Optimization of chemical reaction path via molecular geometry generation using quantum circuits

Shu Kanno*

Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, 226-8501 Yokohama, Japan

ABSTRACT

The search for new tasks related to quantum chemical calculations that can be performed on current quantum computers is important for the development of both quantum computing and quantum chemical calculations. Although chemical reaction calculations have a wide range of applications in quantum chemical calculations, there is no quantum algorithm for obtaining the activation energy ($E_a$), which determines the rate of chemical reactions for any given substance. In this study, we propose a quantum algorithm for obtaining $E_a$ for a given substance by optimizing the reaction path via molecular geometry generation using quantum circuits. The nudged elastic band method was used to optimize a reaction path, and the ground state calculation for each state on the reaction path involved either variational quantum eigensolver (VQE) or exact diagonalization (ED). The proposed algorithm was applied to $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ reaction, and the reaction path was correctly optimized. Moreover, the activation energy was obtained with good accuracy regardless of whether VQE or ED is used for the ground state calculation. The results demonstrate the feasibility of performing the chemical reaction calculations using quantum algorithms.
1. Introduction

Quantum computers have attracted considerable attention as they can perform tasks more inefficiently compared to classical computers. Although quantum computing has been shown can be superior to classical computing in certain tasks,¹ no practical task with quantum advantage (e.g., quantum chemical calculation) has been implemented yet.

Current quantum computers, called noisy intermediate-scale quantum (NISQ) devices,² are composed of tens or hundreds of qubits and have non-negligible noise in quantum gates. Therefore, it is necessary to explore tasks that can be performed using quantum algorithms that are compatible with NISQ devices in order to demonstrate the practicality of quantum computers using NISQ devices.

One of the potential applications of NISQ devices is quantum chemical calculations using the variational quantum eigensolver (VQE).³ VQE is an algorithm that generates a wave function using a parameterized quantum circuit and optimizes the parameters in a classical computer according to the expectation value of Hamiltonian to obtain the eigenvalue information. The multipartite quantum entanglement between the qubits in VQE is expected to enable us to calculate the wave functions that cannot be represented by classical computers efficiently. VQE requires only a similar number of qubits to that of spin orbitals of the simulated system and is resistant to physical noise since we use only short depth quantum circuits and obtain the wave function by a large number of measurements. Thus, VQE is believed to be a suitable algorithm for NISQ devices. The electronic states of molecules have been calculated by NISQ devices.³⁴ Starting from the VQE research,
numerous studies related to quantum chemical calculations (e.g., the ground-state calculation\(^3\) and molecular dynamics\(^5\)) for NISQ devices have been conducted.\(^6,7\) Therefore, the search for new tasks related to quantum chemical calculations for NISQ devices is important for the development of both quantum computers and quantum chemical calculations.

On the other hand, chemical reaction calculations have a wide range of applications in materials development, such as catalysts\(^8,9\) and batteries\(^10\). The reaction rate constant \((k)\) of the chemical reaction depends on the activation energy \((E_a)\) in the form of an exponent as

\[
k \propto \exp \left( \frac{E_a}{RT} \right),
\]

where \(R\) is the gas constant and \(T\) is the temperature. Hence, a high-precision calculation is required for obtaining \(E_a\). However, a common electronic structure calculation method, i.e., density functional theory (DFT), may not always achieve the required accuracy for the prediction of chemical reactions when consideration of the electronic correlation of the system is essential to the calculation. For example, the calculated dissociation energy in a certain ligand using DFT has an error of about 50 kJ/mol (19 mHartree) from the experimental value, which cannot reach the chemical accuracy (about 1 mHartree) required for quantum chemistry calculations.\(^11\) Therefore, if we can obtain \(E_a\) with high accuracy using NISQ algorithms, such as VQE, it will be possible to elucidate the mechanism of chemical reactions in systems whose properties cannot be revealed using classical algorithms. Studies related to quantum algorithmic chemical reactions include proposals about chemical dynamics methods,\(^12-14\) calculations for energy derivatives of atomic coordinates,\(^15-17\) samplings for molecular vibronic spectra,\(^5,18,19\) quantum resource estimations for catalytic reactions,\(^8,20\) and potential energy curve
calculations for a specific reaction path.\textsuperscript{21,22} Although numerous studies on chemical reactions have been performed in this way, no study has yet been performed to optimize the reaction path and obtain activation energy using the quantum algorithm. Therefore, the development of algorithms for NISQ devices that can obtain highly accurate activation energy will expand the application of quantum computers.

