

Quantum Chemistry Simulation on Quantum Computers: Theories and Experiments

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It has been claimed that quantum computers can mimic quantum systems efficiently in polynomial scale. Traditionally, those simulations are carried out numerically on classical computers, which are inevitably confronted with the exponential growth of required resources, with the increasing size of quantum systems. Quantum computers avoid this problem, and thus provide a possible solution for large quantum systems. In this paper, we first discuss the ideas of quantum simulation, the background of quantum simulators, categories of them, and the development in both theories and experiments. We then present a brief introduction to quantum chemistry evaluated via classical computers followed by typical procedures of quantum simulation towards quantum chemistry. Reviewed are not only theoretical proposals but also proof-of-principle experimental implementations, via a small quantum computer, which include the evaluation of the static molecular eigenenergy and the simulation of chemical reaction dynamics. Although the experimental development is still behind the theory, we give prospects and suggestions for future experiments. We anticipate that in the near future quantum simulation will become a powerful tool for quantum chemistry over classical computations.

1 Introduction to quantum simulation

Over the last century, quantum chemistry, benefited from various theoretical approximations in computational simulation, has achieved remarkable success in exploring the electronic configurations of atoms and molecules, and interactions between them for small systems.¹ These methods, elegant and ingenious, ranging from wavefunction approaches to density functional theory, are facing challenges when the system becomes larger or higher accuracy is required. This is because the Hilbert space of quantum system scales exponentially with system size, making computational costs unfeasible within current classical computer architectures. Having realized the computational bottleneck of classical computers, these intrinsically quantum systems would be better simulated on a quantum simulator to reduce the computational difficulties and extract information that is inaccessible with classical computers. For about thirty years since Richard Feynman brought forth the idea of quantum simulation performed inherently via a quantum apparatus,² numerous studies have been done in many aspects of physics,³ including in particular, quantum

chemistry, materials science, quantum many-body problems, condensed matter physics, etc.

In this article, we first introduce the ideas of quantum simulations on quantum simulators and approaches to physical quantum simulators. We also briefly discuss the quantum chemistry and how to implement quantum simulation specifically for quantum chemistry problems. Afterwards we review the recent theoretical scenarios and experimental illustrations for some of the proposed algorithms, including the simulations of static molecules and chemical reactions.

1.1 Advantages of quantum simulators

The driving force in building a quantum simulator is its advantage in solving a vast amount of problems in physics, chemistry, and biology, together with its feasibility within current technological development. Classical computers are limited to small quantum systems, due to the huge demand of memory and processor capability to store and manipulate the states of large quantum systems. This is because the number of parameters defining the quantum states is raised exponentially, with respect to the increasing number of particles involved. Moreover, the number of operations in evolving quantum states also grows exponentially with the size of the system. For instance, to simulate 100 spin-1/2 particles, i.e. number of electrons in a moderate molecule, a conventional computer would need $2^{100} \approx 10^{30}$ bits to describe the state, whilst

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computing the time evolution is effectively doing 2^{100} by 2^{100} matrix arithmetics. Both requirements are beyond the capacity of current computers and even the future ones, since the quantum effect would kick in when the components in electric circuit are small enough, leading to the upper bound on the calculating ability of conventional computers. However, quantum computer, in that case, would only need 100 qubits to implement the simulation, which is greatly fewer than 2^{100} bits. Here, a qubit, a two level quantum system that is analogous to the classical bit, is usually represented by an atom, an electron, a photon, *etc.* Thus quantum simulations on quantum computers could not only release the potential of quantum simulation, yielding results which are unable to calculate on a classical circuit, but also enable us to verify and develop theories and models, especially on microscopic scale.⁴

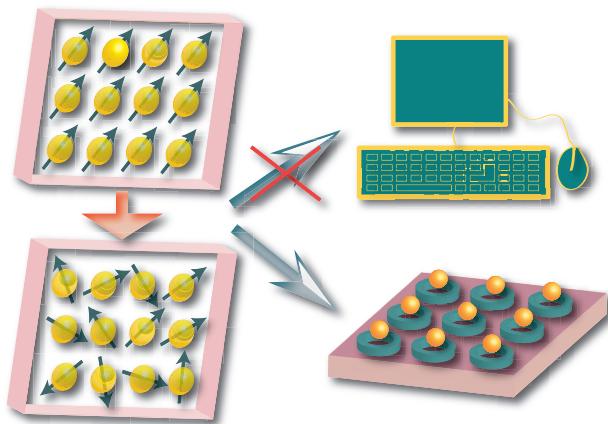


Fig. 1 Quantum phenomena describing the spin-1/2 particles from an ordered state to a random state. For simulating this process of 45 particles with classical computers, the memory required to store the states of the system needs 2^{45} bits = 4 tera byte (TB), which is about the current capacity of hard disks in personal computer. It is hard to imagine when the system scales to 100 particles what a fantastic classical computer we need to merely store the data. Contrarily, a quantum computer of 45 qubits is sufficient to simulate this process.

