Quantum Algorithm for the Direct Calculations of Vertical Ionization Energies

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Highlights	◇　量子コンピュータは量子化学計算を高速に実行できるが、エネルギー計算値の誤差と計算コストが反比例する。 ◇　分子のエネルギーではなく、エネルギー差を直接計算する量子アルゴリズムを開発することで、大きな分子の量子化学計算も低い計算コストで実行できる。 ◇　原子・分子の基本的性質の１つであるイオン化エネルギーを直接計算する手法を提案した。
Supporting Information	The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00283. Definitions of quantum gates, computational conditions for ionization energy calculations, numerical quantum circuit simulations, Trotter decomposition error analysis, ionization energy calculations based on iterative quantum phase estimation, and noisy quantum circuit simulations
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概要	研究チームは、量子コンピュータを用いてスピン量子数が異なる電子状態（スピン状態）間のエネルギー差を直接計算できる量子アルゴリズムを改良し、量子コンピュータ実機に実装しやすくするとともに、中性原子・分子が電子を放出してイオンとなるために必要なエネルギーであるイオン化エネルギーの直接計算へと応用しました。これらの結果は、化学で興味が持たれている大きな分子の量子化学計算を量子コンピュータで効率的に実行するための重要な道筋を示すものといえます。
Description	**<研究の背景>** 　近年、特定の問題をスパコンなどのコンピュータよりも高速に解くことができる量子コンピュータの研究が非常に盛んに行われています。そのなかでも原子・分子のエネルギーを理論的に求め、電子状態を明らかにする量子化学計算は量子コンピュータの近い将来の計算ターゲットとして特に注目されています。しかし、量子コンピュータを用いた量子化学計算ではエネルギー計算値の誤差に反比例して計算コストが増えてしまうため、原子・分子のエネルギーを小さな桁まで正確に決定するのが非常に大変です。そのため、このままでは化学で興味が持たれているような大きな分子のエネルギーを量子コンピュータを用いて正確に決定し、量子コンピュータを化学研究に役立てることが困難です。 　ところで、ほぼ全ての化学の問題は分子の全エネルギーそのものではなく、エネルギー差を議論します。また、分子が大きくなったり、周期表で下の方に現れる重原子が入ったりすると全エネルギーは大きくなりますが、議論したいエネルギー差の大きさは分子サイズにかかわらずほぼ一定という特徴があります。同研究グループは、全エネルギーではなくエネルギー差を量子コンピュータで直接計算することができれば上述した問題が解決でき、量子コンピュータを実際の化学研究に役立てられる未来を創造できると考え、研究を進めています。 **<研究の内容>** 　研究グループは最近、スピン量子数が異なる電子状態（スピン状態）間のエネルギー差を直接計算することができる量子アルゴリズムを開発しました（K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, T. Takui, Chem. Sci. 2021, 12, 2121-2132.）。この量子アルゴリズムはこれまで知られていた量子位相推定と呼ばれる量子アルゴリズムよりも量子論理回路（量子サーキット）が短く、量子コンピュータへの実装が容易ですが、必要な量子ビット数が量子位相推定の2倍程度に増えてしまうという欠点がありました。今回、同研究グループは量子論理回路の改良を行い、実装に必要な量子ビット数を量子位相推定と同程度まで削減することに成功しました。また、この量子アルゴリズムを原子・分子が電子を放出してイオンとなるために必要なエネルギーであるイオン化エネルギーの直接計算へと応用しました。イオン化エネルギーは原子・分子の最も基本的な物性値の1つであり、化学結合の強さや性質、化学反応を理解するための重要な指標にもなります。従来はイオン化エネルギーを求めるには中性状態とイオン化状態それぞれのエネルギーを計算する必要がありましたが、この量子アルゴリズムを使えばイオン化エネルギーを一回の計算で求めることができます。量子論理回路の数値シミュレーションから、

イオン化エネルギー計算値の読み出しにかかる計算コストは原子番号や分子サイズに依存せず一定となること、量子論理回路の長さが量子位相推定の 10 分の 1 以下でイオン化エネルギーを 0.1 eV の高精度で求められることを明らかにしました。