Chemical reaction calculations require a combination of ground-state calculation algorithms and reaction path optimization algorithms. Methods related to the reaction path optimization using a classical algorithm include the Nudged Elastic Band (NEB) method,\textsuperscript{23-25} dimer method,\textsuperscript{26} quadratic synchronous transit method,\textsuperscript{27} and intrinsic reaction coordinate method.\textsuperscript{28} Let us explain the NEB method used in this study. The NEB method searches for a minimum energy path (MEP), which has the smallest energy maximum for the reaction path connecting the reactants and products at a potential energy surface given in reaction coordinates (e.g., bond lengths and bond angles).\textsuperscript{a} Concretely, the method considers the reaction paths on the potential energy surface by generating several intermediate states, called “images”, between the reaction coordinates corresponding to the reactants (initial state) and products (final state). The intermediate images are then optimized so that the maximum energy in the reaction path becomes smaller, and the activation energy is obtained from the optimized reaction path. During the optimization by the NEB method,

\textsuperscript{a} The state corresponding to the position of the energy maximum in the exact MEP is called the transition state. The transition state is a saddle point on the potential energy surface, i.e., it has a local maximum value in one direction and local minimum values in other directions.
the adjacent images are connected by virtual springs along the reaction path to keep the distance between the images equal. Therefore, the images interact with each other, and the handling of the interactions affect the speed of convergence.\textsuperscript{24,29} Hence, if we can generate the atomic structural information (i.e., the position of atoms in each image) for image acquisition using a quantum computer, we can handle the interactions between the images by the entanglement between qubits, which would speed up the calculation. Also, the ground-state calculation using VQE for each state would enable us to obtain the activation energy with high accuracy.

In this study, we propose an algorithm to generate an image using a quantum circuit and optimize the reaction path via the NEB method from the generated image. The algorithm first embeds the molecular geometry of the initial guess of images as the rotation angle of the $R_y$ gate into each qubit, and then entangles these qubits with each other using parameterized unitary gates. Then, the geometry is obtained from the measured value of each qubit, which takes into account the interactions between the images. The reaction path is optimized by repeatedly obtaining an evaluation of the reaction path using images and adjusting the gate parameters that generate the images. VQE and ED are used to calculate the ground state of each image. The algorithm is applied to $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ reactions, and the activation energy is obtained from the optimized reaction path. The results show that the proposed algorithm accurately optimizes the reaction path and correctly obtains the activation energy from the reaction path, even when quantum circuits are used for both molecular geometry generation and ground-state calculations. This result shows that the quantum computer can be used to calculate chemical reactions.
2. Methods

We first give an overview of the NEB method and then explain the proposed reaction path optimization algorithm, which is based on molecular geometry generation using a quantum circuit.

2.1 Overview of the NEB method

We provide an overview of the theory of the reaction path optimization using the NEB method.\textsuperscript{23-25} We first generated $N_{\text{image}}$ images between the reaction coordinate of the reactant (initial state) and the reaction coordinate of the product (final state) at the potential energy surface on the reaction coordinate. Then, we created a reaction path by connecting adjacent images using virtual springs, and the force on each image in the reaction path is obtained. The force on the $i$-th image $F_i$ ($i = 1, 2, \ldots N_{\text{image}}$) is composed of the spring force $F_{i}^s$ and the gradient for the potential energy surface $\nabla E(R_i)$, where $R_i$ is the reaction coordinate in the $i$-th image and $E(R_i)$ is the energy of the system specified by $R_i$. In this study, the evaluation value $\bar{F}$ in the NEB is defined as the average of the norm of the forces on each image using the tangential component for the path of $F_{i}^s$, $F_{i}^s\parallel$ and the tangential perpendicular component of $\nabla E(R_i)$, $\nabla E(R_i)\perp$, as shown below:

$$\bar{F} = \frac{1}{N_{\text{image}}} \sum_{i=1}^{N_{\text{image}}} |F_i| \quad (1)$$

$$F_i = F_{i}^s\parallel - \nabla E(R_i)\perp \quad (2)$$

$$F_{i}^s\parallel = (F_{i}^s \cdot \hat{t}_i)\hat{t}_i = K(|R_{i+1} - R_i| - |R_i - R_{i-1}|)\hat{t}_i \quad (3)$$

$$\nabla E(R_i)\perp = \nabla E(R_i) - \nabla E(R_i) \cdot \hat{t}_i \quad (4)$$
where $K$ is the spring constant. The tangent vector $\mathbf{\hat{t}}_i$ is defined as follows.

$$
\mathbf{\hat{t}}_i = \begin{cases} 
\mathbf{\hat{t}}_i^+ & \text{if } E(R_{i+1}) > E(R_i) > E(R_{i-1}) \\
\mathbf{\hat{t}}_i^- & \text{if } E(R_{i+1}) < E(R_i) < E(R_{i-1}) \\
\end{cases}
$$

else if $E(R_{i+1}) < E(R_i) > E(R_{i-1})$ or $E(R_{i+1}) > E(R_i) < E(R_{i-1})$

$$
\mathbf{\hat{t}}_i = \begin{cases} 
\mathbf{\hat{t}}_i^+ + \mathbf{\hat{t}}_i^+ \Delta E_{i}^{\min} & \text{if } E(R_{i+1}) > E(R_{i-1}) \\
\mathbf{\hat{t}}_i^- + \mathbf{\hat{t}}_i^- \Delta E_{i}^{\max} & \text{if } E(R_{i+1}) < E(R_{i-1}) \\
\end{cases}
$$

$$
\mathbf{\hat{t}}_i^+ = R_{i+1} - R_i \\
\mathbf{\hat{t}}_i^- = R_i - R_{i-1}
$$

$$
\Delta E_{i}^{\max} = \max(|E(R_{i+1}) - E(R_i)|, |E(R_{i-1}) - E(R_i)|) \\
\Delta E_{i}^{\min} = \min(|E(R_{i+1}) - E(R_i)|, |E(R_{i-1}) - E(R_i)|)
$$

The value of $\mathbf{\hat{t}}_i$ needs to be normalized. The tangential perpendicular component of the spring force and the tangential component of the gradient at the potential energy surface are not used in the evaluation value in order to prevent shifting of the image from MEP and the distance between images from being unequal, respectively. The tangent vectors are defined so as to prevent the path from oscillating during the convergence process. In this study, the number of images $N_{image}$ in NEB was set to three or five. The spring constant $K$ was set to 0.1 Hartree/A$^2$.

2.2 Optimization of reaction path by molecular geometry generation using quantum circuits

Here, we provide a detailed description of the algorithm proposed in this work to optimize the reaction path via molecular geometry generation using quantum circuits. Figure 1 shows the algorithm for obtaining the activation energy via geometry generation using
quantum circuits. The outline of the calculation is shown in the following four steps. The capital letters in each step correspond to the letters in Figure 1.

Step A. Generate the geometries that correspond to the images on the reaction path using a parameterized quantum circuit using $\theta$, i.e., generate the reaction path using $\theta$. b

Step B. Calculate the energy value for each image and obtain the evaluation value for the reaction path based on the obtained energy value.

Step C. Calculate the gradients for the parameters $\theta$ of the evaluation value by performing step A and step B by slightly changing the parameters from the original ones and updating $\theta$ based on the gradient.

Step D. Repeat from step A to C until the termination condition is satisfied. After termination, the activation energy is obtained using the geometry and energy on the optimized reaction path.