We see that quantum simulators have great advantages over classical counterparts. To build one in the near future, one of the barriers of developing quantum information processor, the present unperfect achievement of coherent control, may soon be overcome, making it possible for physical realization of quantum simulation.⁵ Additionally, unlike quantum computation which requires either error corrections or explicit quantum gates, quantum simulation is more feasible. Thousands of qubits are necessary to perform a quantum algorithm, like factorizing a modest number with Shor's algorithm, whereas only tens of qubits are required to conduct a useful quantum simulation.⁶⁻⁸

1.2 Categories of quantum simulators

A question comes how the quantum simulator would be implemented? One direct method is to project the evolution of the physical system to be simulated onto the controlled evolution of the simulating system. Therefore, the simulating quantum system will reproduce the physical one. This type of device is referred here as an analogue quantum simulator (AQS).⁸⁻¹¹ In AQS, the accuracy depends on the resemblance between the physical system and the simulating one. Another type of simulators, the digital quantum simulator (DQS), is a quantum circuit, comprised of one- and two-qubit gates for certain unitary transformations.^{6,12,13} This approach has the advantage of universality. However, there remain challenges of the DQS, such as the exponential growth of required gates with the precision of the results.⁴ For this reason, AQS is more favorite in current quantum simulation studies compared to DQS, although in the end we aim to build a universal quantum simulator. In the following subsection, we will discuss, so far, several (potentially) fruitful implementations of AQS for quantum chemical applications.

1.3 Some feasible quantum simulator architectures

- Nuclear Magnetic Resonance (NMR). Since the first simulation of quantum oscillator,¹⁴ a lot of progress have been made on this platform.¹⁵⁻¹⁹ Among them, in the area of quantum chemical simulations, two proof-of-principle experiments have been done on modeling the hydrogen molecule H₂,²⁰ and on simulating the chemical dynamics of a isomerization reaction.²¹ In NMR architecture, nuclear spins are functioned as qubits, and are manipulated and read-out by an NMR spectrometer.²² Although the NMR system may be limited to only few tens of qubits, it has produced a wealth of information and provided a testing platform for experimental realizations of many proposed schemes.^{23,24}

- Quantum Linear Optics. This is a more quantum-mechanical approach than NMR ensemble, and yet starts to show its potential in quantum computation and quantum simulation.²⁵ Indeed, the first experiment in quantum chemistry simulation, a minimal basis model of the hydrogen molecule H₂, was implemented with this system.²⁷ Quantum optics system relies on the different degrees of freedom (DOF) of single photons, i.e. polarizations and paths, as qubits to encode quantum information.^{25,26} It is regarded as an available platform for quantum chemical simulations, despite challenges remaining in hardware, e.g. the reliability of output and detection of a number of coherent single photons.²⁸

- Trapped Ions. As one of the most controllable systems available today, many advanced physical systems, such as quantum magnet and Dirac equations, have been simulated on this platform.^{8,29,30} For this structure, qubits are represented

by the electronic states of cold trapped ions.^{31–33} However, chemical simulations are yet to be realized.

- Superconducting Circuits. Besides synthesizing arbitrary states and implementing simple 2-qubit algorithms in experiment,^{34,35} superconducting circuits are supposed to simulate the phenomena of atom physics,^{36,37} realize the Kitaev model on a honeycomb lattice,³⁸ or simulate Anderson and Kondo models.³⁹ The flowing circulating current in a superconductor can be used as a qubit.^{37,40} Precise control and measurement in this system has been demonstrated, but the scalability problem remains to be solved.

- Quantum Dots. The electron spins in semiconductor quantum dots with discrete energy levels,⁴¹ which are analogous to a real atom binding an electron, have been proved to simulate the Fermi-Hubbard model^{41,42} and the many-fermion problem in high-Tc superconductors.¹⁰ A feasible proposal has also been brought forward to model chemical reactions.¹¹

- Cold Atoms. Neutral atoms in optical lattices are important potential quantum simulators, especially for condensed matter physics. The simulation of the quantum phase transition was firstly implemented in this system, realizing a superfluid transferred to a Mott insulator.⁹ Numerical examples that could be simulated are discussed in the reviewing paper by Lewenstein,³ while experimental approaches can be found in Bloch's paper.⁴⁴

2 Quantum chemistry

2.1 Classical approach to quantum chemistry

Quantum chemistry aims at developing theoretical methods to calculate molecular properties and evolutions on basis of quantum mechanics. Most quantum chemical approaches involve the Born-Oppenheimer approximation to separate electronic and nuclear motions. However, even in this frame, exact solution of the Schrödinger equation requires the computational resources increase exponentially with the molecular size. Because of this, the developments of quantum chemical methods have always adopted various approximations.

The first important task of quantum chemistry is to study static molecular properties, such as electronic structures and eigenenergies, vibrational normal modes, etc. Methods in this aspect include the mean-field Hartree-Fock and various post-Hartree-Fock approaches for the electronic correlations, such as the configuration interaction, coupled cluster, and many-body perturbation theories.⁴⁵ These high-precision calculations can only be performed on very small molecular systems. Density functional theory^{46–48} has a relatively high efficiency and enlarges the system size of application with a certain accuracy. Linear scaling algorithms^{49,50} are also developed to explore systems of thousands of atoms or even larger for certain types of materials. These methods can sometimes predict

chemical properties for large systems, but in some cases they may fail.^{51–54}

Another important task in quantum chemistry is the simulation of chemical dynamics, not only to explore the reaction mechanisms but also to guide the control of chemical reactions.^{55,56} Using conventional methods without approximations, the capacity of investigating chemical reaction dynamics so far is just 9 DOF.⁵⁷ Even the multiconfigurational time-dependent Hartree method,⁵⁸ which is highly sophisticated with various approximations and models, can just deal with tens of DOF. Similarly as in the static case, to simulate quantum dynamics of large molecular systems is currently intractable in classical computers.

