excited state. Another possible cost function, $C_2(\theta)$, that can be used to calculate the first singlet excited state as follows:\textsuperscript{27}

$$C_2(\theta) = \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle + \beta | \langle \Psi(\theta) | \Psi_0 \rangle |^2 + \gamma \langle \Psi(\theta) | \hat{S}^2 | \Psi(\theta) \rangle,$$

where $\gamma$ is a hyperparameter that constrains the search to a singlet. This cost function is useful for calculating organic molecules whose optical functions are mainly determined by the characteristics of the first singlet excited state ($S_1$) and the singlet ground state ($S_0$). With appropriate hyperparameters, the VQD with the cost function $C_2(\theta)$ could give the $S_1$ state, while that with
$C_1(\theta)$ could give the lowest triplet excited state ($T_1$). When the spin multiplicity of the target state is constrained to be a singlet by the ansatz (as mentioned below), however, the VQD with $C_1(\theta)$ could also give the $S_1$ state.

**VQE under automatically-adjusted constraint (VQE/AC)**

Another way to minimize the energy with the constraint of the orthogonality to the ground state is to apply constrained optimization using a linear approximation (COBYLA), which is a numerical optimization method that does not require the derivative of the objective function (i.e., the energy). To obtain the first excited state, the energy expectation value is minimized with the constraint of the overlap such as $|\langle \Psi(\theta)|\Psi_0 \rangle|^2 \leq 10^{-4}$. In other words, the weight of the constraint, which corresponds to $\beta$ in VQD, is automatically adjusted within the algorithm of the COBYLA. We named this excited state calculation VQE under automatically-adjusted constraint (VQE/AC). There are two advantages to VQE/AC. First, the cost function tuning is not required, unlike VQD. The second is the applicability to higher excited state calculations because more than two constraints can be considered in the COBYLA. Because the number of constraints does not increase exponentially, the computational cost of a higher excited state calculation should not be too demanding.

**Spin-restricted ansatz**

The spin multiplicity of the trial wavefunction can be restricted using an ansatz called the spin-restricted ansatz. As an example to illustrate the ansatz that restricts the trial wavefunction to a singlet, consider a wavefunction represented by the electronic configurations obtained by the active space with two electrons in two orbitals (i.e., HOMO and LUMO). Under the constraints of the electron number, $N = 2$, and the spin $z$-projection, $S_z = 0$, the active space can be mapped to the qubit space in the manner of parity mapping as follows:

\[
\begin{align*}
    a_{\text{HOMO}}^\dagger a_{\text{LUMO}}^\dagger |\text{vac}\rangle & \rightarrow |00\rangle, \\
    a_{\text{HOMO}}^\dagger a_{\text{HOMO}}^\dagger |\text{vac}\rangle & \rightarrow |01\rangle, \\
    a_{\text{LUMO}}^\dagger a_{\text{LUMO}}^\dagger |\text{vac}\rangle & \rightarrow |10\rangle, \\
    a_{\text{LUMO}}^\dagger a_{\text{HOMO}}^\dagger |\text{vac}\rangle & \rightarrow |11\rangle,
\end{align*}
\]

(4)

where $a_x^\dagger$ is the generating operator of an electron in spin orbital $X$, $|\text{vac}\rangle$ is the vacuum state, and the up and down arrows represent two spin eigenstates. Here, the singlet and triplet configurations are represented by a linear combination of Eq. (4). The doubly occupied singlet configurations in the HOMO and LUMO correspond to $|01\rangle$ and $|10\rangle$, respectively. The open-shell singlet and triplet configurations are represented by $\frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$ and $\frac{1}{\sqrt{2}}(|00\rangle - |11\rangle)$, respectively. When only the singlet states are focused on, their wavefunctions can be represented by a linear combination of only the singlet configurations. Thus, a quantum circuit that constructs trial functions within the
singlet subspace is efficient in avoiding undesired spin contamination. Figure 1 shows a quantum circuit that constructs the singlet subspace. In this circuit, the Pauli X-gate is applied to the second qubit, \( q_1 \), to prepare the doubly excited configuration, \( |10\rangle \), as the initial state. Then, \( q_0 \) and \( q_1 \) are transformed into \( \sin(\theta_0/2)|01\rangle + \cos(\theta_0/2)|10\rangle \) by the Y-rotation gate, \( R_y(\theta_0) \), combined with the CNOT gate. The \( R_y(\theta_1) \) and \( R_y(-\theta_1) \) pair partly transforms \( |01\rangle - |10\rangle \) into \( |00\rangle + |11\rangle \) to finally produce a superposition of the three singlet configurations as follows:

\[
|\Psi(\theta)\rangle = \frac{1}{\sqrt{2}} \left\{ \sin\left(\frac{\theta_0}{2} + \frac{\pi}{4}\right) - \cos\left(\frac{\theta_0}{2} + \frac{\pi}{4}\right) \cos \theta_1 \right\} |01\rangle + \frac{1}{\sqrt{2}} \left\{ \sin\left(\frac{\theta_0}{2} + \frac{\pi}{4}\right) + \cos\left(\frac{\theta_0}{2} + \frac{\pi}{4}\right) \cos \theta_1 \right\} |10\rangle + \frac{1}{\sqrt{2}} \cos \left(\frac{\theta_0}{2} + \frac{\pi}{4}\right) \sin \theta_1 \left( |00\rangle + |11\rangle \right).
\]

(5)

This ansatz, which is described in a form similar to the hyperspherical expansion,\(^{43}\) is realized by a circuit with minimum gate operations.

\[ \begin{array}{c}
q_0 : |0\rangle \\
q_1 : |0\rangle
\end{array} \quad \xrightarrow{R_y(\theta_0)} \quad \bullet \quad \xrightarrow{R_y(\theta_1)} \quad \begin{array}{c}
q_0 : |0\rangle \\
q_1 : |0\rangle
\end{array} \quad \xrightarrow{X} \quad \oplus \quad \xrightarrow{R_y(-\theta_1)} \quad \begin{array}{c}
q_0 : |0\rangle \\
q_1 : |0\rangle
\end{array} \]

**Fig. 1 Quantum circuit of singlet-restricted ansatz for two electrons in two-orbital system.** X, \( R_y \), and the \( \oplus \) connected to a dot represent the Pauli X-gate, Y-rotational gate, and CNOT gate, respectively. \( q_0 \) and \( q_1 \) are the labels for the two qubits.

To obtain deeper insights into the singlet subspace, we plotted the energy landscape against the circuit parameters \( \theta_0 \) and \( \theta_1 \). Figure 2 shows the energy landscape of ethylene calculated using the CASCI method, whose active space includes two electrons in two orbitals. As shown in Eq. (5), the coefficient of each electronic configuration is represented by the trigonometric functions of parameters \( \theta_0 \) and \( \theta_1 \) (in other words, the coefficient changes periodically with respect to \( \theta_0 \) and \( \theta_1 \)), which results in the periodic energy landscape. In Fig. 2, one of the minimum points, the first-order saddle point, and the second-order saddle point are shown by the white circle, black x, and black triangle, respectively. \( S_0 \) corresponds to the minimum energy points, which can be determined by minimizing the energy value. \( S_1 \) corresponds to the first-order saddle point because it is located at the minimum energy point within the subspace that satisfies the orthogonality to \( S_0 \) (shown by the white solid line in Fig. 2). Therefore, \( S_1 \) can easily be found using a conventional optimization method under orthogonality constraints. In the same way, the higher \( (n\text{-th}) \) singlet excited state, which corresponds to the \( n\text{-th order} \) saddle point, could be obtained by energy minimization within the subspace orthogonal to all the lower singlet states.
Fig. 2 Energy landscape (in Hartree) of ethylene plotted against two circuit parameters $\theta_0$ and $\theta_1$ (in radian). The energies of ethylene were computed at the FC structure using the CASCI/STO-3G method, whose active space included two electrons in two orbitals. One of the minimum energy points ($S_0$), the first-order saddle point ($S_1$), and the second-order saddle point ($S_2$) are shown by the white circle, black x, and black triangle, respectively. The white solid line represents the region where the wavefunction is orthogonal to $S_0$.

Comparison of ansätze

Two quantum circuit simulators implemented in Qiskit were used for all the CASSCF calculations. One was the statevector simulator, which simulated the ideal quantum state and did not involve any noise or readout error. The other was a noisy-QASM simulator that used a realistic device (ibmq_belem) noise model. We expect that the appropriate method provides the negligible energy difference between the statevector and noisy-QASM simulators.