<今後の展開と応用について>

　これまでに報告されている量子化学計算のための量子アルゴリズムのほとんどは、全エネルギーを求めるように設計されているため、化学で興味が持たれているような大きな分子の、小さなエネルギー差を正確に求めることが困難でした。本研究で開発した手法はエネルギー差を直接計算できるので、大きな分子の計算が格段に容易になります。

　本研究で提案した手法は従来のコンピュータに対して計算速度の指数関数的な加速が保証されています。現在利用可能な量子コンピュータはノイズの影響が大きく、長い量子論理回路を正確に実行することが困難ですが、量子コンピュータハードウェアの発展により、従来のコンピュータでは現実時間内に計算ができないような大きな分子の高精度計算が本量子アルゴリズムを用いて実行できるようになると期待されます。

'化学研究に役立つ量子アルゴリズム〜原子・分子のイオン化エネルギーを量子コンピュータで直接計算する手法を開発！' 大阪市立大学. https://www.osaka-cu.ac.jp/ja/news/2020/210317-1. (参照 2021-03-17)

Letter

Quantum Algorithm for the Direct Calculations of Vertical Ionization Energies

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ABSTRACT: Recently, a quantum algorithm that is capable of directly calculating the energy gap between two electronic states having different spin quantum numbers without inspecting the total energy of the individual electronic states was proposed. This quantum algorithm guarantees an exponential speedup, like quantum phase estimation (QPE)-based full-CI, with much lower costs. In this work, we propose a modified quantum circuit for the direct calculations of spin state energy gaps to reduce the number of qubits and quantum gates, extending the quantum algorithm to the direct calculation of vertical ionization energies. Numerical quantum circuit simulations for the ionization of light atoms (He, Li, Be, B, C, and N) and small molecules (HF, BF, CF, CO, O_2, NO, CN, F_2, H_2O, and NH_3) revealed that the proposed quantum algorithm affords the vertical ionization energies within 0.1 eV of precision.
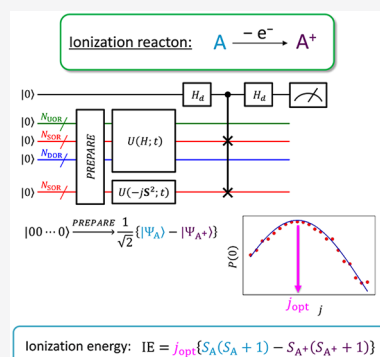
Sophisticated quantum chemical calculations of atoms and molecules are one of the most anticipated applications of quantum computers in the near future. The first quantum algorithm for the full-CI calculation[1] is based on a quantum phase estimation (QPE) algorithm,[2] which is executable in polynomial time against the system size of atoms and molecules. In this approach, the full-CI energy is computed from the relative phase shift caused by the time evolution of a wave function given in eq 1 and inverse quantum Fourier transformation to readout the phase ϕ.

$$\exp(-iHt)|\Psi\rangle = \exp(-iEt)|\Psi\rangle = \exp(-i2\pi\phi)|\Psi\rangle \quad (1)$$

Methods for the construction of the quantum circuit to simulate the time evolution of a wave function can be found in ref 3. Many attempts to reduce the computational costs of QPE-based full-CI calculations have been reported.[4−8] Another important algorithm is a variational quantum eigensolver (VQE),[9,10] in which an approximated wave function is generated via parametrized quantum circuits and the energy expectation value is computed in a statistical manner by iteratively performing the quantum circuit and collect measurement outcomes. When the energy expectation value is obtained on a quantum computer, the variational optimization of parameters is carried out on classical computers. VQE is a quantum−classical hybrid algorithm and has been extensively studied because it is executable on noisy intermediate-scale quantum (NISQ) devices. Apart from these two approaches, many studies of quantum chemical calculations on quantum computers have been reported from both the theoretical and experimental sides. For example, extension of theory for relativistic quantum chemistry,[11] adaptive constructions of parametrized quantum

circuits in VQE,[12,13] quantum chemistry on analog quantum computers,[14] development of spin symmetry-adapted treatments,[15−18] and proof-of-principle demonstrations on real quantum devices[19−23] have been documented. Recent reviews in this research field can be found in the reference.[24−26]