2.2 Typical procedure of quantum simulation towards quantum chemistry

We have introduced the backgrounds for quantum simulation, quantum simulator, and quantum chemistry. In this section, we will discuss the approaches in quantum simulation. Specifically, we will focus on the methods and techniques applied in quantum chemistry simulations, especially those which have been or are likely to be implemented.

In quantum simulation, we are interested in the behaviors and properties of a quantum system, which could be either a stationary molecule or a chemical reaction. The procedure of quantum simulation can be summarized into three steps: a) preparing the quantum state into an initial state, b) evolving the initial state with the system Hamiltonian, and c) measuring the desired properties from the final state.

Before we move on to discuss each of these steps, we recall that the two major schemes in quantum simulation are digital (universal) quantum simulation (DQS) and analogue (dedicated) quantum simulation (AQS). As mentioned in Section 1.2, at current stage, most research groups concentrate on AQS instead of DQS due to the difficulty in performing a DQS. Therefore, the arguments below will mainly apply to AQS, although some of them could also be used on DQS.

2.2.1 Preparing the quantum state into an initial state.

In principle, there are two ways to simulate a chemical system.⁵⁹ One is the second quantization method where Born-Oppenheimer approximation is adopted. It considers that electrons in a molecule are indistinguishable, unlike individually identifiable qubits. The advantage of this approach is that it is economical with quantum resources, as it requires only one qubit per basis. Due to this, the first quantum chemical experiment was performed using this method.²⁷ Nonetheless, this method is not suited if the system is complex which cannot be represented by a small basis set, or if it is a dynamic problem which cannot be associated with a fixed basis set. To overcome this, people also introduce the first quantization method.

First quantization approach does not take account of the Born-Oppenheimer approximation. Instead, it simulates particles altogether including both nuclei and electrons governed by the Schrödinger equation on a grid in real space.^{60–62} Although it may need an excessive amount of resources compared to the second quantization, it has advantages when the system becomes large. Since the Coulomb interaction is operated in different representations, the second quantization method requires $O(P^5)$ gates where P denotes the size of the basis set, while using the first quantization approach the number of gates scales at $O(Q^2)$ for a Q -particle system.^{59,60} It is found the first quantization scheme will be more efficient to simulate reactions of more than four atoms.⁶⁰

2.2.2 Evolving the initial state with the system Hamiltonian. Currently, we select the Trotter formula⁶² and its generalization in high dimensions^{63,64} to generate the unitary evolution on basis of a system Hamiltonian that is to be simulated. Essentially, this formula decomposes the time period in the propagator into small time intervals. The desired evolution is implemented by iterating the process of each step.

2.2.3 Measuring the desired properties from the final state. There are mainly two methods that have been used in experiments to obtain information from the final state. The first one, quantum state tomography, can fully characterize the final state after the evolution. However, the required resources grow exponentially with the size of the state since it reads out the whole Hilbert space of the state. Nevertheless, it provides a valuable method to evaluate the fidelity of the final results for low-dimensional states, especially in those proof-of-principle experiments. Another type of read-out technique is called phase estimation algorithm (PEA).^{65,66} Often the information of the state is encoded in the global phase which is of no use, as it is not observable. Using PEA, the information is transferred to the ancilla qubits and extracted from the latter by performing measurements on the latter. The scalability of this method is universal. However, one thing restricts it from wide use in circuit is the demand for extra ancilla qubits. As it is known that, to date, it is still a technical challenge to generate and manipulate many qubits in any quantum structure. So far, the two experimental realizations of static molecular modeling are performed via an improved version of PEA.^{20,27} Essentially, by iterating PEA process and modifying the parameters, i.e. the pulses in the circuit, accordingly, high-precision results can be achieved. In the contrary, another experiment,²¹ which was on simulating chemical dynamics, turned to quantum state tomography as its measurement technique. It was effective in that experiment since merely three qubits were involved and the associated Hilbert space was small enough. Additionally, quantum tomography provides a direct way to reconstruct the final state and to calculate the fidelity of the results. Nevertheless, this method could not be

conducted when system scales up, for the reason discussed above. PEA and other approaches^{67–70} would be the promising methods for measurements when systems contain tens of qubits or more.

3 Simulation of static molecular energies

3.1 Theoretical designment on simulating the molecular ground state energies

In a quantum system, the most fundamental properties are its energy eigenvalues and eigenstates. Accurate calculations of them request a quantum algorithm. This is the same situation as in quantum chemistry, where given a time-independent Hamiltonian of a molecule, the first task is to calculate the ground state energy, i.e., the lowest eigenvalue of the Hamiltonian. In classical computers, it is a non-deterministic polynomial (NP) problem. All known classical algorithms for it require exponential time. On the other hand, quantum algorithm or quantum simulation is theoretically proved to be able to solve this problem efficiently, in polynomial time.⁶⁵ With the help of quantum fast Fourier transform (FFT), the eigenvalues and eigenstates of a local Hamiltonian can be solved in polynomial time. Adams and Lloyd believed that many interesting problems in atomic physics which are classically intractable can be solved with 50 to 100 qubits.⁶⁵ It means quantum computers in this size would surpass the capacity of classical computers. Recently, Li and Yung *et al.* employed a trial wavefunction, approximating the ground state, to project the ground state by means of PEA, and performed an NMR experimental implementation of this idea to solve the ground-state problem of the Heisenberg spin model.⁷¹ Concerning the static properties of a molecule in quantum chemistry, Aspuru-Guzik *et al.* proposed an algorithm to calculate the energies of molecules in 2005.⁷ Compared to the previous algorithms, the information of eigenenergy in their work is encoded in the phase shift, and measured by a recursive PEA which reduces the number of qubits constituting the readout register from 20 to 4. In this scheme, the number of qubits scales linearly with the number of basis functions, and the number of gates scales polynomially, because the direct mapping from wavefunctions to qubits ensures the whole unitary operator be decomposed into polynomial number of quantum gates. They conclude that quantum simulation with 30 to 100 qubits can exceed the limitations of classical computing.⁷

