NMR Implementation of a Molecular Hydrogen Quantum Simulation with Adiabatic State Preparation

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It is difficult to simulate quantum systems on classical computers, while quantum computers have been proved to be able to efficiently perform such kinds of simulations. We report an NMR implementation simulating the hydrogen molecule (H_2) in a minimal basis to obtain its ground-state energy. Using an iterative NMR interferometer to measure the phase shift, we achieve a 45-bit estimation of the energy value. The efficiency of the adiabatic state preparation is also experimentally tested with various configurations of the same molecule.

Introduction.—It is well known that quantum algorithms provide speedups towards classical algorithms in many problems [1], e.g., Shor's quantum factoring algorithm [2]. In addition to the successful application of quantum computation (QC) in computational study, QC can also be used to simulate other quantum systems, an idea conceived by Feynman [3]. The simulation of realistic quantum systems requires an exponential amount of resources on current computers, due to the exponential-growing dimensionality of Hilbert spaces. However, It is highly efficient to simulate a physical system within the QC architecture [4], i.e., costing only polynomial resources with respect to the size of the target system. Several physical systems were examined using this novel framework [5–11] and some of them have been demonstrated on NMR [8,9,12] and iontrap [13] platforms. Based on the iterative phase estimation, Aspuru-Guzik *et al.* proposed an algorithm [14] to simulate a molecular system and calculate the energies of the molecule. Very recently, Lanyon *et al.* [15] carried out a key step towards the realization of this algorithm on a photonic system to calculate molecular energies with a 20-bit precision.

The calculation of molecular energies is a fundamental problem in computational quantum chemistry. On classical computers, the resources required for a full simulation of the molecular system scale exponentially with the number of atoms involved, limiting such full configuration interaction (FCI) calculations of molecular energies to diatomic and triatomic molecules [16]. Nevertheless, the calculation could be done efficiently on a quantum simulator with Aspuru-Guzik's algorithm [14], where information of the energy is coded to the phase shift of a quantum register and measured by a quantum phase estimation algorithm (PEA).

In this Letter we implement a quantum molecular simulation where all the algorithmic steps, including the adiabatic state preparation (ASP), are completed on an NMR quantum simulator. As a demonstration, the ground-state energy of H_2 molecule has been extracted to a precision of 45 bits. Furthermore, we give an experimental analysis of

ASP's efficiency for different molecular configurations in our example, which matches well with Aspuru-Guzik's theoretical prediction [14].

Hamiltonian of H_2 molecule.—Because of the limitation of current quantum computing technology, it is impossible to demonstrate a large molecular energy calculation in FCI. So we exam the simplest situation: the ground-state energy of Hydrogen molecule in minimal STO-3G basis—a widely used basis set in FCI (for details, see Ref. [17]). The electron's Hamiltonian of H_2 molecule in Born-Oppenheimer approximation is $H = \sum_{i=1}^{2}(T_i + \sum_{j=1}^{2} V_{ij}) + \sum_{\substack{i,j=1 \\ i>j}}^{2} O_{ij}$, where T_i is the kinetic energy of the ith electron, V_{ij} is the Coulomb potential energy be-
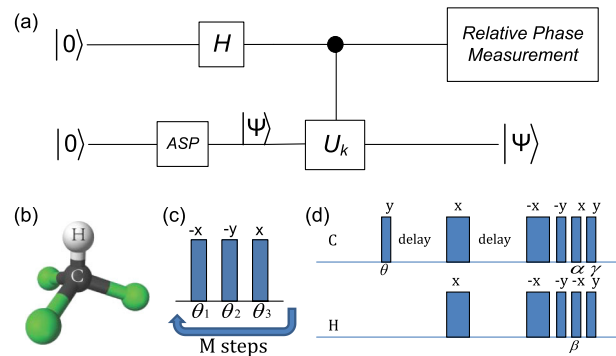