First, to examine the dependency on the ansatz, this study focused on the ground state ($S_0$) energy of ethylene at the FC geometry calculated with the SS-CASSCF method using two types of ansätze, called the heuristic and chemistry-inspired ansätze. Figure 3 shows the $S_0$ energy calculated with three heuristic ansätze, including the real amplitudes (RA) ansatz (with 2 and 6 depth conditions, denoted as RA(2) and RA(6), respectively), the efficient SU2 ansatz, and a chemistry-inspired ansatz, that is, the spin-restricted ansatz. As shown in Fig. 3, when using the statevector simulator, the energy converged to an exact value for all four ansätze. With the noisy-QASM simulator, the calculated energies were higher than the exact value for all the ansätze, but the errors were within 2.5 kcal/mol at most. It should be noted that the error tended to be larger when using a more complex quantum circuit. As shown in Figs. 1 and S1 (in the SI), the quantum circuit for the spin-restricted ansatz was shorter than those of the heuristic ansätze. In addition, the number of the parameters for the spin-restricted ansatz was only two, which was smaller than the numbers used for the heuristic ansätze (6, 14, and 8 for RA(2), RA(6), and efficient SU2, respectively). It is known that calculations using complex circuits (using many gates and parameters) suffer from the dreaded “Barren Plateau” of insolvability, where energy minimization becomes
difficult due to the flat energy landscape.\textsuperscript{53} Thus, the spin-restricted ansatz might have an advantage over the heuristic ansätze by avoiding this problem.

Fig. 3 Comparison of ansätze for the ground state calculation of ethylene. The energy deviations $\Delta E$ (in kcal/mol) from the exact values were calculated at the FC geometry using SS-CASSCF with statevector (in red) and noisy-QASM simulators (in blue). Detailed values are shown in Table S1 in Supplemental Information; SI.

Next, we considered the first singlet excited state ($S_1$), as well as the $S_0$ state of ethylene, at the FC and CI geometries. As summarized in Table 1, the calculation methods depend on the ansatz, geometry, and the electronic state. In the case of heuristic ansatz, the calculation methods depend on the geometry. Focusing on the FC geometry, the $S_0$ can be obtained by the VQE, while the $S_1$ can be obtained by the VQD with the cost function $C_2(\theta)$ in Eq. (3). The hyperparameter $\beta$, which constrained the search within the subspace orthogonal to $S_0$, was manually adjusted and set to 1. The parameter $\gamma$, which constrained the search within the singlet subspace, needed to be positive and adjusted to 1 because triplet excited states could be more stable than $S_1$. Focusing on the CI geometry, where the $S_0$ and $S_1$ energies were equal, the VQE gave the triplet state ($T_1$) because $T_1$ was always more stable than $S_1$. Therefore, to calculate $S_0$, the VQD with the parameters ($\beta, \gamma$) = (0, 1) had to be used instead of the VQE. In the case of the spin-restricted ansatz, on the other hand, the $S_0$ ground state could be obtained by the VQE for any molecular geometry, and the simpler cost function $C_1(\theta)$ in Eq. (2) with $\beta = 1$ could be used because the spin multiplicity was constrained to a singlet by the ansatz.

| Ansatz          | geometry | $S_0$            | $S_1$            |
|-----------------|----------|------------------|------------------|
| Heuristic       | FC       | VQE              | VQD ($C_2(\theta), \beta > 0$) |
|                 | CI       | VQD ($C_2(\theta), \beta = 0$) | VQD ($C_2(\theta), \beta > 0$) |
| Spin-restricted | Any      | VQE              | VQD ($C_1(\theta), \beta > 0$) |

As shown in Fig. 4, when the statevector simulator was used, every calculation at the FC
and CI geometries with any ansatz converged to the exact $S_0$ and $S_1$ energies. However, when using the noisy-QASM simulator, the errors in the $S_0$ and $S_1$ energies differed greatly depending on the ansatz and hyperparameter. Focusing on the energies in Figs. 4(a–c), the errors calculated with the heuristic ansätze were much larger than those found using the spin-restricted ansatz. To understand the reason for the larger errors with the heuristic ansätze, the expected value of spin squared ($\langle \hat{S}^2 \rangle$) was focused on (see Table S2 in the SI). The deviation of the spin squared value from the exact value (i.e., zero) was relatively large when the heuristic ansätze were used. Thus, undesired spin contamination could be one of the reasons for the energy errors. (Note that the errors in the $S_0$ energies calculated by the SA-CASSCF were larger than those calculated by the SS-CASSCF in Fig. 3. It could be understood that inappropriate hyperparameters affected the orbital optimization and eventually both the $S_0$ and $S_1$ energies.) Even though the spin-restricted ansatz was applied, the error in the $S_1$ energy in the CI geometry was as large as 20.96 kcal/mol (see Fig. 4(d)), while the errors in the $S_1$ energy at the FC as well as the $S_0$ energies were small (up to 0.35 kcal/mol). To clarify the large error in the $S_1$ energy, the coefficients of the three singlet electronic configurations were calculated using Eq. (5). As a result, the major component of the excited state at the CI was the doubly excited electronic configuration; in other words, this calculation converged to $S_2$, not $S_1$. This implied that the exploration of the PESs of the excited states using the VQD could be difficult because the parameter $\beta$ would have to be adjusted for each molecular geometry.