The main procedure of simulating molecular energies can be summarized into three steps:

(i) *Encoding and initialization.* All quantum simulation tasks require a proper mapping from the system wavefunction to the state of qubits, to establish a bridge between the simulating system and physical system. The wavefunctions of many-particle system are often represented by single-particle

atomic orbits, which also depend on the choice of basis sets. There are essentially two different mapping methods: direct mapping in which a Fock space of the molecule is mapped onto the Hilbert space of the qubits, and more efficiently, the compact mapping, in which only a subspace of the Fock space is mapped onto the Hilbert space. For instance, to map the wavefunctions of water, with the simplest STO-3G basis set including 7 wavefunctions, the direct and compact mapping methods require 14 qubits and 10 qubits, respectively. If we choose the cc-pVTZ basis set including 58 wavefunctions, the two mapping ways need 116 and 47 qubits, respectively.⁷ The resources required exceed the experimental capacity in current quantum simulation, whereas it would be more possible to realize in the near future, compared to the conventional quantum algorithms which usually need thousands of qubits.

To prepare the initial state, i.e., the ground state $|\psi\rangle$ of a molecular Hamiltonian, the adiabatic state preparation (ASP) algorithm, on basis of the quantum adiabatic theorem,⁷² is a suitable approach. The quantum adiabatic theorem states that, a quantum system remains in its instantaneous eigenstate, if the system Hamiltonian varies slowly enough, and if there is a gap between this eigenvalue and the rest of the Hamiltonian's spectrum.⁷² Therefore we can choose a simple Hamiltonian and prepare the state according to its ground state. We then drive the simple Hamiltonian to the target molecular Hamiltonian sufficiently slowly, in which the non-crossing of all the energy levels are ensured. After the adiabatic process the qubits have been prepared to the initial state, the ground state of the molecular Hamiltonian.

(ii) *Evolution.* The core of evolution is the implementation of PEA to generate a phase shift on the probe qubit which reflects the information of the target eigenvalue. Briefly, applying $U = e^{-iH\tau}$ on the ground state $|\psi\rangle$, a phase will be induced on the exponential term $U|\psi\rangle = e^{-iH\tau}|\psi\rangle = e^{-iE\tau}|\psi\rangle = e^{i2\pi\phi}|\psi\rangle$, where $E = -2\pi\phi/\tau$ is the eigenvalue of the ground state. Experimentally, we confine the phase ϕ between zero and unity by a pre-estimated value of the energy E . If the phase on the probe qubit can be measured tremendously accurate, the resulted eigenvalue would be greatly precise, surpassing the results reached by the classical computers. However, this will cost many qubits in resource.

To overcome that, a modified PEA is proposed⁷ to reduce the number of qubits. The main idea is a recursive PEA, which repeats an arbitrary n -qubit PEA using $V_{k+1} = [e^{-i2\pi\phi_k} V_k]^2$. Here ϕ_k is a lower bound on the constructed shift ϕ at each iterative step k . The initial condition is $V_0 = U = e^{-iH\tau}$. In each step, one additional bit of ϕ is obtained, and a long enough digit can be achieved by repeating this procedure for many times. No matter how small the number of qubits n is (even only one qubit), accurate results can be obtained as long as the iterations of PEA are carried out enough times.

(iii) *Measurement.* Since the ground state energy has been

encoded to the phase of the probe qubits, a direct measurement of this phase is sufficient to obtain the value of the ground state energy. For example, if a four-bit inverse quantum Fourier transform is adopted for the phase measurement, we will need four qubits to obtain one precise bit with successful possibility of 15/16.

Similar to other quantum simulation tasks, in the field of chemical simulation, theory is still ahead of experiment. The present experimental technology is hardly to support the simulation of large molecules, whereas proof-of-principle experiments are available using current quantum simulation devices. As the first and key exemplification of quantum simulation towards quantum chemistry, the simplest but most significant scenario of simulating the ground state energy of hydrogen molecule is a good choice. The first two experiments both selected this problem, using the linear optical system²⁷ and NMR system,²⁰ respectively. We will review these two experiments briefly in the following.

3.2 Experiments of simulating the ground state energies of the hydrogen molecule

In 2010, Lanyon *et al.* demonstrated the quantum simulation of molecular eigenenergies using a linear optical quantum computation architecture for obtaining the energies of the hydrogen molecule in a minimal STO-3G basis.²⁷ In the linear optical system, quantum information is encoded in polarization or path of single photons.^{25,26} In their experiment, two qubits are utilized to implement the simulation, with one to encode the system wavefunction, while another to read out the result of PEA. For each iterative process, one bit precision is obtained. The whole iterative PEA is repeated for 20 times, achieving a high level of 20 bit precision in total. The experimental result matches exactly with the theoretical calculation and promises the chemical application of quantum simulation. Despite the other steps of the algorithm are assisted in a classical computer, the key step of performing the iterative PEA is realized perfectly on a linear optical quantum system, yielding important progress towards simulating quantum chemistry.