FIG. 1 (color online). (a) General schematic circuit for calculating molecular energies. (b) Molecular structure of quantum register ($CHCl_3$). (c) Pulse sequence for the adiabatic process to prepare the ^{13}C nucleus in the ground state $|\Psi\rangle$ of the molecular Hamiltonian H. (d) Pulse sequence to implement the controlled-U_k operation, where $\theta = \arctan(\frac{2H(1,2)}{H(1,1)-H(2,2)}) = 0.226$, $\gamma = \frac{\pi}{2} - \theta = 1.3458$, $\beta = \beta_k^0 - \phi'_{k-1}$ (ϕ'_{k-1} is calculated from the result of last iteration and $\beta_k^0 = -\frac{8^{k-1}\tau}{2}(H(1,1) + H(2,2))$), $\alpha = \frac{8^{k-1}\tau}{2}\sqrt{4H(1,2)^2 + (H(1,1) - H(2,2))^2}$ and $d = \frac{\alpha}{\pi J_{wa}}$ for the kth iteration. Totally 15 iterations are performed in our experiment. The U sequences are optimized as we chose a suitable $\tau = 1.94112172562605$.

tween the ith electron and the jth nucleus, and O_{ij} is the Coulomb potential energy between the ith and jth electron. In this molecule of two nuclei and two electrons, each atom has a $1s$ Gaussian-type function in STO-3G basis. Besides, these two $1s$ functions compose one bonding orbital with gerade symmetry and one antibonding orbital with ungerade symmetry. So there are 4 spin orbitals corresponding to 6 possible configurations. Considering the singlet symmetry and spatial symmetry of its ground state, only two configurations are relevant 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 nuclear distance r is 1.4 a.u.) [18]:

$$H = \begin{pmatrix} \langle\Psi_0|H|\Psi_0\rangle & \langle\Psi_{1\bar{1}}^{2\bar{2}}|H|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \\ \langle\Psi_{1\bar{1}}^{2\bar{2}}|H|\Psi_0\rangle & \langle\Psi_{1\bar{1}}^{2\bar{2}}|H|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \end{pmatrix}$$

$$= \begin{pmatrix} -1.8310 & 0.1813 \\ 0.1813 & -0.2537 \end{pmatrix}$$

of which the theoretical eigenvalue by diagonalization is $-1.851\,570\,929\,351\,19$ a.u.

Calculation of molecular energy.—As shown in Fig. 1(a), the calculation of the molecular energy in our experiment is achieved by three 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.

In the first step, the system qubit of quantum simulator is prepared by ASP to $|\Psi\rangle$, the ground state of the molecular Hamiltonian H. According to the quantum adiabatic theorem [19,20], the qubit starts from the ground state of a simple Hamiltonian and the system Hamiltonian of the qubit varies sufficiently slowly from the simple Hamiltonian to the target Hamiltonian H. If there is 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, a unitary operator $U = e^{-iH\tau}$ is applied to the state $|\Psi\rangle$, generating a phase shift on the probe qubit by a 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 choose τ properly to make the phase ϕ ranges from 0 to 1.

Finally, 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 obtain one precise bit with successful possibility of 15/16 [1]. While in the NMR platform we could use an NMR interferometer, named from the similar apparatus originally used in optics, to measure the relative phase shift of the

quantum states by modulating the spectrum patterns [21,22]. On our NMR interferometer, the phase shift could be evaluated with an error bound of less than $\pm 5°$, much higher precision than the performance of the original four-bit inverse QFT apparatus. Thus we utilize the interferometer to measure the phase shift in our experiment.

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(a), for each iteration k we apply 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 bits exacted in each iteration and $\phi_k' = \max\{\phi_k - \phi_{errbd}, 0\}$ where ϕ_k is the phase shift measured in the kth iteration. Note that n is limited by the precision of the phase measurement in each iteration, i.e., $2^{-n} \geq 2\phi_{errbd}$.

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 ^{1}H was for the probe qubit. The molecular structure is shown in Fig. 1(b). The natural Hamiltonian of this two-qubit system is given by

$$\mathcal{H}_{NMR} = \frac{\omega_p}{2}\sigma_z^p + \frac{\omega_s}{2}\sigma_z^s + \frac{\pi J_{ps}}{2}\sigma_z^p\sigma_z^s \qquad (1)$$

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

(A) *Preparation of the initial state.*—Starting from the thermal equilibrium state, we first created a pseudopure state (PPS) $\rho_{00} = \frac{1-\epsilon}{4}\mathbf{I} + \epsilon|\uparrow\uparrow\rangle\langle\uparrow\uparrow|$ using the spatial average technique [23], with $\mathbf{I}$ representing the 4×4 unity operator and $\epsilon \approx 10^{-5}$ the polarization. Then, we prepared the system qubit on $|\Psi\rangle$ by the ASP process and the probe bit on the state $|+\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$ by a pseudo-Hadamard gate $R_y^p(\pi/2)$.