b In this study, the symbols that represent the parameters (i.e., $\theta$, $\varphi$, and $\lambda$) are generic terms. When dealing with individual parameters, they are written as $\varphi_m$ (where $m$ is the qubit index).
**Figure 1.** The computational flow of the reaction path optimization and activation energy acquisition by molecular geometry generation using quantum circuits. Two-atom molecules are depicted as a picture. In step A, we generate the geometries needed to obtain the reaction path using a quantum circuit. Each rotation angle of the $R_y$ gate in the geometry-generating quantum circuit (center) is determined based on the structural information of each image in the initial guess (the initial reaction path, left side). The rotation angle of the $R_y$ gate is fixed once determined during the reaction path optimization. Each qubit is initialized with $|0\rangle$, and then the $R_y$ gate is computed, followed by a quantum gate $U_g(\theta)$ with the parameters $\theta$ to entangle each geometrical information (center). New geometries in each state are generated (right side) based on the wave function $|\psi'(\theta)\rangle$ (center) from the quantum circuit. In step B, we calculate the energy in each state and the evaluation value.
value. The ground-state calculations in each geometry were performed following two patterns: VQE and ED. In step C, we obtain the gradients for the evaluation value by performing step A and step B with a small change in $\theta$, and then by updating $\theta$. In step D, we repeat the step from A to C until the termination condition (100 iterations in this study) is met, and the activation energy $E_a$ is obtained using the reaction path in the final iteration.

The details for each step are shown below:

Step A. molecular geometry generation by a quantum circuit

After explaining the embedding of the structural information into a quantum circuit, we describe the transformation of wave functions into structural information.

**Figure 2** shows the proposed algorithm of embedding the structural information into a quantum circuit and transforming the wave function into structural information. First, we explain the embedding method of the structural information in a quantum circuit using an example of three hydrogen atoms aligned in one dimension, which we are dealing with in this study. The three hydrogen atoms are named $H_A$, $H_B$, and $H_C$ from left to right, and the position of $H_A$ is used as the origin. The distances between $H_AH_B$, $H_BH_C$, and $H_AH_C$ are written as $R_{AB}$, $R_{BC}$, and $R_{AC}$, respectively. The three distances have a relation $R_{AB} + R_{BC} = R_{AC}$. These distances in absolute coordinates are divided by the reference length $R_{ref} \geq R_{AC}$ to convert them to the fractional coordinates of $[0,1]$. Then, the origin 0 of the fractional coordinate is converted to $|0\rangle$, the maximum length 1 is converted to $|1\rangle$, and the distance between 0 and 1 is regarded as a wave function of the linear combination of $|0\rangle$ and $|1\rangle$, making the fractional coordinate correspond to the rotation angles $\varphi$ of $R_y$. In the
present case, the coordinates of \( H_A, H_B, \) and \( H_C \) are converted from absolute coordinates \( 0, R_{AB}, \) and \( R_{AC} \) to the fractional ones \( 0, R_{AB}/R_{ref}, \) and \( R_{AC}/R_{ref}, \) respectively, and the corresponding wave functions are \( |0\rangle, \sqrt{R_{AB}/R_{ref}}|0\rangle + \sqrt{1 - R_{AB}/R_{ref}}|1\rangle, \) and \( \sqrt{R_{AC}/R_{ref}}|0\rangle + \sqrt{1 - R_{AC}/R_{ref}}|1\rangle, \) respectively, and the rotation angles \( \varphi \) of \( R_y \) are 0, \( 2\arccos(\sqrt{R_{AB}/R_{ref}}), \) and \( 2\arccos(\sqrt{R_{AC}/R_{ref}}), \) respectively. The root sign is used for wave function normalization. \( \varphi \) are determined so that \( |0\rangle \) multiplied by \( R_y(\varphi) \) is the wave function corresponding to the fractional coordinate. That is,

\[
R_y(2\arccos(0))|0\rangle = |0\rangle \\
R_y(2\arccos(\sqrt{R_{AB}/R_{ref}}))|0\rangle = \sqrt{R_{AB}/R_{ref}}|0\rangle + \sqrt{1 - R_{AB}/R_{ref}}|1\rangle \\
R_y(2\arccos(\sqrt{R_{AC}/R_{ref}}))|0\rangle = \sqrt{R_{AC}/R_{ref}}|0\rangle + \sqrt{1 - R_{AC}/R_{ref}}|1\rangle
\]