The Hamiltonian of the hydrogen molecule in the minimal STO-3G basis is block-diagonal with 2×2 submatrices, conducting one qubit to represent the system wavefunction and another to represent the phase information. Exact eigenstates are first encoded, which are preliminarily calculated through a classical computer. For imperfect eigenstate encoding, the algorithm is robust and still works well. The quantum state $|0\rangle$ and $|1\rangle$ are represented via the horizontal and vertical polarization $|H\rangle$ and $|V\rangle$, respectively. Single rotating gate is implemented using birefringent wave plates, and two-qubit gate is implemented by combining the phase shifters and beam splitters with projective measurement. The quantum circuit model can be found in Fig.2(a). The ground state energy is obtained

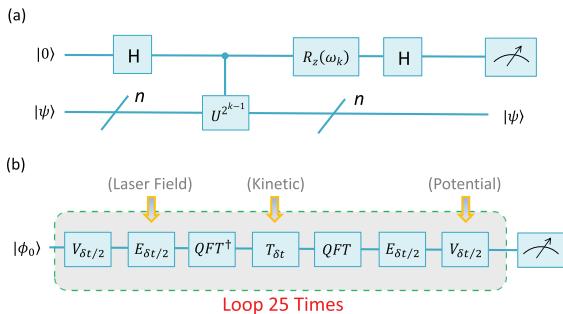


Fig. 2 (a) Network of the iterative phase estimation algorithm for the calculation of the hydrogen molecular energies. (b) Network of simulating the isomerization dynamics from the reactant state $|\phi_0\rangle$ where the whole process is divided into 25 loops.

as $-535.58 \pm 0.03 \text{ kJ mol}^{-1}$, which agrees well with the result calculated from a classical computer.

Almost simultaneously to the optical experiment, the proposal of simulating the ground state energies of hydrogen molecule is demonstrated via the NMR quantum computer.²⁰ The basis is selected as the widely used minimal STO-3G as well, and a two-qubit sample of ^{13}C -labeled chloroform dissolved in d_6 acetone is employed in the NMR spectrometer. Qubits are represented by ^{13}C (system qubit) and ^1H (probe qubit) nuclear spins. ASP⁷³ is tested for various bond distances with $r = 1.4$ a.u. is found the most suited to be used to prepare the initial state, i.e., the ground state of the hydrogen molecule in the minimal basis. A 15-step iterative PEA process is implemented as the essential part of the algorithm, with a 3-bit precision extracted per iteration, achieving totally a 45-bit precision. The readout is performed through an NMR interferometer,^{74–76} to obtain the phase shift of the probe qubit. The experimental result of the ground state energy is exact where uncertainty is only in the last and also the least important bit.

Considering the singlet symmetry and spatial symmetry, the Hamiltonian of the hydrogen molecule in the STO-3G basis can be simplified as⁴⁵

$$\begin{aligned} H &= \begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_{1\bar{1}}^{2\bar{2}} | H | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \\ \langle \Psi_{1\bar{1}}^{2\bar{2}} | H | \Psi_0 \rangle & \langle \Psi_{1\bar{1}}^{2\bar{2}} | H | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \end{pmatrix} \\ &= \begin{pmatrix} -1.8310 & 0.1813 \\ 0.1813 & -0.2537 \end{pmatrix}, \end{aligned} \quad (1)$$

whose eigenvalue is -1.85157092935119 a.u. Spin ^{13}C is used to modulate the system Hamiltonian. In NMR architecture, the logical states $|0\rangle$ and $|1\rangle$ are represented by the nuclear spin up $|\uparrow\rangle$ and spin down $|\downarrow\rangle$, respectively. Single rotating gate is realized by applying short accurate hard pulse for arbitrary angle and two qubit gate is realized by modeling the free evolution of the NMR internal Hamiltonian combined with the decoupling technique.²³ The whole experiment is divided into three parts: the adiabatic preparation of the system qubit ^{13}C to the ground state of the Hamiltonian; the application of the controlled evolution of the Hamiltonian to produce a phase shift on the probe qubit; and the measurement of the phase shift to obtain the value of the ground state energy. The network and the corresponding pulse sequence is displayed in the Figure 1 of Du's paper.²⁰ Instead of taking tomography of the probe qubit, an NMR interferometer equipment is utilized to measure the phase shift accurately, since the error bound of it is less than $\pm 5^\circ$. After 15 iterations the ground state energy of the molecular Hamiltonian is extracted as -1.851570929351124 a.u. ultimately. The intermediate results after each iteration are shown in Fig.3.

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	Iteration k	Binary value
ϕ_{exp}	0	0.100 10001110110010101000011001000011111110110
	2	0.100100100111010111001011010011000101001001110
	5	0.10010010011100000001101001110110111101101001
	8	0.100100100111000000010100001110100010001111110
	11	0.100100100111000000010100001101111001110000000
	14	0.100100100111000000010100001101111001101010110
ϕ_{th}		0.100100100111000000010100001101111001101010110

Fig. 3 Experimental ϕ values (ϕ_{exp}) measured in iterations, compared to the theoretical expectation ϕ_{th} (brown). The numbers in bold (blue) are the bits obtained from the experiment, where 3 bits are extracted in each iteration. Through 15 iterations, we ultimately obtain 45 bits of ϕ , whose value is exactly the same as the theoretical result.

