

# 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.<sup>1</sup> 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 systems scale 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,<sup>2</sup> numerous studies have been done in many aspects of physics,<sup>3</sup> 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 simulations of static molecules and chemical reactions.

### 1.1 Advantages of quantum simulators

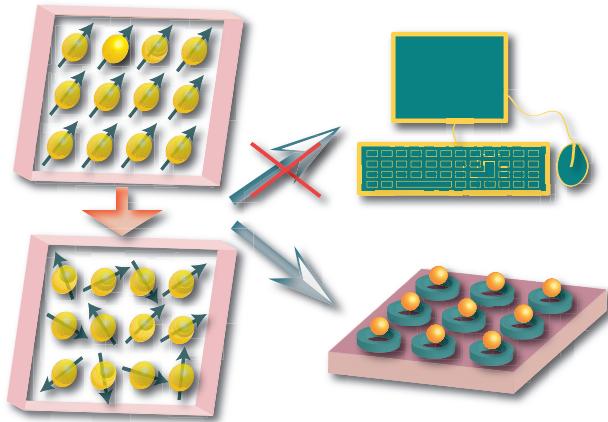
The driving force in building a quantum simulator is its advantage in solving a vast amount of problems in physics, chemistry, and biology, together with its feasibility within current technological development. Classical computers are limited to small quantum systems, due to the huge demand of memory 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. the number of electrons in a moderate molecule, a conventional computer would need  $2^{100} \approx 10^{30}$  bits to describe the state, whilst computing the

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time evolution is effectively doing  $2^{100}$  by  $2^{100}$  matrix arithmetics. Both requirements are beyond the capacity of current computers and even future ones, since quantum effects 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 computers, 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 scales.<sup>4</sup>



**Fig. 1** (color online) Quantum phenomena describing 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 computers. It is hard to imagine when the system scales to 100 particles what a fantastic classical computer we need to merely store the data. However, a quantum computer of 45 qubits is sufficient to simulate this process.

We see that quantum simulators have great advantages over classical counterparts. The present unperfect achievement of coherent control, as one of the barriers to built a quantum information processor, may soon be overcome.<sup>5</sup> Therefore it is possible for the physical realization of quantum simulation in the near future. 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.<sup>6-8</sup>

## 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 to an analogue quantum simulator (AQS).<sup>8-11</sup> 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.<sup>6,12,13</sup> This approach has the advantage of universality. However, there remain challenges for the DQS, such as the exponential growth of required gates with the precision of the results.<sup>4</sup> For this reason, AQS is more favored in current quantum simulation studies, compared to DQS, although at 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

In this section, we consider some different physical systems which can be used to implement quantum simulation tasks.<sup>14,15</sup>

- Nuclear Magnetic Resonance (NMR). Since the first simulation of quantum oscillators,<sup>16</sup> a lot of progress has been made on this platform.<sup>17-21</sup> Among them, in the area of quantum chemical simulations, two proof-of-principle experiments have been done on modeling the hydrogen molecule H<sub>2</sub>,<sup>22</sup> and on simulating the chemical dynamics of a isomerization reaction.<sup>23</sup> In NMR architecture, nuclear spins are functioned as qubits, and are manipulated and read-out by an NMR spectrometer.<sup>24</sup> 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.<sup>25,26</sup>

- 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.<sup>27</sup> Indeed, the first experiment in quantum chemistry simulation, a minimal basis model of the hydrogen molecule H<sub>2</sub>, was implemented with this system.<sup>29</sup> 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.<sup>27,28</sup> 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.<sup>30</sup>

- 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.<sup>8,31,32</sup> For this structure, qubits are represented by the electronic states of cold trapped ions.<sup>33–35</sup> However, chemical simulations are yet to be realized.

