Implementation of a Quantum-simulation Algorithm of Calculating Molecular Ground-state Energy on an NMR Quantum Computer

Jiangfeng Du*, Nanyang Xu, Xinhua Peng, Pengfei Wang, Sanfeng Wu, Dawei Lu
Hefei National Laboratory for Physical Sciences at Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
*To whom correspondence should be addressed; E-mail: dfj@ustc.edu.cn

Introduction. — It is well known that quantum algorithms provide an excellent speedup towards classical algorithms in many problems [1]. Among these, the most famous example is the Shor’s algorithm [2], which solves the factoring problem exponentially faster than classical methods. Besides the success of quantum computation (QC) applied in computational problems, another important application of QC is the simulation of quantum systems, an idea conceived by Feynman [3]. Simulation of realistic quantum systems requires an exponential amount of resources to handle the large number of coupled Schrödinger equations used to describe the particles in the system. However, within the QC architecture it was shown that universally simulating an physical system is efficient, i.e., costing polynomial resources with the size of the target system.

Quantum simulation allows us to examine several new frameworks such as the many-particle systems [5]–[8], pairing-Hamiltonian systems [7] and etc. [8, 9, 10]. Specifically, several quantum-simulation algorithms were proposed to determine properties like thermal rate constant [11] and molecular energies [12] in quantum chemistry. The calculation of molecular energies is a fundamental problem focused in computational quantum chemistry. On classical computer, resources for a full simulation of the molecular system scale exponentially with the number of atoms involved, limiting such full configuration interaction calculations of molecular energies to diatomic and triatomic molecules [13]. However the calculation could be efficient if it is performed on a quantum simulator using the algorithm proposed by Aspuru-Guzik et al [12], where information about the energy is transferred onto the phase shift of a quantum register and measured by a quantum phase estimate algorithm (PEA) iteratively.

Because of the practical importance of QS, experimental demonstrations of these algorithms are not only of fundamental interests, but also a cornerstone of emerging field of new technologies. Previous experiments have been performed to simulate some small systems on NMR [8, 9, 14] or ion-trap [15] platforms. However no such demonstrations have been performed till now due to the requirement of controlling sufficient number of qubits for simulation a molecule in original Aspuru-Guzik’s algorithm.

In this letter, we adopt two methods to overcome the challenges: 1) choosing simplest case of the smallest molecule, i.e., $H_2$; 2) utilizing the mature technology on NMR platform - the NMR interferometer - to measure the phase shift. We also adopt a improved iterative scheme to extend the precision to a high level. By these methods, we realize this algorithm and calculate the ground-state energy of $H_2$ molecule to a precision of 17 bits. We also find that the precision of the result got from this algorithm is limited by the imperfection of simulating the operators in experiment.

The Hamiltonian of $H_2$ molecule. — Limited by the current technology, to calculate a large molecular energy in Full Configuration Interaction is not possible, so we choose the simplest situation: the ground-state energy of Hydrogen molecule in the minimal STO-3G basis [16]. The electron’s Hamiltonian of $H_2$ molecule with Born-Oppenheimer approximation is shown as follows [16],

$$H = \sum_{i=1}^{2} (T_i + \sum_{j=1}^{2} V_{ij} + \sum_{i,j=1 \atop i \neq j}^{2} O_{ij})$$

where $T_i$ is the kinetic energy of the $i$th electron, and $V_{ij}$ is the coulomb potential energy between the $i$th electron and the $j$th nucleus, while $O_{ij}$ is the coulomb potential energy between the $i$th and $j$th electron. In this two-nucleus and two-electron molecule in STO-3G basis, each atom has a 1s Gaussian-type function, and the two 1s functions compose one bonding orbital with gerade symmetry and one antibonding orbital with ungerade symmetry. So there are 4 spin orbitals which can form 6 configurations. Considering the singlet symmetry and the spatial symmetry of $H_2$ exact ground state, only two configurations...
configurations are acting in fact in the calculation: the ground state configuration \( |\Psi_0\rangle \) and the double excitation configuration \( |\Psi_{11}\rangle \). Thus, the Hamiltonian matrix is (in atom units, the nucleus distance is 1.4 a.u., only the electron’s energy):

\[
H = \begin{pmatrix}
\langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_{11} | H | \Psi_2 \rangle \\
\langle \Psi_{11} | H | \Psi_0 \rangle & \langle \Psi_{11} | H | \Psi_{11} \rangle
\end{pmatrix} = \begin{pmatrix}
-1.8310 & 0.1813 \\
0.1813 & -0.2537
\end{pmatrix}
\]

(1)

whose theoretical eigenvalue is -1.8516 a.u.

