Simulate the H_2 Molecule 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: djf@ustc.edu.cn

The difficulty to calculate molecular energies in quantum chemistry with classical algorithms grows exponentially with the size of molecule. But quantum computers dramatically reduce the complexity of this problem. We made a demonstration of simulating H_2 molecule in an NMR quantum computer to calculate the energy of its ground state. We use the iterative method to get more precise bits of the value and for each iteration we utilized the NMR interferometry to get the energy information. Finally we get 17 precise bits of the energy value. Besides, we also show the bottleneck of such quantum algorithms where the precision upper bound limited by the imperfection of the operators in experiment.

Quantum computer have been shown in principle more powerful than classical computers in many problems. The most famous example is the factoring problem, which has a polynomial complexity in the Shor's quantum factoring algorithm[1] while no efficient classical method is available till now[2]. Another type of classically hard problem is the simulation of real quantum systems[3]. On classical computers, simulation of *Schödinger* equation of a quantum system need an exponentially growing resource with the size of the system. In 1982, Feynman proposed that quantum systems may be well simulated by a quantum computer[4]. Then S. Lloyd show that an universal quantum computer could simulate other quantum systems efficiently. Sequently a few demonstrated examples were shown to simulated the small quantum systems such as oscillators[5], Many-Body Fermi Systems[6], Heisenberg spin chain[7] and *etc.*.

The main task in computational quantum chemistry is to calculate the molecular properties. The difficulty for calculation of the molecular energies with classical algorithms scales exponentially with the molecular size[8]. Recently in 2005, Aspuru-Guzik and Dutoi *et al.* (AD)[8] proposed a new algorithm to simulate the molecules in quantum computers, which could calculate the energy of the molecule with polynomial resources. The algorithm transferred the energy information to the phase of the quantum states and adopted a quantum phase estimate algorithm to measure the relative phase shift of the state, and the process is iterated many times to get more precision of bit from the molecular energy. They use the H_2O and LiH molecules as examples to show the usefulness of their algorithm, which need at least 12 and 15 qubits in realizations. However, this requirement excess the ability of today's quantum computation technology, so no such experiment have been done till now.

In this letter, we firstly simulate the H_2 molecule in experiment and calculate the ground energy to a precision of 17 bits. For this work, we use the interferometry for the evaluation of the phase shift and adopt similar iterative scheme as in the AD's proposal. we also find that the precision of the result got from this algorithm limited by the imperfection of operators in experiments.

As shown in Fig.1a, the general routines to calculate the molecular ground energy in AD's proposal have four steps: 1) map the molecular wave function to the qubits' space; 2) apply the molecular Hamiltonian on the qubits which are prepared in its ground state to generate only phase shift on the qubits; 3) measure the phase shift and extract the energy information. 4) iterate the procedure more time with compensating the value get from the above loops to get more precise bit from the energy. For the scheme we implemented in the experiment, We will introduce the later three steps first and leave the chemistry issues behind.

In the second step, the quantum simulator's work qubit is prepared by Adiabatic State Preparation (ASP) to $|\Psi\rangle$, the ground state of the molecular Hamiltonian H. An unitary operator $U = e^{-iH\tau}$ is applied to the state $|\Psi\rangle$, with only generating a phase shift to the ancillary qubit by the controlled operation. Here $U|\Psi\rangle = e^{-iH\tau}|\Psi\rangle = e^{i2\pi\phi}|\Psi\rangle$ where $E = -2\pi\phi/\tau$ is the energy of H's ground state. Note that the energy E is negative so we make the phase ϕ to be positive and τ is chosen properly to make the phase ϕ ranges from 0 to 1.

In the measurement step, originally a four-bit inverse Quantum Fourier Transform (QFT) is adopted as the Relative Phase Measurement to evaluate the phase shift to get the energy value. This apparatus need four qubits as ancilla to get on precise bit with successful possibility of 15/16[9]. However, it is hard to handle so many extra qubits in today's technology. At the same time, 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[10, 11]. The principles of NMR interferometer is shown in Fig.1b. Very similarly with the optical area, the NMR interferometry measures the phase shift by modulating the spectrum patterns and

the phase shift could be evaluated with an error bound of $\pm 5°$ in our experiment, 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.