- Superconducting Circuits. Besides synthesizing arbitrary states and implementing simple 2-qubit algorithms in experiment,<sup>36,37</sup> superconducting circuits are supposed to simulate phenomena in atomic physics,<sup>38,39</sup> realize the Kitaev model on a honeycomb lattice,<sup>40</sup> emulate large-spins,<sup>41</sup> or simulate the Anderson and Kondo models.<sup>42,43</sup> The flowing circulating current in a superconductor can be used as a qubit.<sup>39,44–46</sup> 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,<sup>47</sup> which are analogous to a real atom binding an electron, have been proved to simulate the Fermi-Hubbard model<sup>47,48</sup> and the many-fermion problem in high-Tc superconductors.<sup>10</sup> A feasible proposal has also been brought forward to model chemical reactions.<sup>11</sup>

- 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 first implemented in this system, realizing a superfluid transferred to a Mott insulator.<sup>9</sup> Numerical examples that could be simulated are discussed in the review paper by Lewenstein,<sup>3</sup> while experimental approaches can be found in Bloch's paper.<sup>50</sup>

## 2 Quantum chemistry

### 2.1 Classical approach to quantum chemistry

Quantum chemistry aims at developing theoretical methods to calculate molecular properties and evolutions on the 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.<sup>51</sup> These high-precision calculations can only be performed on very small molecular systems. Density functional theory<sup>52–54</sup> has a relatively high efficiency and enlarges the system size of application with a certain accuracy. Linear scaling algorithms<sup>55,56</sup> are also developed to

explore systems of thousands of atoms or even larger for certain typies of materials. These methods can sometimes predict chemical properties for large systems, but in some cases they may fail.<sup>57–60</sup>

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 reaction-s.<sup>61,62</sup> Using conventional methods without approximations, the capacity of investigating chemical reaction dynamics so far is just 9 DOF.<sup>63</sup> Even the multiconfigurational time-dependent Hartree method,<sup>64</sup> 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 using 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 approaches used 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 the near future.

In quantum simulation, we are interested in the behavior 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 in 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, currently 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.<sup>66</sup> One is the second quantization method where the 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.<sup>29</sup> Nonetheless, this method is not suited if the system is complex and 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.

The first quantization approach does not take into account 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.<sup>67–69</sup> 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.<sup>66,67</sup> It is found that the first quantization scheme will be more efficient to simulate reactions of more than four atoms.<sup>67</sup>

**2.2.2 Evolving the initial state with the system Hamiltonian.** Currently, we select the Trotter formula<sup>69</sup> and its generalization in high dimensions<sup>70,71</sup> to generate the unitary evolution of a system Hamiltonian that is to be simulated. Assume that the system Hamiltonian can be written as  $H = \sum_{m=1}^M H_m$ , where  $H_m$  is local interaction Hamiltonian. The unitary operator of the evolution would be  $U(t) = e^{-iHt}$ , whose decomposition is usually difficult. By using the first-order Trotter formula and small time intervals  $\delta t \rightarrow 0$ ,

$$\begin{aligned} U(\delta t) &= e^{-iH\delta t} = \prod_{m=1}^M e^{-iH_m\delta t} + \mathcal{O}(\delta t^2) \\ &\approx \prod_{m=1}^M e^{-iH_m\delta t}. \end{aligned} \quad (1)$$

Noting that the accuracy of this formula can be improved by choosing very small  $\delta t$  or choosing higher-order decompositions, both of which will produce a large number of logical gates and accumulate the errors due to the imperfection of each gate in experiment.

**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 its 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).<sup>72–75</sup> Often the information of the state is encoded in the global phase which is of no use, as it is not observable. Using the 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, the demand for

extra ancilla qubits restricts it from wide use in circuit. As it is known, 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 the PEA.<sup>22,29</sup> Essentially, by iterating the PEA process and modifying the parameters, i.e. the pulses in the circuit, accordingly, high-precision results can be achieved. However, another experiment,<sup>23</sup> which was on simulating chemical dynamics, turned to quantum state tomography as its measurement technique. It was effective in that experiment since only three qubits were involved and the associated Hilbert space was small enough. Additionally, quantum tomography provided a direct way to reconstruct the final state and to calculate the fidelity of the results. Nevertheless, this method could not be conducted when the system scales up, for the reason discussed above. The PEA and other approaches<sup>76–79</sup> 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.<sup>72</sup> With the help of quantum fast Fourier transform (FFT), the eigenvalues and eigenstates of a local Hamiltonian can be solved in polynomial time. Abrams and Lloyd<sup>72</sup> believed that many interesting problems in atomic physics which are classically intractable can be solved with 50 to 100 qubits. This means that quantum computers in this size would surpass the capacity of classical computers. Recently, Li *et al.*<sup>80</sup> employed a trial wavefunction, approximating the ground state, to project the ground state by means of the PEA, and performed an NMR experimental implementation of this idea to solve the ground-state problem of the Heisenberg spin model. Concerning the static properties of a molecule in quantum chemistry, Aspuru-Guzik *et al.*<sup>7</sup> proposed an algorithm to calculate the energies of molecules in 2005. 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 a polynomial number of quantum gates. They conclude<sup>7</sup> that quantum simulation with 30 to 100 qubits can exceed the limitations of classical computing.