**Fig. 4** Comparison of ansätze for the ground and excited state calculations of ethylene. Energy deviations $\Delta E$ (in kcal/mol) from the exact values for $S_0$ at the FC (a), $S_1$ at the FC (b), $S_0$ at the CI
(c), and S₁ at the CI (d) were calculated using the SA-CASSCF method. The errors in energy obtained by the statevector and noisy-QASM simulators are shown in red and blue, respectively. The results labeled with an "*" indicate that the maximum number of orbital rotations was reached. The parameters were $\beta = 1$ for all the ansätze, $\gamma = 1$ for the heuristic ansätze. Detailed values are shown in Table S2 in the SI.

**Comparison of calculation methods for excited states**

Next, we examined the performance of VQD with different $\beta$ and compare them with our proposed excited state calculation method, the VQE/AC. As shown in Fig. 5, we calculated S₀ and S₁ energies of ethylene with the spin-restricted ansatz and compared these excited state calculation methods. Focusing on the VQD, the S₁ energy heavily depended on the parameter $\beta$. When the parameter $\beta$ was set to 1, the excited state at the CI geometry converged to the undesired S₂ state, as mentioned above. With the $\beta$ set to 2.5, both S₀ and S₁ were calculated successfully. When the $\beta$ was larger than 5, even the statevector simulator (and of course the noisy-QASM simulator) gave inaccurate energy values, indicating that these $\beta$ values were not appropriate. Thus, the parameter $\beta$ needed to be carefully and manually adjusted and was 2.5 for ethylene. Although higher excited states such as S₂ were beyond the scope of this study, it can be expected that the cost functions could be more difficult to adjust because they must involve constraints on all the lower excited states. On the other hand, when the VQE/AC was applied, the errors in energies at both the FC and CI obtained with the noisy-QASM simulator were very small (up to 0.45 kcal/mol). It should be emphasized that VQE/AC does not require the tuning of the cost function, unlike the VQD. Therefore, the VQE/AC could be used to describe smooth PESs even when using the noisy-QASM simulator, i.e., under realistic device noise.
Fig. 5 Comparison of VQD with different parameter $\beta$ and VQE/AC for ethylene. Energy deviations $\Delta E$ (in kcal/mol) from the exact values for $S_0$ at the FC (a), $S_1$ at the FC (b), $S_0$ at the CI (c), and $S_1$ at the CI (d) were calculated using the SA-CASSCF method. The errors in energy obtained by the statevector and noisy-QASM simulators are shown in red and blue, respectively. The results labeled with an "*" indicate that the maximum number of orbital rotations was reached. Detailed values are shown in Table S3 in the SI.

Application to phenol blue

As previously described, the combination of the spin-restricted ansatz and the VQE/AC enabled to give $S_0$ and $S_1$ energies with an error of less than 1 kcal/mol, even under the realistic device noise model. Next, to verify the applicability of this method to photofunctional molecules, the study focused on a robust dye called phenol blue (see Fig. 6). Focusing on the performance of the VQD method, the most suitable $\beta$ value for both the FC and CI geometries was 1 (in contrast to the value of 2.5 for ethylene), which indicated that the most appropriate value for this parameter heavily depended on the molecule. The errors in energy calculated by the VQD method with parameter $\beta = 1$ were only 0.22 kcal/mol at most even when using the noisy-QASM simulator. In the case of the VQE/AC, the errors in the $S_0$ and $S_1$ energies were only 0.14 kcal/mol at most. Therefore, it can be stated that the proposed strategy (VQE/AC with spin-restricted ansatz) is efficient in calculating the excited states, as well as the ground states, of large molecules. This method gave a small error at any geometry without any hyperparameter tuning, which indicated that it is applicable to describe potential energy surfaces of the ground and excited states.
Fig. 6 Comparison of VQD with different parameter $\beta$ and VQE/AC for phenol blue. Energy deviations $\Delta E$ (in kcal/mol) from the exact values for $S_0$ at the FC (a), $S_1$ at the FC (b), $S_0$ at the CI (c), and $S_1$ at the CI (d) were calculated using the SA-CASSCF method. The errors in energy obtained by the statevector and noisy-QASM simulators are shown in red and blue, respectively. Detailed values are shown in Table S4 in the SI.