Therefore, to embed the one-dimensional molecular geometry of three hydrogen atoms in a circuit, we first initialize all three qubits corresponding to each atom to \( |0\rangle \) and then apply the \( R_y \) gate with a rotation angle, corresponding to each atom’s position. \( R_{ref} \) is set to be 6.00 Å. In the NEB method, it is necessary to embed multiple geometries in a quantum circuit. In this case, the qubits and \( R_y \) gates corresponding to the geometries of each image are arranged in order. However, it is not necessary to embed the information of the atoms that do not change the coordinate\(^c\) in the optimization of the reaction path in NEB. As an

\(^c\) Excluding small changes in the reaction coordinates during the gradient calculation on the potential energy surface in step B.
example, Figure 2 shows the initial guess (the initial reaction path) of NEB with three images used in this study and the quantum circuit with the structural information embedded in it. In addition to the initial and final states, the positions of HA are fixed at the origin (shown in black in Figure 2(a)). The unfixed atoms are shown in red, indicating that six qubits are required for the geometry generation.\(^d\) The rotation angle of the \(R_y\) gate is shown in Figure 2(b), \(\varphi_m (m = 1, 2, \ldots 6)\) is determined by the position of the atoms in the red circle in Figure 2(a). For example, H\(_C\) of the 4-th index in Figure 2(a) has a distance \(R_{AC}\) with \(R_{AC} = R_{AB} + R_{BC} = 0.73 + 0.73 = 1.46\, \text{Å}\), and the corresponding rotation angle of the \(R_y\) gate \(\varphi_4\) is as follows.

\[
\varphi_4 = 2\arccos\left(\frac{R_{AC}}{R_{ref}}\right) = 2\arccos\left(\frac{1.46}{6.00}\right) \approx 2.11
\]

We describe a method for extracting the structural information from a wave function. We let the probability \(P_m\) obtained by measuring the \(m\)-th qubit with \(\langle 0|\) correspond to the fractional coordinate of the \(m\)-th atom for the wave function \(|\psi'(\theta)\rangle\) obtained from the quantum circuit.

\[
P_m = \langle 0|_m |\psi'(\theta)\rangle^2 \quad (5)
\]

\(\langle 0|_m\) represents \(\langle 0|\) acting on the qubits of the index \(m\). The definition of \(P_m\) comes from the fact that if the qubits are not entangled with each other and a single-qubit wave function

\(^d\) Since we are dealing with a one-dimensional system, the number of qubits required per atom is one. And if we are dealing with an \(N\)-dimensional system, we can make the same argument as above for the embedding using \(N\) qubits per atom. The number of qubits required for the geometry generation of an \(N\)-dimensional system is \(N \times (\text{The number of unfixed atoms})\).
for the $m$-th atom with the fractional coordinate $a$ can be expressed as $|\psi'\rangle = \sqrt{a}|0\rangle + \sqrt{1-a}|1\rangle$, then applying Equation 5 results in $P_m = a$. Fractional coordinate $a$ is converted to absolute coordinates by $a \times R_{ref}$. As shown in Figure 2(b), we can obtain the wave functions of the entangled structural (i.e., atomic positional) information by embedding the structural information in $R_y$ and then multiplying it by unitary gates with parameters represented as $U_g(\theta)$. Thus, through the circuit in Figure 2(b), the coordinates obtained using Equation 5 can be considered as ones that incorporate interactions between images.\(^c\)

All qubits of the geometry generation in Figure 2(b) are initialized with $|0\rangle$. The parameterized unitary gate $U_g(\theta)$ was created based on Hardware Efficient Ansatz.\(^30\) All initial parameters $\theta$ of $U_g(\theta)$ were set to 0, and the depth of the geometry generating circuit $D_g$ (right side of Figure 2(b)) was set to 2. All quantum circuit simulations in this work are implemented using Blueqat.\(^31\)