In the ASP process, we started from an initial Hamiltonian $H_0 = \sigma_x$ and prepared the system qubit on its ground state $|-\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle)$ by a conjugated pseudo-Hadamard gate $R_y^s(-\pi/2)$. Then we drove the system Hamiltonian slowly from H_0 to H by a linear interpolation $H_{ad} = (1 - s)H_0 + sH$, where $s = \frac{t}{T}$ and the time t grows from 0 to T. The state of system qubit $|\Psi_{asp}\rangle$ after ASP approaches $|\Psi\rangle$ as T increases [19]. We numerically characterized the dependency of the fidelity of ASP (defined as $|\langle\Psi|\Psi_{asp}\rangle|^2$) on the total evolution time T in Fig. 2(a). In our experiment, we chose $T = 5.52$ a.u. [denoted by the triangle in the Fig. 2(a)] to ensure the

TABLE I. Experimental ϕ values (ϕ_{exp}) measured in iterations, compared to the theoretical expectation ϕth. The numbers in bold are the bits obtained from the experiment, where 3 bits are extracted in each iteration. Through 15 iterations, we ultimately obtained 45 bits of ϕ.

	k	Binary value
ϕ_{exp}	0	**0.100**100011101100101010000110010000011111110110
	2	**0.100100100**1110101110010110100110001010010011110
	5	**0.100100100111000000**011010011101101111011101001
	8	**0.100100100111000000010100001**110100010001111110
	11	**0.100100100111000000010100001101111001**110000000
	14	**0.100100100111000000010100001101111001101010110**
ϕth		0.100100100111000000010100001101111001101010110101

success of ASP [24,25]. The unitary evolution for each adiabatic step is $U_m^{\text{ad}} = e^{-i(\delta/2)(1-s_m)\sigma_x}e^{-is_m H\delta} \times e^{-i(\tau/2)(1-s_m)\sigma_x} + O(\delta^3)$, where the duration $\delta = T/(M+1)$ and $s_m = \frac{m}{M+1}T$. In our experiment, U_m^{ad} can be implemented by a pulse sequence $R_{-x}^s(\theta_1) - R_{-y}^s(\theta_2) - R_x^s(\theta_3)$ in Fig. 1(c) and the total evolution of ASP can be realized by applying U_m^{ad} in sequence. To clearly illustrate the efficiency of ASP, we also tested the fidelities of ASP vs evolution times T for nuclear distances r in the hydrogen molecule.

(B) *The controlled-U_k operation.*—The controlled U_k has the form of $\mathcal{U}_k = |\!\uparrow\rangle\langle\uparrow| \otimes I + |\!\downarrow\rangle\langle\downarrow| \otimes U_k$. For the first iteration (i.e., $k = 0$), $U_0 = e^{-iH\tau}$. Thus, the $\mathcal{U}_0$ operation transforms the initial state $|\psi_{\text{in}}\rangle = \frac{1}{\sqrt{2}}(|\!\uparrow\rangle + |\!\downarrow\rangle)|\Psi_{\text{asp}}\rangle$ into $|\psi_f\rangle = \frac{1}{\sqrt{2}}(|\!\uparrow\rangle + e^{i2\pi\phi}|\!\downarrow\rangle)|\Psi_{\text{asp}}\rangle$ where $\phi = -E\tau/2\pi$ with the energy E. In 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 probe qubit, which can be read out directly in NMR [21,22]. The value
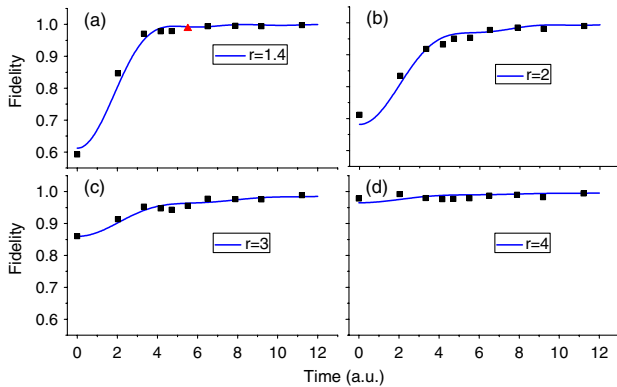
of τ, in principle, can be arbitrarily chosen to make $\phi \in (0, 1)$. For experimental convenience, we chose $\tau = [\pi/\sqrt{(2H(1, 2))^2 + (H(1, 1) - H(2, 2))^2}]$, and the pulse sequence to implement the controlled-U_k operator is shown in Fig. 1(d). The different $\mathcal{U}_k$ in each iteration is realized by adjusting the parameters α, β, and d.