For a useful application in the quantum chemistry, the precision of the energy should be extendable, so the above process should be iterated to get more precise bits from the real value. We made a little modification to the original AD's proposal to improve its reliability. In our experiment for the kth iteration we perform the measurement, we get the phase shift ϕ_k with an error bound of $\pm\phi_{errbd}$. Then we perform the $(k+1)$th iteration by choosing another operator $U_{k+1} = [e^{-i2\pi\phi_0'}U_k]^{2^n}$, where n is the number of extra bits we want to attain in the $(k+1)$th iteration. Of course n is limited by the error bound in the experiment. Here $\phi_k' = max\{\phi_k - \phi_{errbd}, 0\}$. This is because we have to make sure that ϕ_k' is less than the theoretical value of ϕ which is generated by the operator U_k in each iteration and if ϕ_k is less than error bound then no phase is necessary to be eliminated. Initial the iteration begins with $U_0 = U$, and by iterate the procedures, the energy value could be accurate with a large number of bits.

However, the precision of the measurement could not be arbitrarily high, because the imperfection of the experimental operations. To get the kth bit of the energy, we have to perform the operator U with 2^k times, so the error of operator U scales exponentially with the bits of precision. So in experiments, the precision of the energy we got relies on the precision we could perform the operators.

For the chemistry issues, because of the limitation in quantum computation technologies, to calculate a large molecule's energy in not possible for the time being. So we choose to calculate the ground energy of H_2 molecule for our demonstration. The Hamiltonian of H_2 molecular is shown as follows,

$$H = \Sigma_i(T_i + \Sigma_j V_{ij}) + \Sigma_{i>j}O_{ij}$$

where T_i is the kinetic energy of electron i, and V_{ij} is the coulomb potential energy between the ith electron and the jth nucleus, while O_{ij} is the coulomb potential energy between electrons i and j. Here we choose the simplest situation: H_2 in the minimal STO-3G basis. In this two-nucleus and two-electron molecule, each atom has a $1s$ Guassian-type function, and the two functions compose one abonding orbital with gerade symmetry and one antibonding orbital with ungerade symmetry. So there are 4 spin orbital and these 4 spin orbital can form 6 configurations. Considering the singlet symmetry and the spatial symmetry of H_2 exact ground state, only two configurations are acting in fact in the calculation: the ground state configuration $|\Psi_0\rangle$ and the double excitation configuration $|\Psi_{1\bar{1}}^{2\bar{2}}\rangle$. Thus, the Hamiltonian matrix

is(in atom units, the nucleus distance is $1.4a.u.$, only the electron's energy) :[12]

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

whose theoretical eigenvalue is -1.8516 $a.u.$.

FIG. 1: (a) general schematic circuit for calculating molecular energies. (b)The sample used in experiment $CHCl_3$. ^{13}C nucleus is used for the work qubit while ^1H is for ancillary qubit. (c) Principle of NMR interferometry, which is used for the Relative Phase Measurement section in our experiment. (d) The pulse sequence to implement the Adiabatic State Preparation (ASP) process. After ASP, the ^{13}C nucleus is prepared in the state $|\Psi\rangle$–the ground state of the Molecular Hamiltonian H.(e) The pulse sequence to implement the controlled-U_k operation.

Now, we start to realize this simulation in a two-qubit NMR quantum computer. The two qubits are represented by ^{13}C and ^1H nuclear spins in the chloroform $(CHCl_3)$,respectively. The molecular structure is shown in Fig.1b, where the two qubits are marked out. The natural Hamiltonian of this two-qubit system is:

$$\mathcal{H}_{NMR} = \frac{\omega_H}{2}\sigma_z^H + \frac{\omega_C}{2}\sigma_z^C + \frac{\pi J_{CH}}{2}\sigma_z^H\sigma_z^C \quad (2)$$

where $\omega_H/2\pi$ and $\omega_C 2\pi$ are the Larmor frequencies and J_{CH} represents the weak coupling constant, typically, $J_{CH} = 214.6Hz$. To implement interferometer, we set ^1H as an ancillary qubit and ^{13}C for the work qubit, and the experiment was actually divided into two parts: (1) to prepare the initial state of the two qubits, i.e. $\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ for ^1H and $|\psi\rangle$ for ^{13}C; (2) to perform the controlled-U_k gate for each of iteration on initial state and measure the phase shift referring to initial state(see in Fig1a). In this experiment, as the error bound of the interferometer is beneath $\pm 5°$, we chose to extract $n = 3$ precise bits from the molecular energy in each iteration, and performed six iterations to get 18 bits overall, although only 17 bits of them are precise which we shall analyze later. For each iteration, the experiment was divided into three steps as following:

A) Adiabatic State Preparation and pseudo-Hadamard operation. Starting from the thermal equilibrium state, we created a pseudo-pure state (PPS) $\rho_{00} = \frac{1-\epsilon}{4}\mathbf{I} + \epsilon|00\rangle\langle00|$ using the spatial average technique[?], with $\mathbf{I}$ representing the $r \times 4$ unity operator and $\epsilon \approx 10^{-5}$ the polarization.

In order to prepare the initial state, first we apply $R_y^H(\pi/2)$ on H channel to perform Hadamard gate. Then

an adiabatic evolution should be perform on the ^{13}C qubit. Before adiabatic evolution, the qubit should be prepare in state $|0> - |1>$(the ground state of σ_x) by a pulse $R^H_{-y}(\pi/2)$. The adiabatic evolution is to vary the system Hamiltonian slowly enough (*i.e.* adiabatically) from an initial Hamiltonian σ_x to the required Hamiltonian H and after the evolution the qubit will on the ground state of H. For our experiment, we divided the adiabatic passage averagely into $M = 5$ step and the total evolution time $T = 5.4$, and linearly interpolate the time-dependent system Hamiltonian by $H_ad = (1-s)\sigma_x + sH$ with $s = \frac{t}{T}$. For each step m, we simulate the adiabatic evolution by an unitary operator U_m with Trotters' formula:

$$U_m = e^{-i\frac{\epsilon}{2}(1-s(t))\sigma_x}e^{-is(t)H\epsilon}e^{-i\frac{\epsilon}{2}(1-s(t))\sigma_x} + O(\epsilon^3), \quad (3)$$

where $\epsilon = \frac{1}{M+1}$. So in experiment, we implement the evolution for each step by a pulse sequence: $R^C_{-x}(\theta_1) - R^C_{-y}(\theta_2) - R^C_x(\theta_3)$, which is also shown in Fig.1d. The overall fidelity of the state we got towards theoretical expectation is 0.996.

B) The controlled-U_k operation. The controlled-U_k has the form of $|0\rangle\langle0| \otimes I + |1\rangle\langle1| \otimes U_k$ and transfers the phase shift to the ancillary qubit, which is the essential part of this simulation. Considering the form of U, i.e. $U = e^{-iH\tau}$, where τ is arbitrary. So for experimental convenience, we choose $\tau = 1.941122$, and the pulse sequence to implement the controlled-U_k operator is shown in Fig.1e.

C) Measurement and result. In the experiment, we take the state of ^1H qubit after the preparation in A) as a reference phase of the successor states, which contained the information of the interested energy. The result of the experiment is showed in Fig.2.

FIG. 2: Spectrums of the experiment. Starting from thermal equilibrium, we first created a pseudopure state and the spectrum after a read-out pulse on observed nuclear ^1H is showed as Spectrum 1). We use the phase of this spectrum as a reference of the successor spectrums. Spectrum 2) is obtained after adiabatic evolution and the quantum state at this time is $\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \otimes |\psi\rangle$. As showed in the figure, the spectrum is similar to that of PPS, which is because that $|\psi\rangle$ is closed to state $|0\rangle$. The following six spectrums are observed after the six iterations, which present us visible phase information. The relative phase of each of the six spectrums to Spectrum 2) are the experiment result of the correspond iteration, that is, the phase is used to calculate the parameter for the next iteration and to calculate the energy E.

After each iterate the above procedure, we measure the phase shift and thereby prepare the operator for the next iteration with the scheme described before. Additionally, we stored the value ϕ'_k in each iteration for further use. After measured the all six phases, we uses a recursive method to rebuild the ϕ as the experiment result. The recursive method is formulate as follows,

$$\phi_i^{result} = \phi_{i+1}^{result}/\phi_{errbd} + \phi'_i, \phi_5^{result} = \phi_5,$$

where ϕ_i is the measured phase in each iteration i and the method iterates from $i = 5$ to 0.