Finally, the ground and excited state energies of phenol blue were measured on the ibm_kawasaki device using the VQE/AC. The energies of the FC and CI geometries were measured twice each as shown in Table 2. All the calculations converged relatively smoothly: the numbers of orbital update iterations were less than 10 in all the calculations. Though the deviations from the exact solutions were larger than those estimated with the noisy-QASM simulator, they were at most 2 kcal/mol and 0.5 kcal/mol for the state energies and excitation energies, respectively. It should be noted that the energy deviations at the CI geometry were as small as 0.5 kcal/mol, which were surprisingly small and showed the high potential to achieve the exploration of the CI geometries. The deviations at the FC geometry, on the other hand, were larger than those at the CI. This could be attributed to the fact that the Hamiltonian structure (Pauli string) at the FC geometry was more sensitive to the device noise than that at the CI geometry. Though precise geometry optimization may still be difficult with an error of 2 kcal/mol, it could be improved by developing methodologies of purification and error mitigation as well as hardware.
Table 2. Energy deviations $\Delta E$ (in kcal/mol) from the exact values of phenol blue for the $S_0$ and $S_1$ energies at the FC and CI geometries measured on the ibm_kawasaki device.

| Entry | Geometry | $\Delta E$ ($S_0$) | $\Delta E$ ($S_1$) |
|-------|----------|---------------------|---------------------|
| 1     | FC       | 1.68                | 1.64                |
| 2     | FC       | 1.82                | 2.03                |
| 3     | CI       | 0.37                | 0.04                |
| 4     | CI       | 0.49                | 0.01                |

Concluding statements

This study investigated a new ground and excited state calculation method that can tolerate NISQ devices. Two methods were combined, a chemistry-inspired spin-restricted ansatz with parity mapping and a new excited-state calculation method, called the VQE/AC method. The advantage of the spin-restricted ansatz was that the wavefunction could be constructed within the subspace of the target spin multiplicity, which reduced the undesired spin contamination. The VQE/AC used a constrained optimization called COBYLA, with the constraint that the overlap integral between the target state and the ground state was smaller than a threshold such as $10^{-4}$. To validate this strategy, the CASSCF method was used for the singlet ground and excited states of ethylene and phenol blue at the FC and CI geometries. The small errors were obtained in the singlet ground and first excited states ($i.e.$, $S_0$ and $S_1$) on a realistic device noise model ($< 0.5$ kcal/mol) and the real device “ibm_kawasaki” ($< 2$ kcal/mol). The present calculation results are superior to the previous ones using quantum circuits (at least 2-3 kcal/mol).\textsuperscript{33,35} Unlike the conventional excited state calculation method called VQD, the VQE/AC does not require any parameter tuning for the cost function. Thus, the VQE/AC could have the advantage of higher excited state calculations (though this was beyond the scope of this study) compared to the VQD. Moreover, it should be emphasized that the ground and excited state energies could be computed with the same calculation condition for any molecular geometry because parameter tuning was not required. Therefore, the VQE/AC could be used to explore PESs of the ground and excited states, even under a realistic device noise model. In other words, the VQE/AC has much potential for achieving geometry optimization of critical structures on and between the ground and excited states using real NISQ devices.

Method

Workflow and classical computations

In all the CASSCF calculations,\textsuperscript{54,55} the active space included two electrons in two orbitals such as HOMO and LUMO. When only the ground state was focused on, the state-specific (SS) CASSCF was applied. To compute both the ground and first excited states, the state-averaged (SA) CASSCF was applied, in which the average energy of these two states was minimized. The initial
(guess) molecular orbitals for the CASSCF were obtained using the Hartree–Fock (HF) method (see Fig. S2 in SI). The basis sets used for ethylene and phenol blue were STO-3G and 6-31G(d), respectively. The molecular geometries of ethylene at the FC and CI were optimized at the same level of theory using the classical CASSCF method (without using the quantum circuit) implemented in the MOLPRO and GRRM programs. The geometries of phenol blue were obtained from a previous study.

Figure 7 shows the workflow of the CASSCF calculation in this study. As shown in (i) in Fig. 7, we started from calculating the one-body and two-body integrals $h_1$ and $h_2$ (in MO basis) based on the input geometries, spin, and the basis set using the PySCF package. Next, the Qiskit package was used (ii) to prepare the Hamiltonian $\hat{H}$ and the spin-squared operator $\hat{S}^2$ in the second-quantized form and to map them to qubit operators. Then, the VQE for $S_0$ (iii) and VQD for $S_1$ (iv) were conducted, in which the expectation values of the energy (or the cost function) and constraints (for VQE/AC) were measured, and the parameters in the ansatz were updated until the energy/cost function converged. The COBYLA optimizer in the SciPy package was used to update the parameters, and the convergence threshold and the maximum number of iterations were set to $10^{-4}$ atomic units and 100, respectively. When iterations reached the maximum, the result at the last step was taken. Each VQE/VQD was followed by state-tomography (ST) and purification (see below). After the calculations for $S_0$ and $S_1$, (v) the one- and two-particle reduced density matrix (1-RDM and 2-RDM) elements for $S_0$ and $S_1$ were measured using the converged parameters. These RDMs were then averaged with weights of $(S_0, S_1) = (1, 0)$ and $(0.5, 0.5)$ for the SS-CASSCF and SA-CASSCF calculations, respectively. If averaged RDMs and the similarly averaged energy were not converged, the orbitals were updated by modules in the PySCF package and repeated the procedure (ii-v). For the calculations on the simulators, the convergence threshold for the orbitals was set to $10^{-4}$ atomic units for the energy, CI gradients, and orbital rotation gradients. They were altered to $10^{-3}$ atomic units for the energy, $5 \times 10^{-2}$ atomic units for the gradients in the calculations on the real device.