Note that the direct implementation of the operator U_k led to the same length of pulse sequences in our small-scale demonstration. However, in a large-scale application, the powers of U in U_k could not be simply decomposed directly. In general, U^j should be realized by applying U with j times [14] (also see Appendix in Ref. [15]); thus, the experimental difficulty and operational error will be amplified with the iterations.

(C) *Measurement.*—The relative phase shift is obtained if we measure the NMR signal of the probe qubit: $\langle\sigma_p^-\rangle = \langle\psi_f|\sigma_p^-|\psi_f\rangle = \cos(2\pi\phi) + i\sin(2\pi\phi)$. 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 ψ_{in} as the reference phase. Some of the experimental spectra are shown in Fig. 3(b).

FIG. 2 (color online). Fidelity of ASP as a function of evolution time T for different nucleus distances r in a single run. The solid lines represent numerical simulations while the squares and the triangle are data points. The triangle in (a) denotes the configuration of ASP for our molecular simulation. The fidelity approaches 1 as the evolution time grows according to the *adiabatic theorem*. The adiabatic evolution is divided into 100 steps in numerical simulations and 8 steps in the experiments.
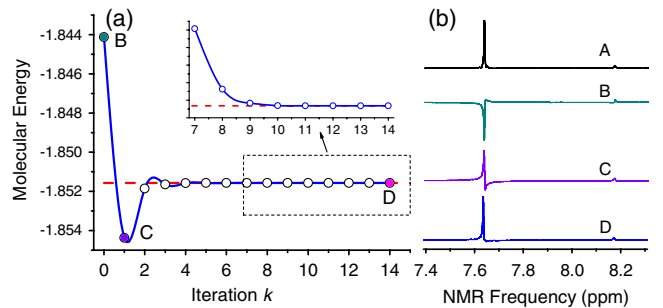

FIG. 3 (color online). (a) Measured energy values for 15 iterations. The solid blue line denotes the spline fit of experimental values (the circles) and the dash red line denotes the theoretical expectation. The experimental value approaches theoretical expectation exponentially. (b) Experimental ^{1}H spectra. The reference spectrum (A) from initial state $|\psi_{\text{in}}\rangle$ and (B)–(D) the spectra observed after iterations $k = 0$, 1, and 14, which provide the relative phase information. The phase measured in each iteration is used in its next iteration.

After each iteration of the above procedure, we measure the phase shift and prepare the operator for the next iteration. After measuring the phases, we use a recursive method to rebuild ϕ as the experiment result. The recursive method is formulated as $\phi_{i-1}^c = \phi_i^c / \phi_{\mathrm{errbd}} + \phi_{i-1}'$ for the result ϕ_{exp} after kth iteration, where ϕ_i^c is the intermediate value only for calculation. The recursive variable i iterates from $i = k$ to 1 with $\phi_k^c = \phi_k$ where ϕ_k is the measured phase in the kth iteration. And finally we get the result by $\phi_{\mathrm{exp}} = \phi_0^c$.

The result of the iteration is shown in Fig. 3(a) and Table I. The value ϕ_{exp} we obtained from experiment approaches the theoretical value of ϕth rapidly as the iterations proceeds. Finally the molecular energy extracted all the 45 significant bits of ϕ in 15 iterations is $-1.851\,570\,929\,351\,124$.

Conclusions.—We performed a proof-of-principle demonstration of quantum-simulation algorithm to calculate the ground-state energy of the hydrogen molecule on an NMR quantum computer up to a precision of 45 bits. In the experiment, the initial ground state was prepared by adiabatic passage. We confirmed that this adiabatic state preparation is efficient at different configurations of nuclear distances in hydrogen molecule. We also verified that the adopted phase estimation works well for obtaining the energy level of the equilibrium configuration.