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 systems 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 maps would need 116 and 47 qubits, respectively.<sup>7</sup> The resources required exceed the experimental capacity in current quantum simulations, whereas it would be more possible to realize in the near future, compared to 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, using the quantum adiabatic theorem,<sup>81</sup> 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.<sup>81</sup> 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 all the energy levels are ensured to be noncrossing. 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 the evolution is the implementation of the 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  $\phi$  between zero and unity by a pre-estimated value of the energy

$E$ . If the phase on the probe qubit can be measured with high accuracy, the resulting eigenvalue would be very precise, surpassing the results reached by the classical computers. However, this will cost many qubits in resource.

To overcome this, a modified PEA is proposed<sup>7</sup> 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  $\phi_k$  is a lower bound on the constructed shift  $\phi$  at each iterative step  $k$ . The initial condition is  $V_0 = U = e^{-iH\tau}$ . In each step, one additional bit of  $\phi$  is obtained, and a long enough digit can be achieved by repeating this procedure 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.

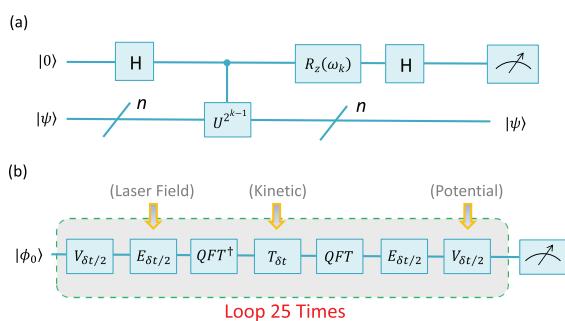
(iii) *Measurement.* Since the ground state energy has been encoded in the phase of the probe qubits, a direct measurement of this phase is sufficient to obtain the value of the ground state energy. For example, if a four-bit inverse quantum Fourier transform is adopted for the phase measurement, we 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 simulations, theory is still ahead of experiments. The present experimental technology cannot 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 for simulating the ground state energy of the hydrogen molecule is a good choice. The first two experiments both selected this problem, using a linear optical system<sup>29</sup> and an NMR system,<sup>22</sup> respectively. We will review these two experiments briefly in the following section.

### 3.2 Experiments for simulating the ground state energy of the hydrogen molecule

In 2010, it was demonstrated that the ground state energies of the hydrogen molecule in a minimal STO-3G basis could be simulated using a linear optical quantum computation architecture.<sup>29</sup> In the linear optical system, quantum information is encoded in polarization or path of single photons.<sup>27,28</sup> In the experiment, two qubits were utilized to implement the simulation, with one to encode the system wavefunction, while another to read out the result of the PEA. For each iterative process, one bit precision was obtained. The whole iterative PEA was repeated for 20 times, achieving a high level of 20 bit precision in total. The key step of performing the iterative PEA was realized on a linear optical quantum system, and the other steps of the algorithm including initial state preparation were assisted by a classical computer. The authors discussed how the technique could be expanded to solve large-scale chemical

problems that lie beyond the reach of modern supercomputers, and claimed that the experimental results represented an early practical step toward a powerful tool with a broad range of quantum-chemical applications.