![Fig. 7 Schematic diagram of SA-CASSCF program.](image)

Green, blue and orange boxes indicate that PySCF, Qiskit and SciPy packages were used, respectively.
Quantum circuits and quantum simulations

The details of the quantum circuit and measurement were as follows. The parity mapping\(^{49}\) was used to map the molecular orbitals to qubits. It exploited the symmetry wherein the total electron number and total alpha electron number should be conserved and allowed the qubits to be reduced by two. Therefore, four spin-orbital calculations were conducted on two qubits. The initial parameters were set to \(\theta = (0, \pi)\) for the spin-restricted ansatz (which corresponded to the HF state) and all zero for the other ansatzë. Note that the overlap between two states \(|\Psi(\theta)\rangle\) and \(|\Psi_0\rangle\), \(\langle\Psi(\theta)|\Psi_0\rangle^2\), was obtained by measuring the quantum circuit of inverted \(|\Psi(\theta)\rangle\) combined with \(|\Psi_0\rangle\). To measure the expectation values, we used the “ibm_kawasaki” device and two simulators in the Qiskit\(^{50}\) package: the statevector simulator, which simulated an ideal quantum state without any noise or readout error, and noisy-QASM simulator, which employed the realistic noise model from “ibmq_belem” device. For the noisy-QASM simulator and the ibm_kawasaki device, the expectation value was obtained using 8192 shots. The measurement error mitigation implemented in Qiskit was applied for the measurements on the noisy-QASM simulator, otherwise not applied for those on the ibm_kawasaki device because the update of the calibration matrix affected the result. The quantum state-tomography and purification after each VQE/VQD calculation was executed by the following procedure, as found in a previous study\(^{35}\).

1. Measure density matrix \(\rho\).
2. Diagonalize \(\rho\) to obtain eigenvalues and eigenvectors with the classical algorithm in SciPy.
3. Assume that the eigenvector \(|\psi\rangle\) corresponding to the maximum eigenvalue is the exact state, and re-evaluate the energy as \(\langle\psi|H|\psi\rangle\).
4. Update parameter set \(\theta\) by minimizing \(|\langle\psi|\Psi(\theta)\rangle|^2 - 1\).

Acknowledgments
This work was supported by JSPS KAKENHI Grant no. JP17H06445 and 20K05438. We also acknowledge the computer resources provided by the Academic Center for Computing and Media Studies (ACCMS) at Kyoto University and by the Research Center of Computer Science (RCCS) at the Institute for Molecular Science.

Author contributions
S.G., H.N., Q.G., T.K., T.I., and M.H. conceived the idea of this work. S.G. developed the VQE/AC and performed calculations on the classical and quantum computers. H.N. developed the spin restricted ansatz code. All authors contributed to the discussions and approved the final version of the manuscript.
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Supporting Information

Fig. S1 The quantum circuits used for the CASSCF calculations of ethylene with the RA ansatz with depth 2 (a), that with depth 6 (b), and the efficient SU(2) ansatz (c).

Fig. S2 The geometries and the active orbitals (HOMO and LUMO) of ethylene at the FC (a) and the CI (b) geometries, and phenol blue at the FC (c) and the CI (d) geometries.