Quantum simulations were proposed as the first applications of quantum computers [3]. Compared to quantum algorithms such as Shor's factoring algorithm [2] requiring thousands of qubits, quantum simulations on a few tens of qubits (30–100 qubits) can be expected to exceed the limitation of classical computing [14]. Here we made an experimental step towards the goal of a rapid quantum chemistry calculation by quantum computers. For larger molecular sizes, two issues are relevant in the scalability of this algorithm: (i) the efficient decomposition of the molecular evolution operator U and (ii) the complexity of the adiabatic state preparation. The first issue has been addressed by Lanyon *et al.* [15]. On the second issue, although it is difficult to achieve a decisive mathematical analysis so far, some numerical simulations of the adiabatic evolutions have been performed showing a polynomial growth of the median runtimes with the system size, e.g., the simulation up to 128 qubits [26]. On the other hand, the polynomial time complexity has been analytically obtained when the adiabatic evolution is performed to have the phase transitions of second or higher orders [27]. Therefore, this quantum-simulation algorithm is in principle feasible on medium molecular sizes where quantum information is exploited to speed up quantum chemistry calculations, when the necessary technical difficulties are overcome in building a medium-scale quantum computer.

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[1] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge Univ. Press, Cambridge, U.K., 2000).

[2] P. Shor, in *Proceedings of the 35th Annual Symposium on Foundations of Computer Science* (IEEE Computer Society Press, New York, Santa Fe, NM, 1994), p. 124.

[3] R. P. Feynman, Int. J. Theor. Phys. **21**, 467 (1982).

[4] S. Lloyd, Science **273**, 1073 (1996).

[5] C. Zalka, in *ITP Conference on Quantum Coherence and Decoherence* (Royal Soc. London, Santa Barbara, California, 1996), pp. 313–322.

[6] D. S. Abrams and S. Lloyd, Phys. Rev. Lett. **79**, 2586 (1997).

[7] L. A. Wu, M. S. Byrd, and D. A. Lidar, Phys. Rev. Lett. **89**, 057904 (2002).

[8] X. H. Peng, J. F. Du, and D. Suter, Phys. Rev. A **71**, 012307 (2005).

[9] S. Somaroo, C. H. Tseng, T. F. Havel, R. Laflamme, and D. G. Cory, Phys. Rev. Lett. **82**, 5381 (1999).

[10] A. Y. Smirnov, S. Savel'ev, L. G. Mourokh, and F. Nori, Europhys. Lett. **80**, 67008 (2007).

[11] D. A. Lidar and H. Wang, Phys. Rev. E **59**, 2429 (1999).

[12] C. Negrevergne, R. Somma, G. Ortiz, E. Knill, and R. Laflamme, Phys. Rev. A **71**, 032344 (2005).

[13] A. Friedenauer, H. Schmitz, J. T. Glueckert, D. Porras, and T. Schaetz, Nature Phys. **4**, 757 (2008).

[14] A. Aspuru-Guzik, A. D. Dutoi, P. J. Love, and M. Head-Gordon, Science **309**, 1704 (2005).

[15] B. P. Lanyon, J. D. Whitfield, G. G. Gillet, M. E. Goggin, and M. P. Almeida *et al.*, arXiv:quant-ph/09050887.

[16] L. Thogersen and J. Olsen, Chem. Phys. Lett. **393**, 36 (2004).

[17] I. N. Levine, *Quantum Chemistry* (Prentice-Hall, Inc., Upper Saddle River, NJ, 2000), 5th ed.

[18] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (Dover Publications, Inc., New York, 1996).

[19] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1976).

[20] T. Kato, J. Phys. Soc. Jpn. **5**, 435 (1950).

[21] J. F. Du, P. Zou, M. J. Shi, L. C. Kwek, J. W. Pan, C. H. Oh, A. Ekert, D. K. L. Oi, and M. Ericsson, Phys. Rev. Lett. **91**, 100403 (2003).

[22] X. H. Peng, X. W. Zhu, D. Suter, J. F. Du, M. L. Liu, and K. L. Gao, Phys. Rev. A **72**, 052109 (2005).

[23] D. G. Cory, A. F. Fahmy, and T. F. Havel, Proc. Natl. Acad. Sci. U.S.A. **94**, 1634 (1997).

[24] M. Steffen, W. van Dam, T. Hogg, G. Breyta, and I. Chuang, Phys. Rev. Lett. **90**, 067903 (2003).

[25] X. H. Peng, Z. Y. Liao, N. Y. Xu, G. Qin, X. Y. Zhou, D. Suter, and J. F. Du, Phys. Rev. Lett. **101**, 220405 (2008).

[26] A. P. Young, S. Knysh, and V. N. Smelyanskiy, Phys. Rev. Lett. **101**, 170503 (2008).

[27] R. Schutzhold and G. Schaller, Phys. Rev. A **74**, 060304 (R) (2006).