**Fig. 2** (color online) (a) Network of the iterative phase estimation algorithm for the calculation of the hydrogen molecular energies. Reproduced from Lanyon *et al.*, *Nat. Chem.*, 2010, **2**, 106–111.<sup>29</sup> (b) Network of simulating the isomerization dynamics from the reactant state  $|\phi_0\rangle$  where the whole process is divided into 25 loops. Reproduced from Lu *et al.*, *Phys. Rev. Lett.*, 2011, **107**, 020501.<sup>23</sup>

The Hamiltonian of the hydrogen molecule in the minimal STO-3G basis was block-diagonal with  $2 \times 2$  submatrices, conducting one qubit to represent the system wavefunction and another to represent the phase information. Exact eigenstates were first encoded, which were preliminarily calculated through a classical computer. For imperfect eigenstate encoding, the algorithm was robust and still works well. The quantum state  $|0\rangle$  and  $|1\rangle$  were represented via the horizontal and vertical polarization  $|H\rangle$  and  $|V\rangle$ , respectively. A single rotating gate was implemented using birefringent wave plates, and a two-qubit gate was 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 was obtained as  $-535.58 \pm 0.03$  kJ mol<sup>-1</sup>, 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 was demonstrated via an NMR system.<sup>22</sup> The basis was selected as the widely used minimal STO-3G as well, and a two-qubit sample of <sup>13</sup>C-labeled chloroform dissolved in *d*<sub>6</sub> acetone was employed in the NMR spectrometer. Qubits were represented by <sup>13</sup>C (system qubit) and <sup>1</sup>H (probe qubit) nuclear spins. ASP<sup>82</sup> was tested for various bond distances, with  $r = 1.4$  a.u. being 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 was implemented as the essential part of the algorithm.

m, with a 3-bit precision extracted per iteration, achieving a 45-bit precision. The readout was performed through an N-MR interferometer,<sup>83–85</sup> to obtain the phase shift of the probe qubit. The experimental result of the ground state energy is exact, with the uncertainty being 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 could be simplified as<sup>51</sup>

$$H = \begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_{11}^{2\bar{2}} | H | \Psi_{11}^{2\bar{2}} \rangle \\ \langle \Psi_{11}^{2\bar{2}} | H | \Psi_0 \rangle & \langle \Psi_{11}^{2\bar{2}} | H | \Psi_{11}^{2\bar{2}} \rangle \end{pmatrix} = \begin{pmatrix} -1.8510 & 0.1813 \\ 0.1813 & -0.2537 \end{pmatrix}, \quad (2)$$

whose eigenvalue is  $-1.85157092935119$  a.u. Here this eigenvalue was given with 15 significant figures to show the contrast between the theoretical value and experimental value clearly. Spin <sup>13</sup>C was used to modulate the system Hamiltonian. In NMR architecture, the logical states  $|0\rangle$  and  $|1\rangle$  were represented by the nuclear spin up  $|\uparrow\rangle$  and spin down  $|\downarrow\rangle$ , respectively. A single rotating gate was realized by applying short accurate hard pulses for arbitrary angles and a two qubit gate was realized by modeling the free evolution of the NMR internal Hamiltonian combined with the decoupling technique.<sup>25</sup> The whole experiment was divided into three parts: the adiabatic preparation of the system qubit <sup>13</sup>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 were displayed in Figure 1 of Du's paper.<sup>22</sup> Instead of taking tomography of the probe qubit, an NMR interferometer equipment was utilized to measure the phase shift accurately, since the error bound of it was less than  $\pm 5^\circ$ . After 15 iterations the ground state energy of the molecular Hamiltonian was extracted as  $-1.851570929351124$  a.u. The intermediate results after each iteration are shown in Fig.3.

The overview of the two proof-of-principle experiments lead us to consider larger molecular size and scale the algorithm to carry out complicated simulations of 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 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.<sup>29</sup> 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, which is also the

	Iteration k	Binary value
$\phi_{exp}$	0	<u>0.100</u> 100011101100101010000110010000011111110110
	2	<u>0.100100100</u> 111010111001011010011000101001001110
	5	<u>0.100100100111000000</u> 011010011101101111011101001
	8	<u>0.100100100111000000010100001110100010001111110</u>
	11	<u>0.10010010011100000001010000110111001101011001</u> 110000000
	14	<u>0.10010010011100000001010000110111001101010110</u> 10
$\phi_{th}$		0.10010010011100000001010000110111001101010110