The overview of the two proof-of-principle experiments lead us to consider larger molecular size and scale the algorithm to carry out complicated simulation of the molecular energies that are impossible via classical computers. We conclude that the dream may come true if the following two difficulties can be overcome in the future. One is the more efficient decomposition of the evolution operator of the molecular Hamiltonian and the other is the less complexity of the ASP. For the first issue, an overview of the operator-splitting technique is given in the supplementary material of Lanyon's paper.²⁷ They find that the number of the quantum logical gates decomposed to simulate an arbitrary molecule is N^5 , where N is the number of involved single-particle basis functions that is also the number of necessary qubits. On the second issue, some numerical simulations of the adiabatic evolutions have been performed showing a polynomial growth with the system size up to 128 qubits,⁷⁷ and the polynomial time complexity has also been analytically obtained when the adiabatic evolution is performed to have the phase transitions of second or higher orders.⁷⁸ Thus, when the necessary hardware and technical

difficulties are overcome, the quantum simulation of ground state energy of medium-size molecule is feasible in principle.

4 Simulation of chemical reaction dynamics

4.1 Theoretical designment on simulating chemical reaction dynamics

Having discussed about the experiments on the static molecular energy simulation, we now concentrate on the second important task in quantum chemistry, the simulation of chemical dynamics. It is a fundamental problem in quantum chemistry to understand and analyze the mechanism of chemical reactions. As discussed above, the main obstacle of quantum dynamics simulation by classical computers is the exponentially required resources with the size of system, which makes simulating a dynamic process more difficult than simulating a stationary model since a dynamic process involves more atoms and molecules and hence has greater complexity. Nonetheless, in 2008, Ivan Kassal *et al.* proposed an algorithm which could reduce this problem to be a polynomial complexity one on quantum computers.⁶⁰ They adopted the first-quantization methods which directly simulates electronic and nuclear interaction evolving in time without applying the Born-Oppenheimer approximation. It turns out that this approach is more efficient on a quantum computer than on a classical computer, given the number of atoms in reaction is more than 4.

In their algorithm, they represent the system by wavefunctions in coordinate representation, which are discretized with qubits. For simplicity, Hamiltonian is assumed to be time independent whose potential only depends on position. In other words, $\hat{H} = \hat{T} + \hat{V}$, where $\hat{T} = \hat{p}^2/2m$ and $\hat{V} = V(\hat{x})$ are kinetic and potential energy operators, respectively. In practice, the split-operator technique⁶² is applied to decompose the propagator $\hat{U}(t)$ into contributions from kinetic \hat{T} and potential \hat{V} components separately. For sufficient small time interval δt , the propagator \hat{U} could be separated, up to the first order of δt , as

$$\hat{U}(\delta t) = e^{-i\hat{H}\delta t} = e^{-i\hat{T}\delta t} e^{-i\hat{V}\delta t} + O(\delta t^2)$$

From now on, we set $\hbar = 1$. Undoubtedly, using higher order decomposition of the propagator^{63,64} would increase the accuracy of implementation.

It is noticed that the operators $e^{-i\hat{T}\delta t}$ and $e^{-i\hat{V}\delta t}$ are diagonal in the momentum and coordinate representations, respectively. They can be transformed easily from one to another via the quantum Fourier transformation (QFT)⁷⁹ on a quantum computer,

$$|\psi(t + \delta t)\rangle = \hat{U}(\delta t)|\psi(t)\rangle \approx \text{QFT}e^{-i\hat{T}\delta t}\text{QFT}^\dagger e^{-i\hat{V}\delta t}|\psi(t)\rangle$$

Here, the kinetic $e^{-i\hat{T}\delta t}$ operator is transformed. Transforming either the kinetic or potential part has no influence on the final result. The step is iterated to evolve the system wavefunction from an initial $|\psi(t_0)\rangle$ to $|\psi(t_f)\rangle$.

In their work,⁶⁰ Ivan Kassal *et al.* introduce also ancillary qubits to reduce the complexity of decomposing operators into elementary gates, via a set of additional arithmetics. This is a crucial step when the system involves not just a few qubits. The number of ancilla qubits needed is the same as the number of qubits to reproduce the wavefunction. By careful analysis, they prove the scheme is of polynomial time complexity.

4.2 Experiment of simulating isomerization reaction

So far, we have a generic method for simulating chemical dynamics in polynomial time complexity. In order to demonstrate it on a particular reaction, we select systems with low DOF, as presently the available number of qubits is still not sufficient to support even a modest reaction. Therefore, we implemented the simulation on an isomerization reaction described by only one DOF.⁸⁰ In the theoretically proposed control scheme,⁸⁰ the process is driven by ultrashort laser pulses with three consecutive stages. Initially, laser field is switched on such that the wave function, the state of the molecule, is converted into a superposition of near-degenerate delocalized states from the initial reactant state. In the next stage, the laser field is approximately constant till the wavefunction has tunneled through the barrier into the product domain. Finally, laser field is switched off for the state to be stabilized in the target product region. There are two merits of this approach, in comparison to the conventional pump-dump method. One is that the required time-integrated laser field intensity is about fifty times smaller, which avoids the Keldysh limit.⁸¹ The other is that higher excited states are much less involved during the reaction.