The calculation of molecular energy. — As shown in Fig. 1, the calculation of the molecular energy in our experiment is described by four steps: 1) adiabatic preparation of the system qubit to the ground state of the Hamiltonian \( H \) 2) application of the time evolution of the molecular Hamiltonian on the qubits to generate the phase shift on the probe qubit; 3) measurement of the phase shift on the probe qubit to extract the energy information. We will introduce the three steps in detail as follows.

In the first step, the quantum simulator’s system qubit is prepared by Adiabatic State Preparation (ASP) to \( |\Psi\rangle \), the ground state of the molecular Hamiltonian \( H \). According to the quantum adiabatic theorem [17], the qubit is prepared on an simple Hamiltonian’s ground state and the systematic Hamiltonian of the qubit varies slowly enough from the simple Hamiltonian to \( H \), if there’s an energy gap between the ground state and the first excited state, the qubit will stay on the instantaneous ground state of the system Hamiltonian. Thus the qubit finally is prepared on the ground state of \( H \) after the ASP.

In the second step, An unitary operator \( U = e^{-iH\tau} \) is applied to the state \( |\Psi\rangle \), with only generating a phase shift to the probe qubit by the controlled operation. Here \( U|\Psi\rangle = e^{-iH\tau}|\Psi\rangle = e^{-\pi\phi/T}|\Psi\rangle \) where \( E = -2\pi\phi/T \) is the energy of \( H \)’s ground state. Note that the energy \( E \) is negative so we make the phase \( \phi \) to be positive and \( \tau \) is chosen properly to make the phase \( \phi \) ranges from 0 to 1.

Finally in the measurement step, a four-bit inverse Quantum Fourier Transform (QFT) is adopted as the Relative Phase Measurement to evaluate the phase shift in the Aspuru-Guzik’s proposal. This apparatus needs four qubits as probe qubits to get one precise bit with successful possibility of 15/16[1]. While in the NMR platform there’s a mature technology NMR interferometer, named from the similar apparatus originally used in optics, which could easily measure the relative phase shift of the quantum states by modulating the spectrum patterns[19, 20]. On our NMR interferometer, the phase shift could be evaluated with an error bound of less than \( \pm 5^\circ \), much more precise than the performance of the original four-bit inverse QFT apparatus. Thus we utilize the interferometry to measure the phase shift in our experiment.

The iterative scheme. — For useful practical application, it should be possible to iterate the above process to achieve arbitrary precision in the molecular energy. We made a small modification to the iterative scheme in Aspuru-Guzik’s algorithm to improve its reliability. As shown in Fig. 1(h), for each iteration \( k \) we applied the controlled-\( U_k \) and measure the phase shift. We start the iterations from \( U_0 = U \) and iterate the process by choosing \( U_{k+1} = [e^{-i2\pi\phi_k U_k}]^{2^n} \). Here, \( n \) is the number of bit attained in each iteration and \( \phi_k = \max\{\phi_k - \phi_{\text{errbd}}, 0\} \) where \( \phi_k \) is the phase shift measured in the \( k \)th iteration. Note that \( n \) is limited by the precision of the phase measurement in each iteration, i.e., \( 2^{-n} \geq 2\phi_{\text{errbd}} \).

The experimental implementation. — We used the \( ^{13}C \)-labeled chloroform dissolved in \( d_6 \)-acetone as a two-qubit NMR quantum computer, where \( ^{13}C \) nucleus was used for the system qubit while \( ^1H \) is for the probe qubit. The molecular structure is shown in Fig. 1(b). The natural Hamiltonian of this two-qubit system is given by:

\[
H_{\text{NMR}} = \frac{\omega_1}{2}\sigma_x^a + \frac{\omega_2}{2}\sigma_z^a + \frac{J_{ps}}{2}\sigma_z^a\sigma_z^b
\]

(2)

where \( \omega_1/2\pi \) and \( \omega_2/2\pi \) are the Larmor frequencies of nucleus \( ^{13}C \) and \( ^1H \), and \( J_{ps} \) represents the \( J \) coupling constant, typically, \( J_{ps} = 214.6Hz \). The experiments
were carried out at room temperature on a Bruker AV-400 spectrometer. Let us now describe the experiment in detail.