\(^c\) Note that the expressible reaction path by the circuit does not change with or without the entanglement (i.e., the $CZ$ gate). The expectations for quantum entanglement in the geometry generating circuit are to improve the expressive power of the reaction path update, not the reaction path itself, and to speed up the evaluation value convergence (see supplementary information).
Figure 2. The initial guess for the $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ reaction and the quantum circuit used to generate the molecular geometry. (a) Initial guess set up. In this figure, the number of images between the initial state and the final state is three. The position of $\text{H}_A$ is set to the origin $O$, and the right direction is positive (arrow from $O$ to $x$ at the top of the figure). The values of $(R_{AB} (\text{Å}), R_{BC} (\text{Å}))$ in the initial state (IS), intermediate point (IMP), and final state (FS) are set to $(0.73, 3.27)$, $(0.73, 0.73)$, and $(3.27, 0.73)$ respectively. In this study, the numbers of images are three or five. When three (five) images, one (two) image(s) was (were) interpolated between IS and IMP, and between IMP and FS, respectively. Atoms with fixed positions in the reaction path optimization calculations are shown in black, and atoms with changed positions are shown in red. The number assigned to each atom in red corresponds to the qubit index in (b). (b) Details of the circuit used to generate the geometry, the qubits were initialized to $|0\rangle$. After the $R_y$ gate operation was performed on
each qubit using the rotation angles, corresponding to each of the atomic positions shown in (a) in red, the qubits are entangled with each other using $U_g(\theta)$ (left side). $U_g(\theta)$ was constructed based on Hardware-efficient ansatz,\textsuperscript{30} and the block composed $R_y$, $R_z$, and $CZ$ gates surrounded by the dashed line (right side) was repeated $D_g$ times.

Step B. Calculate the energy values for each image and obtain the evaluation value for a reaction path.

To obtain the evaluation values in Equation 1, the values of energies and gradients on the potential energy surface for each image, i.e., $E(R_i)$ and $\nabla E(R_i)$, respectively, are required. Therefore, we calculate the ground state of the geometry, corresponding to the reaction coordinates of each image and the coordinates around the reaction coordinates. We choose the reaction coordinates on the potential energy surface as $R_{AB}$ and $R_{BC}$. The Hamiltonians used in the ground-state calculations were generated using OpenFermion package.\textsuperscript{32} The molecular wavefunctions of the converged Hartree-Fock calculations by STO-3G were used, and the number of spin orbitals was six, i.e., two per hydrogen atom. For the comparison, the ground-state calculation was obtained using VQE and ED, respectively.

The optimization of the quantum circuit in the VQE ground-state calculation was based on the gradient-free method, Rotoselect.\textsuperscript{33} Figure 3 shows the quantum circuit used in the ground state calculation using VQE. Rotoselect optimizes not only the parameters but also the types of the rotation gates in the circuit.\textsuperscript{33} The initial parameters of Rotoselect were set to be random numbers of [0.0, 0.1) and the initial rotation gates were set to be $R_x$. The depth $D_e$ of the quantum circuit shown in Figure 3 was set to five. The energy evaluation
of VQE was repeated until the energy difference became less than $10^{-4}$ Hartree. The gradient on the potential energy surface for each image was obtained using the central difference method, and the difference value for each reaction coordinate was set to 0.1 Å. By obtaining the energy and gradient values for each image, we can obtain the evaluation values in Equation 1.

Step C. Calculate the parameter gradients of the evaluation value and update the parameters $\theta$.

By performing steps A and B with parameters whose values were changed slightly, we calculated the gradients of the evaluation value for the parameters $\theta$ and used the gradients to update $\theta$. The gradients of the evaluation value were obtained using the central difference method, the parameter difference value was set to 0.001, and the parameter update was done using Adam$^{34}$ at a learning rate of 0.01.

Step D. Obtain the activation energy for an optimized reaction path

Steps A to C were repeated until the termination condition was met, and after the termination, the activation energy was obtained using the energy of each state on the reaction path in the final iteration. The termination condition was set at 100 iterations. In this study, $E_a$ is defined as the difference between the energy of the image with the highest energy among all states and the energy of the initial state (i.e., reactant).
Figure 3. A quantum circuit used in the VQE ground-state calculation. In the quantum circuit, six qubits were used (the number of qubits is the same as the number of spin orbitals of the system). All the qubits were initialized to |0⟩. $U_e(\lambda)$ was composed of blocks of $R_l$ ($l = x, y, z$), and $CNOT$ gates in the dashed line on the right of the figure, and the number of the block repetitions was $D_e$. The parameters and the kinds of rotation gates were optimized using Rotoselect.\textsuperscript{33}