This chemical isomerization reaction has been successfully exemplified as the first experimental realization of quantum simulation on chemical dynamics, via a NMR quantum simulator.²¹ In our case, the reaction has one DOF, hence modeled as an one-dimentional object, and described by qubits. The laser controlled dynamics is to relocate hydrogen of non-symmetric substituted malonaldehydes,⁸⁰ as shown in Fig.4(a). For our implementation, we would like to discuss it in the following aspects: initial state preparation of the molecule, time evolution under Hamiltonian operator, and the measurement during and after the experiment, followed by the conclusion and the future prospect.

Beginning with the state initialization, the system Hamiltonian operator was originally time independent, before the laser field. Nevertheless, to exploit the “hydrogen-subway” effect under the influence of laser field, the new Hamiltonian needs

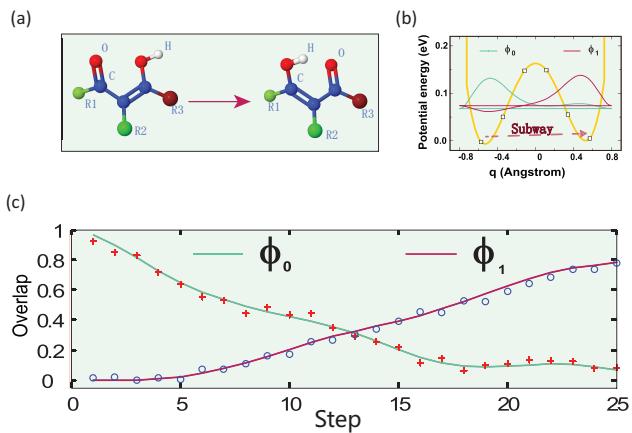


Fig. 4 (a) Isomerization reaction of nonsymmetric substituted malonaldehydes. (b) Potential energy curve, together with the eigenfunctions of the ground (green) and the first excited (red) states. The subway represents the procedure of the hydrogen tunneling approach. (c) Measured probabilities of the reactant (ground) and product (first excited) states to give 25 snapshots of the reaction dynamics. The red plus symbols represent measured results of percentages of the reactant and the blue circles represent those of the product during the time evolution, both in agreement with the theoretical smooth curves.

to take the external electric field into consideration. That is

$$H = T + V + E(t)$$

where $E(t)$ is the time-dependent laser-molecule interaction and T and V are the time-independent kinetic and potential energy operators, respectively. As illustrated in Fig. 4(b), the potential function V is of a double-well shape. From the asymmetry of the shape, i.e. the difference in the well depths, it is assumed that the initial state as the ground state of the system is located in the left potential well, whereas the product state as the first excited state is in the right potential well. The “hydrogen-subway” approach offers an implementation of laser controlled tunneling process for the reaction to take place when the energy of the molecule is below the barrier height.

Here, the kinetic energy operator is given as $T = p^2/(2m)$, whilst the potential counterpart is described as

$$V = \frac{\Delta}{2q_0}(q - q_0) + \frac{V^\ddagger - \Delta/2}{q_0^4}(q - q_0)^2(q + q_0)^2 \quad (2)$$

The laser field interaction is $E(t) = \mu\epsilon(t)$ where $\mu = eq$ is the dipole moment operator and $\epsilon(t)$ represents the driving electric field:

$$\epsilon(t) = \begin{cases} \epsilon_0 \sin^2(\frac{\pi t}{2s_1}); & 0 \leq t \leq s_1 \\ \epsilon_0; & s_1 < t < s_2 \\ \epsilon_0 \sin^2[\frac{\pi(t_f-t)}{2(t_f-s_2)}]; & s_2 \leq t \leq t_f \end{cases} \quad (3)$$

with $s_1 = 5\text{ fs}$, $s_2 = 32.5\text{ fs}$ and $t_f = 37.5\text{ fs}$.

At the start of the simulation, $t = 0$, the molecule should be prepared under the bare Hamiltonian $T + V$, before the action of laser field taking place. To do this, we manipulated a pseudo state from the thermal equilibrium state, by applying a radio-frequency (rf) pulse using spatial average technique,⁹⁵ generated via the GRadient Ascent Pulse Engineering (GRAPE) algorithm,^{22,82,83} with a high fidelity of 0.995. So far we have obtained the reactant state, or the initial state, which was checked by a full state tomography and then a fidelity test. Following the definition of the fidelity $F(\rho_1, \rho_2) \equiv \text{Tr}(\rho_1\rho_2)/\sqrt{(\text{Tr}(\rho_1^2)\text{Tr}(\rho_2^2))}$, we obtain $F[\rho_0, \rho_{\text{exp}}(0)] = 0.950$, where ρ_0 is the theoretical reactant state and $\rho_{\text{exp}}(0)$ is the experimentally obtained initial state. The tomographic results of them demonstrated a high agreement between the theoretical reactant state and the prepared one. Hence we were confident in moving onto the time evolution of experiment from this initial state.

In the next step, we applied the propagator of Hamiltonian, U , to the system, which, in a small enough time interval, follows

$$U(t + \delta t, t) \approx e^{-iH(t+\delta t/2)\delta t}$$

where $H = T + V + E(t)$. The potential was quantized with 8 discrete points, represented by 3 qubits. Undoubtedly, more elaborate discretization would improve the precision of simulation. Nonetheless the availability of qubits limited our choices of the number of quantized points. To avoid the direct operation of the whole Hamiltonian, the propagator is implemented by taking Trotter formula,^{62–64}

$$U(t + \delta t, t) \approx e^{-iV\delta t/2} e^{-iE(t+\delta t/2)\delta t/2} e^{-iT\delta t} \times e^{-iE(t+\delta t/2)\delta t/2} e^{-iV\delta t/2}. \quad (4)$$

Hence the propagator is decomposed into simple forms, consisting only of unitary diagonal operators in either the position or momentum representation. In quantum computer, we could conduct QFT to realize transformations between them easily.