The result of the iteration is shown in Fig.3a. The value ϕ we got from experiment approaches the theoretical value of ϕ with the iterations processing. But there's still a gap between theoretical expectation and experimental value which could be seen in the zoom-in part in Fig.3a. The detail information is listed in Tab.I which shows the precision of the binary value ϕ_{exp} in the iterations. Note that, although we could get 18 bit value of ϕ in the overall six iterations, only 17 bit is precise with theoretical expectations. So the finally ϕ in our experiment is -1.851569, a little different from theoretical value -1.8516.

The reason for this difference is the error caused by experimental imperfections. As mentioned before, the evaluation could not be arbitrarily precise because of the error in operation U_k. To this end, we analyze the imperfection of U_k and figured out the error caused by this imperfection in Fig.3b. So after the 5th iteration, the value will not be corrected as the U_k caused error is too large. Finally we get 17 bits of precise ϕ which have already been the upper bound in our experiment.

FIG. 3: (a)The value ϕ approaches theoretical expectation as the iteration performs. The green line is the fit of triangles which denotes the experimental ϕ value in the iterations. The dash red line is theoretical expectation of ϕ. The experimental value approaches theoretical expectation exponentially. (b) zooming in part of the approaching process too show the limitation of precision caused by experimental imperfection.(c) The error of ϕ caused by imperfection of U_k in our experiment. Because the operation U could not be arbitrarily precise, by applying U with 8^k times, the error could be scale exponentially with k.

	iteration	binary values
ϕ_{exp}	0	0.01000 11100 10010 11000 10010
	1	0.01001 00100 00111 01110 01001
	2	0.01001 00100 11001 01010 11010
	3	0.01001 00100 11011 10011 10001
	4	0.01001 00100 11011 11110 11100
	5	0.01001 00100 11100 00000 01001
ϕ_{th}		0.01001 00100 11100 00101 01100

TABLE I: The Comparison of ϕ in Theoretical Expectation and Experimental result in the Iterations. All the values are presented by binary value. The experiments get 3 more bits in each iteration. The bits with an underline in each ϕ_{exp} denotes the precision of the value. Overall, we get 17 bits of precision rather than 18 bits.

In conclusion, we simulate the H_2 molecule in our NMR quantum computer. This is the first time simulating chemical interested molecular energies in experiment. The result matches well with theoretical expectation and we also find the precision limitation of this algorithm in experiments which is caused by the imperfection of operators. In fact, the extracted precision relies exponentially with the precision of operator, which maybe the bottleneck of this algorithm in applications.

[1] P. Shor, p. 124 (1994).
[2] D. E. Knuth, *The Art of Computer Programming Vol. 2, Seminumerical Algorithms* (Addison-Wesley, Reading, Massachusetts, 1998).
[3] S. Lloyd, Science **279**, 1117 (1998).
[4] R. P. Feynman, International Journal of Theoretical Physics **21**, 467 (1982).
[5] S. Somaroo, C. H. Tseng, T. F. Havel, R. Laflamme, and D. G. Cory, Physical Review Letters **82**, 5381 (1999).
[6] D. S. Abrams and S. Lloyd, Physical Review Letters **79**, 2586 (1997).
[7] X. H. Peng, J. F. Du, and D. Suter, Physical Review A **71**, 4 (2005).
[8] A. Aspuru-Guzik, A. D. Dutoi, P. J. Love, and M. Head-Gordon, Science **309**, 1704 (2005).
[9] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge Univ. Press, Cambridge, 2000).
[10] J. F. Du, P. Zou, M. J. Shi, L. C. Kwek, J. W. Pan, et al., Physical Review Letters **91**, 4 (2003).
[11] X. H. Peng, X. W. Zhu, D. Suter, J. F. Du, M. L. Liu, et al., Physical Review A **72**, 11 (2005).
[12] A. Szabo, N. S. Ostlund, *Modern Quantum Chemistry*, vol. 238 (Dover publications, Inc.).