Table S1. Energy deviations from the exact value $\Delta E$ (in kcal/mol), and spin squared values $S^2$ of the ground state of ethylene at the FC geometry calculated at the SS-CASSCF level of theory.

| Entry | Simulator | Ansatz        | $\Delta E$ (kcal/mol) | $S^2$ |
|-------|-----------|---------------|-----------------------|-------|
| 1     | Statevector | RA(2)         | 0.00                  | 0.00  |
| 2     |            | RA(6)         | 0.00                  | 0.00  |
| 3     |            | EfficientSU2(1) | 0.01                | 0.00  |
| 4     |            | Spin restricted | 0.00                 | 0.00  |
| 5     | Noisy-QASM | RA(2)         | 0.27                  | 0.01  |
| 6     |            | RA(6)         | 1.51                  | 0.10  |
| 7     |            | EfficientSU2(1) | 2.37                | 0.04  |
| 8     |            | Spin restricted | 0.34                 | 0.03  |
Table S2. Energy deviations from the exact value\(^a\) \(\Delta E\) (in kcal/mol), and spin squared values \(S^2\) of the \(S_0\) and \(S_1\) states of ethylene at the FC and CI geometries calculated at the SA-CASSCF level of theory.

| Entry | Geometry | Simulator | Ansatz                  | \(\Delta E(S_0)\) (kcal/mol) | \(S^2(S_0)\) | \(\Delta E(S_1)\) (kcal/mol) | \(S^2(S_1)\) |
|-------|----------|-----------|-------------------------|-------------------------------|--------------|-------------------------------|--------------|
| 1     | FC       | Statevector | RA(2)                  | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 2     |          |            | RA(6)                  | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 3     |          |            | EfficientSU2(1)         | 0.01                          | 0.00         | 0.00                          | 0.00         |
| 4     |          |            | Spin restricted         | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 5     |          | Noisy-QASM | RA(2)                  | 9.43                          | 0.10         | -9.92                         | 0.03         |
| 6     |          |            | RA(6)                  | 10.16                         | 0.10         | -4.00                         | 0.07         |
| 7     |          |            | EfficientSU2(1)         | 5.98                          | 0.02         | -1.23                         | 0.02         |
| 8     |          |            | Spin restricted\(^b\)  | 0.11                          | 0.02         | 0.11                          | 0.01         |
| 9     |          |            | Spin restricted\(^c\)  | 0.29                          | 0.01         | -0.09                         | 0.02         |
| 10    | CI       | Statevector | RA(2)                  | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 11    |          |            | RA(6)                  | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 12    |          |            | EfficientSU2(1)         | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 13    |          |            | Spin restricted         | 0.00                          | 0.00         | 0.00                          | 0.00         |
| 14    |          | Noisy-QASM | RA(2)                  | 0.69                          | 0.03         | 0.48                          | 0.03         |
| 15    |          |            | RA(6)                  | 10.25                         | 0.06         | 0.25                          | 0.09         |
| 16    |          |            | EfficientSU2(1)         | 5.68                          | 0.04         | 1.23                          | 0.01         |
| 17    |          |            | Spin restricted\(^b\)  | 0.35                          | 0.02         | 20.96                         | 0.01         |
| 18    |          |            | Spin restricted\(^c\)  | 0.06                          | 0.00         | 0.96                          | 0.01         |

a) The exact energy differences from \(S_0\) at FC were 325.68 kcal/mol and 125.44 kcal/mol for \(S_1\) at FC and CI, respectively. b) \(\beta = 1\). c) \(\beta = 2.5\).
Table S3. Energy deviations from the exact value\(^a\) \(\Delta E\) (in kcal/mol), and spin squared values \(S^2\) of the \(S_0\) and \(S_1\) states of ethylene at the FC and CI geometries calculated at the SA-CASSCF level of theory with the spin restricted ansatz.