3. Results
For the $H_2 + H \rightarrow H + H_2$ reaction, we show the results of the reaction path optimization of NEB with three and five images via molecular geometry generation using a quantum circuit (see the supplementary information on the change in the evaluation values for each iteration). Figure 4 shows the reaction paths on the potential energy surface with the hydrogen-atom distances ($R_{AB}$, $R_{BC}$) as the reaction coordinates. Figures (a) and (c) show that the paths obtained by NEB using VQE and ED energy evaluations, written as Eval_VQE (green line) and Eval_ED (red line), respectively, changed from the initial guess (black dotted line) to closer paths to the saddle point (the maximum energy in the exact MEP, blue cross mark) and smoother paths of curvature in both image numbers three and five (a smoother path was obtained for the five images than three images). Furthermore, in Figures (b) and (d), the maximum energies of the reaction paths for both Eval_VQE (green line) and Eval_ED (red line) were lower than those of the initial guess (black dotted line), which were close to the value of the saddle point (blue cross mark). Therefore, it can be seen that the reaction path was correctly optimized by the molecular geometry
generation method using quantum circuits. Furthermore, the Eval_VQE results show that the NISQ device can be used to optimize the reaction path since the activation energy is correctly obtained even when the quantum circuit is used for both molecular geometry generation and ground-state calculation.

Finally, we note the effect of the convergence condition of the ground-state calculation on \( E_a \). Table 1 shows the obtained evaluation values \( \bar{F} \) (the average of the forces on images), \( R_{AB}, R_{BC} \), activation energy, and absolute values of the difference from the exact activation energy \( |\Delta_{saddle}| \) for each calculation condition in three and five images. Although the values of \( |\Delta_{saddle}| \) were sufficiently small compared to the initial guess for both Eval_ED and Eval_VQE, the value of Eval_VQE was slightly larger than the chemical accuracy (about 1 mHartree). Particularly, in the case of five images using Eval_VQE, the value was about 8 mHartree. The error can be solved by tightening the convergence condition in VQE. For example, we executed VQE in the geometry of the saddle point and found that the absolute value of the error from the exact value decreases from 4.5 mHartree to 0.031 mHartree when the convergence condition was changed from the default value of \( 10^{-4} \) Hartree in this study to \( 10^{-6} \) Hartree. The convergence conditions in this study were a little loose due to saving the calculation time. The conditions need to be tightened when calculating the activation energy with higher precision than the accuracy of the results obtained in this study.
Figure 4. Reaction paths on the potential surface before and after the optimization of the reaction path by NEB for three and five images and the energies of each state in the reaction path. (a)(b) and (c)(d) are the results for three and five images, respectively. (a)(c) are reaction paths on the potential surface at the reaction coordinates $R_{AB}, R_{BC}$. The value of the energy on the potential surface is shown as a contour plot. The initial guess shown in Figure 2(a) is indicated by black triangle marks and dotted lines, and the path Eval_VQE (Eval_ED), optimized using the energy evaluation by VQE (ED), is indicated by red circle marks, (green square marks) and straight lines. The marks denote each state. The saddle point (the maximum energy in the exact MEP) is indicated by a blue cross mark. The reaction proceeds from the initial state at the upper left to the final state at the lower right.
(b)(d) show the energy in each state during the reaction. The energy along each reaction path in (a) and (c) is shown on the horizontal axis, and the length of each reaction path was normalized to compare different length reaction paths (the horizontal axis was written as “Reaction coordinate” due to convention). The types of marks and lines correspond to those of (a) and (c). The reaction proceeds from the initial state on the left to the final state on the right. Since the potential surface in (a) and (c) are symmetrical with respect to the 45° line (symmetrical with respect to the replacement of $R_{AB}$ and $R_{BC}$) and the saddle point was on the 45° line, the horizontal axis of the saddle point mark in (b) and (d) was set to 0.5.