A) Preparation of the initial state: Starting from the thermal equilibrium state, we first created a pseudo-pure state (PPS) \( |\psi_0\rangle = \frac{1}{\sqrt{2}} |\uparrow\rangle + e\epsilon |\downarrow\rangle \) using the spatial average technique\[21\], with \( I \) representing the 4 \times 4 unity operator and \( \epsilon \approx 10^{-5} \) the polarization. However, the simulation algorithm requires the system qubit is in the ground state \( |\psi_g\rangle \) of the Hamiltonian of the \( H_2 \) molecule \([\text{Eq. (2)}]\); while the probe bit is in the ground state \( |\uparrow\rangle \) prepared by an adiabatic procedure where we start from a simple initial Hamiltonian \( H_0 \) whose ground state \( |\psi_0\rangle \) is easily constructed. The adiabatic theorem tells that if the system Hamiltonian \( H_{ad}(t) \) varies slowly enough so that the adiabatic condition is satisfied \[17\], the system remains in its instantaneous ground state. Therefore, if \( H_{ad}(t) \) reaches the Hamiltonian \( H \) at \( t = T \), the system is prepared the ground state \( |\psi_g\rangle \) of \( H \). The time-dependent Hamiltonian during the adiabatic passage is obtained by linear interpolation: \( H_{ad} = (1-s)\sigma_x + sH \) with \( s = \frac{t}{T} \). Here we chose the initial Hamiltonian \( H_0 = \sigma_x \) whose ground state is \( |\downarrow\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle - |\downarrow\rangle) \) prepared by the conjugated pseudo-Hadamard gate \( R_y^{H}(-\pi/2) \). We implemented the adiabatic preparation by discretizing the continuous adiabatic passage with the optimized parameters \[22\] \[23\]: the discrete steps \( M + 1 = 6 \) and the total time \( T = 5.4ns \). Therefore the unitary evolution for the discrete adiabatic passage is then \( U_{ad} = \prod_{m=0}^{M} U_{ad}^{m} = \prod_{m=0}^{M} e^{-iH_{ad}T} \), where the duration of each step is \( \delta = T/(M + 1) \). For each step,

\[
U_{ad}^{m} = e^{-i\frac{\delta}{2}(1-s_m)\sigma_x} e^{-is_mH\delta} e^{-i\frac{\delta}{2}(1-s_m)\sigma_x} + O(\delta^3), \tag{3}
\]

where \( s_m = \frac{m}{M + 1} T \). Consequently, \( U_{ad}^{m} \) can be implemented by the pulse sequence \( R_x^{C} (\theta_1) - R_y^{C} (\theta_2) - R_x^{C} (\theta_3) \) shown in Fig.1(c). The fidelity of the state obtained by the adiabatic preparation is around 98.93\% comparing with the theoretical expectation 0.996.

B) The controlled-\( U_k \) operation. The controlled-\( U_k \) has the form of

\[
U_k = |\uparrow\rangle \langle\uparrow| \otimes I + |\downarrow\rangle \langle\downarrow| \otimes U_k.
\]

For the first iteration, i.e., \( k = 0 \), \( U_0 = e^{-iH_{ad}T} \). Thus, the \( U_0 \) operation transforms the initial state \( |\psi_m\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle + |\downarrow\rangle) \) into \( \psi_{f} = \frac{1}{\sqrt{2}} (|\uparrow\rangle + e^{2\pi i \phi} |\downarrow\rangle) \) where \( \phi = -E\tau/2\pi \) with the energy \( E \). As an interferometer, the controlled logic gate effectively introduces a relative phase shift \( 2\pi \phi \) between ‘two paths’: the \( |0\rangle \) and \( |1\rangle \) states in the initially prepared superposition of the auxiliary qubit, which can be read out directly in NMR \[19\] \[20\]. The value of \( \tau \), in principle, can be arbitrarily chosen to make \( \phi \in (0, 1) \). For experimental convenience, we chose \( \tau = \frac{\pi}{\sqrt{2(2H(1.2)^2 + (H(1.1) - H(2.2))^2}} = 1.941122 \), and the pulse sequence to implement the controlled-\( U_k \) operator is shown in Fig.1(d). The different \( U_k \) in each iteration is realized by adjusting the parameters \( \alpha, \beta \) and delay .