**Fig. 3** (color online) Experimental  $\phi$  values ( $\phi_{exp}$ ) measured in iterations, compared to the theoretical expectation  $\phi_{th}$  (brown). The numbers with underlines are the bits obtained from the experiment, where 3 bits are extracted in each iteration. Through 15 iterations, we ultimately obtain 45 bits of  $\phi$ , whose value is exactly the same as the theoretical result. These results are from Du *et al.*, *Phys. Rev. Lett.*, 2010, **104**, 030502.<sup>22</sup>

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,<sup>86</sup> and the polynomial time complexity has also been analytically obtained when the adiabatic evolution is performed to have phase transitions of second or higher orders.<sup>87</sup> Thus, when the necessary hardware and technical difficulties are overcome, the quantum simulation of ground state energies of medium-size molecules is feasible in principle.

## 4 Simulation of chemical reaction dynamics

### 4.1 Theoretical designment on simulating chemical reaction dynamics

Having discussed experiments on static molecular energy simulations, 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 the system.<sup>88</sup> This makes simulating a dynamic process more difficult than simulating a stationary model, because a dynamic process involves more atoms and molecules and hence has greater complexity. Nonetheless, in 2008, an algorithm (DQS) was proposed to reduce this problem to be a polynomial complexity one on quantum computers.<sup>67</sup> 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, when the number of atoms in the reaction is more than 4.

In their algorithm, they represent the system by wavefunc-

tions in coordinate representation, which are discretized with qubits. For simplicity, the Hamiltonian is assumed to be time-independent, and the 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 the kinetic and potential energy operators, respectively. In practice, the split-operator technique<sup>69–71</sup> is applied to decompose the propagator  $\hat{U}(t)$  into contributions from the kinetic  $\hat{T}$  and potential  $\hat{V}$  components separately, which are discussed in Section 4.2 in detail.

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)<sup>89</sup> 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  $|\psi(t_f)\rangle$ .

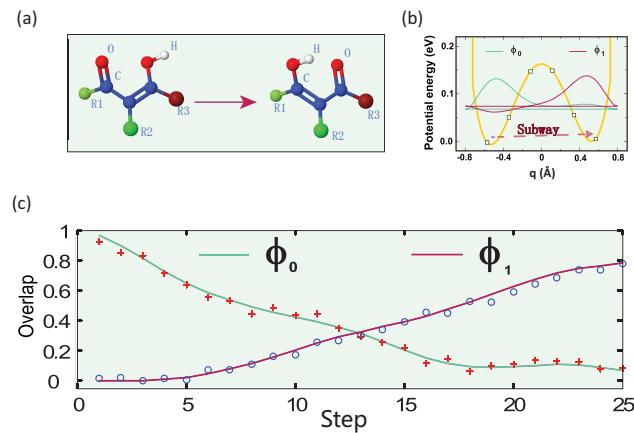
In the work,<sup>67</sup> ancillary qubits are introduced to reduce the complexity of decomposing operators into elementary gates, via a set of additional arithmetics. This is a crucial step when the system involves not just a few qubits. The number of ancilla qubits needed is the same as the number of qubits to reproduce the wavefunction. By careful analysis, they prove that the scheme is of polynomial-time complexity.

Besides the above proposal which belongs to DQS, it would be possible to simulate chemical reactions using AQS. In semiconductor quantum dots,<sup>11</sup> as coupled quantum dots can be seen as "artificial molecules", various reaction regimes and different reaction products can be achieved by varying the speed of voltage changes applied to the gates forming quantum dots. In ultracold atoms on a waveguide,<sup>90</sup> the quantum three-body collinear chemical reactions can be simulated by the motion of single ultracold atoms or a weakly interacting Bose-Einstein condensate on an *L*-shaped waveguide.

### 4.2 Experiment for simulating an 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.<sup>91</sup> In the theoretically proposed control scheme,<sup>91</sup> the process is driven by ultrashort laser pulses with three consecutive stages. Initially, a 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 until the wavefunction has tunneled through the barrier into the product domain. Finally, the 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.<sup>92</sup> The other is that higher-excited states are much less involved during the reaction.