Table 1 List of obtained evaluation values $\bar{F}$ (the average force acting on images), $R_{AB}$, $R_{BC}$, activation energy $E_a$, and the absolute value of the difference from the exact activation energy $|\Delta_{saddle}|$ for three and five images after the optimization termination. If the values of three images and five images were different, the result for five images was written in parentheses.

| 3 Images (5 Images) | $\bar{F}$ (Ha/Å) | $R_{AB}$ (Å) | $R_{BC}$ (Å) | $E_a$ (mHa) | $|\Delta_{saddle}|$ (mHa) |
|---------------------|------------------|--------------|--------------|-------------|------------------|
| Initial guess       | 0.17 (0.12)      | 0.73         | 0.73         | 83          | 50               |
| Eval_VQE            | 0.02 (0.03)      | 0.82 (0.91)  | 1.09 (1.01)  | 38 (41)     | 5 (8)            |
| Eval_ED             | 0.00 (0.00)      | 0.94 (0.87)  | 0.95 (1.04)  | 33 (31)     | 0 (2)            |
| Saddle Point        | -                | 0.94         | 0.94         | 33          | -                |
4. Conclusions

In this study, we proposed an algorithm for the optimization of the reaction path for obtaining the activation energy based on the generation of molecular geometries using quantum circuits. In the geometry generating method, the coordinates of each atom in each state of the initial reaction path were embedded in a quantum circuit as the rotation angle of an $R_y$ gate. We extracted the structural information from the measured probabilities for each qubit in the wave function obtained from the quantum circuit. The NEB method was used for the reaction path optimization. The states in the reaction path can be interacted with each other by connecting between qubits using $CZ$ gates. We applied the algorithm to optimize the reaction path for the $\text{H}_2+\text{H} \rightarrow \text{H} + \text{H}_2$ reaction. We used ground-state calculations in each state using VQE (hardware efficient ansatz) and ED in the NEB evaluation. It was found that the reaction paths were optimized and the activation energy values that are close to the saddle point (exact) values were obtained in both the cases. The results show that it is possible to perform chemical reaction calculations using quantum algorithms. Future studies will include the confirmation of the convergence speed-up using a quantum circuit (as mentioned about the convergence in the supplementary information), application of the algorithm to large scale systems, and adaptation of the geometries generation method to other algorithms (e.g., geometry optimization algorithms).

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*Email: kanno.s.ac@m.titech.ac.jp.*
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Supplementary information

The convergence of the evaluation value, and entangler’s contribution to the convergence speed

First, we describe a convergence of the evaluation value (the average force acting on images). Figure S1 shows the changes in the evaluation values of the optimization of parameter $\theta$ for each iteration. Figures (a) and (c) show the results for three and five images, respectively. In both cases, the evaluation values tend to converge as the number of iterations increases. The use of ED for the ground-state calculation (red line) converged faster than that of VQE (green line), indicating that the speed of convergence is related to the accuracy of the ground state calculation.

Next, we discuss the influence of the entangler $CZ$ gates on the convergence of the evaluation values. In this study, we used the $CZ$ gates in the quantum circuit (Figure 2(b)) for molecular geometry generation to interact between images (and atomic positions). Also, as mentioned in the introduction section, the treatment of interactions between images can affect the speed of convergence. Thus, the presence or absence of the $CZ$ gates may change the speed of convergence. The purple dotted line in Figure S1 shows the change in the evaluation value for each iteration when the reaction path is optimized by removing the $CZ$ gate from $U_g(\theta)$. The ground-state calculation is based on ED. Although there is almost no significant difference between the case with $CZ$ gates (red line) and the case without (purple dotted line) in Figures S1(a) and S1(c), the enlarged Figures S1(b) and S1(d) show that after about 50 iterations, and the value with $CZ$ gates (red line) tends to be lower
than that without CZ gates (purple dotted line). Therefore, the effect of the CZ gate entanglement between images (and between atomic positions) would be affected after the NEB evaluation values converge to some extent. The application of our algorithm to various systems or theoretical analyses would confirm the quantum advantage of the proposed algorithm.

**Figure. S1** The evaluation value (the average force acting on images) for each iteration.

(a)(b) and (c)(d) are the results for three and five images, respectively. (b) and (d) are enlarged views of the vertical axes in (a) and (c), respectively. The green and red lines are
The results of ground-state calculation with VQE and ED, respectively, as used in the main text. The dotted purple line shows the reaction path optimization by removing the CZ gate from the geometry generating quantum circuit in Figure 2(b). The ground-state calculation in the purple line was performed using ED.