Alternatively, ancilla⁶⁰ could be introduced to the loop. However for the reason stated before, extra qubits are required for ancilla method, which, again, were not available at the time of the experiment. Instead, within low dimensions of state functions, the GRAPE approach has been proved to be successful on a NMR simulator. Although its prospect is not promising on high-dimensional density matrices, it may be possible to produce a GRAPE pulse via feedback learning control, exploiting the quantum evolution of NMR system itself. Nonetheless, when system scales up, the ancilla approach is likely to provide a feasible solution to simplify operators.

The final result at t_f was obtained by iterating the loop of Eq.(4) for 25 times with $\delta t = 1.5\text{ fs}$. The limiting factor for the number of loop was at first the operation time of applying rf

pulse for each operator and the decoherence time of the NMR system. A solution to it is to combine a series of rf pulses for operators in one loop into one single rf pulse using high fidelity GRAPE method, which is a facile job for a 3-qubit system. With this we were able to decrease the overall operation time, as well as reduce the technical complexity, while prevent serious decoherence effects and other experimentally inevitable errors. As the result, we achieve a high fidelity end product.

For the purpose of observing the conversion from the reactant to the product, the overlaps were measured between density matrices during the experiment and those of the theoretical initial and final states. This information was obtained more simply by a digitalization technique⁷ to measure the populations, rather than the full state tomography that demands much more resources. The trend of overlap is shown in Fig.4(c).

After the propagation, for the final product, we conducted a close inspection of the discrepancy between the theory and the experiment. A full state tomography on the final state density matrix is carried out to compare with the theoretical one, in an eight dimensional Hilbert space. Provided with a high fidelity of the GRAPE pulse (0.995), the experimental final state and the theoretical one agreed with each other to a great extent, with fidelity of 0.957. Furthermore, for the product state, the experimental density matrix elements and the theoretical ones are also consistent with high fidelity.

Therefore, the result in Fig.4(c) achieved from our quantum simulator demonstrates the time evolution of reactant and product state probabilities. The product-to-reactant ratio rises gradually with time. A 77% probability of the product state is reached at the end of the simulation.

To summarize, an archetype chemical reaction driven by laser was successfully emulated by our 3-qubit NMR system. Furthermore, as the operations of gates were merged via the GRAPE pulses, the whole number of operations was reduced. We emphasize that the simulation time, 30 ms, was considerably shorter than our system spin decoherence time. The insignificant difference between the theory and the experiment may be caused by the falseness of GRAPE pulses, the inhomogeneity in rf pulses, and the inconsistency in the static magnetic field.

5 Conclusion and perspective

In the paper we have reviewed the development of quantum simulation towards quantum chemistry, in both theory and experiment. Unlike the quantum computation algorithm which usually requires thousands of qubits to display the superiority of polynomial complexity of quantum computers, quantum simulation architectures are expected to surpass the classical computers with just 30-100 qubits. Even though, this requirement is still beyond the current experimental equipment. As proof-of-principle but pioneer experiments to demonstrate the

simulations of static molecular energy⁷ and dynamical chemical reaction,⁵⁹ the quantum simulation of hydrogen molecular ground state energies in linear optics²⁷ and NMR,²⁰ and the quantum simulation of an one-dimensional isomerization chemical reaction in NMR,²¹ have exhibited elementary superiority of quantum simulation as a powerful tool to investigate quantum chemistry. The main challenges of quantum simulation on quantum chemistry for large systems are just the challenges of building a practical quantum computer. They include the preparation of initial states, decomposition and application of arbitrary qubit evolutions, measurement on the final states, and ways to overcome noise and decoherence. Although the current limitations of technique and hardware forbid us to build a universal quantum simulator exceeding classical computers at present, we propose in the following the possible improvements in the two directions of applications: simulation on static molecular energies of larger molecules and simulation on more complicated chemical reactions.

For larger molecules, since the simple and important hydrogen molecule has been simulated successfully, the next one taken into account could be the water molecule H₂O. In the original scheme,⁷ if choosing the minimal STO-3G basis set, it is declared that simulating H₂O requires 8 qubits, which is already available in some quantum systems. Subsequently, a quantum algorithm to obtain the energy spectrum of molecule based on the multiconfigurational self-consistent field is presented,⁸⁴ with which the excited states are accessible. As an example, the quantum simulation of the ground state and the first singlet excited state of the water molecule using the cc-pVDZ basis set⁸⁵ is demonstrated, where 14 qubits are required on a quantum simulator. This could be an accessible object in the near future.

In the dynamic chemical simulations, the next potential step could be extending the system into two dimensions. Obviously the Hamiltonian, with its potential and kinetic energy operators, would then be expressed in two dimensions. If the system is quantized with a 16×16 grid, the required number of qubits is 8, which would be feasible in near future. However, if we apply the spilt-operator method^{63,64} to the two dimensional problems, the number of quantum gates would be hundreds or even thousands, beyond the capacity of current quantum systems. Nevertheless, it may be possible to make algorithmic progress on other models, rather than the quantum circuit model. For instance, the topological quantum computing,^{86,87} quantum walks,^{88–91} and one-way quantum computing^{92–94} may boost the quantum chemical dynamics simulation of systems beyond one dimension.

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