**Fig. 4** (color online) (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 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. Reproduced from Lu *et al.*, *Phys. Rev. Lett.*, 2011, **107**, 020501.<sup>23</sup>

This chemical isomerization reaction has been successfully exemplified as the first experimental realization of quantum simulation on chemical dynamics, via a NMR quantum simulator.<sup>23</sup> In our case, the reaction has one DOF, hence modeled as an one-dimensional object, and described by qubits. The laser-controlled dynamics is to the relocate hydrogen of non-symmetric substituted malonaldehydes,<sup>91</sup> 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 the Hamiltonian operator, and the measurement during and after the experiment, followed by conclusions and future prospects.

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 the laser field, the new Hamiltonian needs 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 a double-well. 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

$$V = \frac{\Delta}{2q_0}(q - q_0) + \frac{V^\ddagger - \Delta/2}{q_0^4}(q - q_0)^2(q + q_0)^2 \quad (3)$$

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:

$$\epsilon(t) = \begin{cases} \epsilon_0 \sin^2(\frac{\pi t}{2s_1}); & 0 \leq t \leq s_1 \\ \epsilon_0; & s_1 < t < s_2 \\ \epsilon_0 \sin^2[\frac{\pi(t_f-t)}{2(t_f-s_2)}]; & s_2 \leq t \leq t_f \end{cases} \quad (4)$$

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 the laser field takes place. To do this, we manipulated a pseudo-pure state from the thermal equilibrium state, by applying a radio-frequency (rf) pulse using the spatial average technique,<sup>93</sup> generated via the GRadient Ascent Pulse Engineering (GRAPE) algorithm,<sup>24,94,95</sup> 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  $\rho_0$  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 the 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 eight discrete points, represented by three qubits. Undoubtedly, more elaborate discretization would improve the precision of the 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 the Trotter formula,<sup>69–71</sup>

$$U(t + \delta t, t) \approx e^{-iV\delta t/2} e^{-iE(t+\delta t/2)\delta t/2} e^{-iT\delta t} \\ \times e^{-iE(t+\delta t/2)\delta t/2} e^{-iV\delta t/2}. \quad (5)$$

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

Alternatively, an ancilla<sup>67</sup> could be introduced to the loop. However for the reason stated before, extra qubits are required for the ancilla method, which, again, were not available at the time of the experiment. Instead, within low dimensions of the Hilbert space, the GRAPE approach has proved to be successful on an 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 the 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.(5) for 25 times with  $\delta t = 1.5$  fs. The limiting factor for the number of loops 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 the 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 preventing serious decoherence effects and other experimentally inevitable errors. As a result of this, 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 diagonalization technique<sup>23</sup> 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 the 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 lasers was successfully emulated by our 3-qubit NMR system. Furthermore, as the operations of gates were merged via the GRAPE pulses, the total 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 theories and experiments. 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 classical computers with just 30–100 qubits. However, this requirement is still beyond the current experimental equipment. As proof-of-principle but pioneer experiments to demonstrate the simulations of static molecular energy<sup>7</sup> and dynamical chemical reaction,<sup>66</sup> the quantum simulation of hydrogen molecular ground state energies in linear optics<sup>29</sup> and NMR,<sup>22</sup> and the quantum simulation of an one-dimensional isomerization chemical reaction in NMR,<sup>23</sup> 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 two directions of applications: simulations of static molecular energies of larger molecules and simulations of 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 H<sub>2</sub>O. In the original scheme,<sup>7</sup> if choosing the minimal STO-3G basis set, it is declared that simulating H<sub>2</sub>O requires 8 qubits, which is already available in some quantum systems. Subsequently, a quantum algorithm to obtain the energy spectrum of a molecule based on the multiconfigurational self-consistent field is presented,<sup>96</sup> 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 set<sup>97</sup> is demonstrated, where 14 qubits are required on a quantum simulator. Recently, it is demonstrated that for simulating the water molecule it just requires 6 qubits to obtain the energy spectrum instead of the ground state energy.<sup>98</sup> This could be an accessible object in the near future.

In 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<sup>70,71</sup> 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, topological quantum computing,<sup>99,100</sup> quantum walks,<sup>101–104</sup> and one-way quantum computing<sup>105–107</sup> may boost the quantum chemical dynamics simulation of systems beyond one dimension.

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