| Entry | Geometry | Simulator | Excited state calculation | \(\Delta E(S_0)\) (kcal/mol) | \(S^2(S_0)\) | \(\Delta E(S_1)\) (kcal/mol) | \(S^2(S_1)\) |
|-------|----------|-----------|---------------------------|-----------------------------|-------------|-----------------------------|-------------|
| 1     | FC       | Statevector | VQD \((\beta = 1)\)     | 0.00                        | 0.00        | 0.00                        | 0.00        |
| 2     | FC       | Statevector | VQD \((\beta = 2.5)\)   | 0.00                        | 0.00        | 0.00                        | 0.00        |
| 3     | FC       | Statevector | VQD \((\beta = 5)\)     | 0.09                        | 0.00        | -0.01                       | 0.00        |
| 4     | FC       | Statevector | VQD \((\beta = 10)\)    | 0.21                        | 0.00        | -0.01                       | 0.00        |
| 5     | FC       | VQE/AC     |                            |                            |             |                              |             |
| 6     | Noisy-QASM | VQD \((\beta = 1)\) | 0.11                    | 0.02                        | 0.11        | 0.01                        |             |
| 7     | Noisy-QASM | VQD \((\beta = 2.5)\) | 0.29                    | 0.01                        | -0.09       | 0.02                        |             |
| 8     | Noisy-QASM | VQD \((\beta = 5)\) | 0.71                     | 0.02                        | -0.63       | 0.02                        |             |
| 9     | Noisy-QASM | VQD \((\beta = 10)\) | 1.25                     | 0.02                        | -2.02       | 0.03                        |             |
| 10    | Noisy-QASM | VQE/AC   |                            |                            |             |                              |             |
| 11    | CI       | Statevector | VQD \((\beta = 1)\)     | 0.00                        | 0.00        | 0.00                        | 0.00        |
| 12    | CI       | Statevector | VQD \((\beta = 2.5)\)   | 0.00                        | 0.00        | 0.00                        | 0.00        |
| 13    | CI       | Statevector | VQD \((\beta = 5)\)     | 0.00                        | 0.00        | 0.01                        | 0.00        |
| 14    | CI       | Statevector | VQD \((\beta = 10)\)    | 0.00                        | 0.00        | 0.11                        | 0.00        |
| 15    | CI       | VQE/AC     |                            |                            |             |                              |             |
| 16    | Noisy-QASM | VQD \((\beta = 1)\) | 0.35                    | 0.02                        | 20.96       | 0.01                        |             |
| 17    | Noisy-QASM | VQD \((\beta = 2.5)\) | 0.06                    | 0.00                        | 0.96        | 0.01                        |             |
| 18    | Noisy-QASM | VQD \((\beta = 5)\) | 0.20                     | 0.02                        | 44.20       | 0.02                        |             |
| 19    | Noisy-QASM | VQD \((\beta = 10)\) | 0.19                     | 0.01                        | 44.32       | 0.01                        |             |
| 20    | Noisy-QASM | VQE/AC   |                            |                            |             |                              |             |

\(^a\) The exact energy differences from \(S_0\) at FC were 325.68 kcal/mol and 125.44 kcal/mol for \(S_1\) at FC and CI, respectively.
Table S4. Energy deviations from the exact value\(^a\) \(\Delta E\) (in kcal/mol), and spin squared values \(S^2\) of the \(S_0\) and \(S_1\) states of phenol blue at the FC and CI geometries calculated at the SA-CASSCF level of theory with the spin restricted ansatz.

| Entry | Geometry | Simulator | Excited state calculation | \(\Delta E(S_0)\) (kcal/mol) | \(S^2(S_0)\) | \(\Delta E(S_1)\) (kcal/mol) | \(S^2(S_1)\) |
|-------|----------|-----------|---------------------------|-----------------------------|------------|-----------------------------|------------|
| 1     | FC       | Statevector | VQD (\(\beta = 1\))    | -0.01                       | 0.00       | 0.01                        | 0.00       |
| 2     |         |           | VQD (\(\beta = 2.5\))  | -0.01                       | 0.00       | 0.01                        | 0.00       |
| 3     |         |           | VQD (\(\beta = 10\))   | -0.01                       | 0.00       | 0.02                        | 0.00       |
| 4     |         |           | VQE/AC                    | 0.02                        | 0.00       | -0.03                       | 0.00       |
| 5     | Noisy-QASM |         | VQD (\(\beta = 1\))    | 0.08                        | 0.01       | 0.22                        | 0.01       |
| 6     |         |           | VQD (\(\beta = 2.5\))  | -0.14                       | 0.02       | 0.16                        | 0.02       |
| 7     |         |           | VQD (\(\beta = 10\))   | 0.00                        | 0.02       | 6.12                        | 0.02       |
| 8     |         |           | VQE/AC                    | 0.08                        | 0.01       | 0.07                        | 0.01       |
| 9     | CI       | Statevector | VQD (\(\beta = 1\))    | 0.00                        | 0.00       | 0.00                        | 0.00       |
| 10    |         |           | VQD (\(\beta = 2.5\))  | 0.00                        | 0.00       | 0.00                        | 0.00       |
| 11    |         |           | VQD (\(\beta = 10\))   | 0.00                        | 0.00       | 0.01                        | 0.00       |
| 12    |         |           | VQE/AC                    | -0.02                       | 0.00       | 0.02                        | 0.00       |
| 13    | Noisy-QASM |         | VQD (\(\beta = 1\))    | 0.14                        | 0.02       | -0.03                       | 0.03       |
| 14    |         |           | VQD (\(\beta = 2.5\))  | 0.17                        | 0.02       | 2.05                        | 0.03       |
| 15    |         |           | VQD (\(\beta = 10\))   | -0.16                       | 0.00       | 26.41                       | 0.03       |
| 16    |         |           | VQE/AC                    | 0.00                        | 0.02       | 0.14                        | 0.01       |

\(a\) The exact energy differences from \(S_0\) at FC were 85.85 kcal/mol and 46.39 kcal/mol for \(S_1\) at FC and CI, respectively.