C) Measurement. The relative phase shift is obtained if we measure the NMR signal of the auxiliary qubit (\( \langle \sigma_{\alpha}^{-} \rangle \)):

\[
\langle \sigma_{\alpha}^{-} \rangle = \langle \psi_f | \sigma_{\alpha}^{-} | \psi_f \rangle = \cos(2\pi \phi + i \sin(2\pi \phi)).
\]

As a result, the quadrature detection in NMR serves as a phase detector, i.e., the Fourier-transformed spectrum gives the relative phase information. Here we take the initial state of \( \psi_m \) as the reference phase. The experimental spectra for each interaction are showed in Fig.2

![FIG. 2: Experimental $^1H$ spectra for all six iterations along with the reference spectrum of the initial state $\psi_m$ (denoted by $k = 1$ as the dashed line). The following spectra $(k = 0 \sim 5)$ are observed after each iteration, which provides the relative phase information. The phase measured in this iteration is used in the next iteration.](image-url)

After each time iteration of the above procedure, we measure the phase shift and prepare the operator for the next iteration. After measured the phases, we uses a recursive method to rebuild the $\phi$ as the experiment result. The recursive method is formulated as follows, for the result $\phi_{exp}$ after kth iteration,

\[
\phi_{i-1} = \phi_{i} / \phi_{errbd} + \phi_{i} / \phi_{errbd}.
\]

$\phi_i$ is the intermediate value only for calculation. The recursive variable $i$ iterates from $i = k$ to 1 with $\phi_k \neq \phi_k$ where $\phi_k$ is the measured phase in the $k$th iteration. And finally we get the result by $\phi_{exp} = \phi_0$.

The result of the iteration is shown in Fig.3 and Tab.1.

The value $\phi_{exp}$ we got from experiment approaches the theoretical value of $\phi_{th}$ rapidly as the iterations proceeds. However, there’s still a gap between $\phi_{exp}$ and $\phi_{th}$ which
quantum-simulation algorithms for chemical-interested quantum computer. This is one of early researches of algorithm to calculate the molecular energies on an 2-bit value $-1.8516$. with 17 precise bits towards the theoretical finally the molecular energy got from our experiment is enough and we can not get any more precise bits. Finally the molecular energy of the experimental value and theoretical expectation. (b) The error of exponentially with $uk$ and this simulation could not be arbitrarily precise. Thus $-1$ is larger than $2^k$ which contains $2^k$’s power of $U_k$ in the iterations. The error scales exponentially with $k$ due to the imperfection of the operator $U$.

TABLE I: The Theoretical Expectation and Experimental result of $\phi$ after each Iteration. The experiments get 3 bits of $\phi$ in each iteration. The bits with an underline in each $\phi_{exp}$ denotes the precision of the value. Overall, we get 17 bits of precision by 6 iterations.

| iteration | binary values |
|-----------|---------------|
| 0         | 0.01001 01100 11001 00110 01100 00100 |
| 1         | 0.01000 00100 00111 01110 01001 01100 |
| 2         | 0.01000 00110 11001 01010 11010 01001 |
| 3         | 0.01000 01010 11001 10011 01001 01001 |
| 4         | 0.01000 01000 11011 11100 00100 01001 |
| 5         | 0.01000 01000 11100 00100 01001 01001 |

is larger than $2^{-18}$ after 6 iterations. This means that although we get 18 bits from the experiment, only 17 bits of them are precise.

This is because the time evolution of molecular Hamiltonian $H$ is simulated by $U = e^{-iH\tau}$ in the experiment and this simulation could not be arbitrarily precise. Thus the error of $U_k$, which contains $2^k$’s power of $U$, scales exponentially with $k$. We figure out this error in Fig.3b, which shows that in the 5th iteration the error is large enough and we can not get any more precise bits. Finally the molecular energy got from our experiment is $-1.851569$, with 17 precise bits towards the theoretical value $-1.8516$.

Conclusions. — We have demonstrated a quantum algorithm to calculate the molecular energies on an 2-bit quantum computer. This is one of early researches of quantum-simulation algorithms for chemical-interested problems and could move this field significantly forward. We also found that the precision of interested properties attained by this algorithm relies on the precision of implementing the time evolution of the molecular Hamiltonian in the experiment. Anyway, we made this early experimental progress towards the long-term goal of a rapid quantum chemistry calculation by quantum computers.

Note that, we have learned of a similar work[24] done concurrently on photonic system since writing this paper.

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