From the viewpoint of the applications of quantum computers for chemistry as practical use, direct calculation of the energy gap between two electronic states is a promising approach.[27−29] This is because most of problems in chemistry focus on the energy difference between two states or structures, rather than total energies themselves. For example, the activation energy of a chemical reaction is calculated as the energy difference between equilibrium and transition structures, the absorption wavelengths of optical spectra are computed as the energy gaps between the ground and excited states, the problem of finding the most stable conformer is solved by comparing the energies of different structural isomers.

In this work, we focus on the energy gaps between neutral and cationic states of atoms and molecules, namely ionization energies. Accurate calculations of ionization energies are important because they govern the electron transfer and oxidation processes in chemistry and biology.[30] Knowledge of ionization energies is also used to understand nature and strength of chemical bonds. Note that the knowledge of the
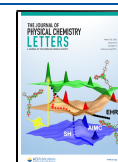
energy spectra of electron-attached (anionic) and removed (cationic) states is needed to construct many body Green's functions, and any quantum algorithm for the direct calculation of ionization energy can be used as a subroutine in the quantum algorithm for Green's functions.[31] Another motivation of the direct calculation of energy gaps on a quantum computer is relevant to computational costs for energy evaluation, which are inversely proportional to ε and ε^2 for QPE and VQE, respectively, where ε is the energy precision. The computational cost increases steeply when we try to evaluate the energy in fine digits. Importantly, the total energy increases as the system size, but the energy gap to be discussed remains almost the same magnitude in most of chemistry problems. In other words, we have to discuss the similar magnitude of energy differences regardless of the system size. A strategy of direct energy gap calculations becomes more important for larger molecules and molecules containing heavier atoms. Quantum computers utilize quantum superpositions as computational resources, which allow us to construct quantum algorithms for the direct energy gap calculations.

Recently, we proposed a quantum algorithm "<u>B</u>ayesian e<u>x</u>change coupling parameter calculator with <u>b</u>roken-symmetry wave functions (BxB)" for the direct calculation of spin state energy gaps on quantum computers without inspecting total energies of individual spin states.[27] Numerical quantum circuit simulations revealed that the BxB algorithm allows us to compute the exchange coupling parameter J defined by the two-site Heisenberg spin Hamiltonian given in eq 2 at the full-CI level within 1 kcal mol^{-1} of precision, with noticeably lower computational costs than the conventional approach based on QPE.

$$H_{\text{Heisenberg}} = -2J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \tag{2}$$

The BxB quantum algorithm has many advantages compared with QPE. The BxB algorithm does not need controlled time evolution operation that is necessary in QPE. The evolution time required to achieve chemical precision (the energy precision of the energy gap becomes less than 1 kcal mol^{-1}) is about 300 atomic unit which is considerably shorter than that in QPE ($t \sim 4000$ au).[27] The quantum algorithm is based on Bayesian inference and it is very robust against measurement errors.[32,33] The BxB algorithm is also expected to be robust against random and imperfect gate errors because it uses the wave function in quantum superposition. Noises and errors originating from imperfect gate operations and decoherence act simultaneously and similarly on the two electronic states, and thus, the errors can be canceled out to some extent when calculating the energy difference.[27] It should be noted that the BxB algorithm is applicable to other problems, if two electronic states have different spin quantum numbers and if the approximate wave function that is the superposition of the two electronic states can easily be prepared.

The BxB quantum algorithm, or more generally, the quantum algorithm for the direct calculations of spin state energy gaps is based on the eigenvalue problem of the shifted Hamiltonian H' in eq 3, which consists of Hamiltonian of the system H and the penalty term $j\mathbf{S}^2$. Here, $\mathbf{S}^2$ is the electron spin operator giving an eigenvalue $S(S + 1)$, where S denotes a spin quantum number. The eigenvalue problem of H' is written as in eq 4.

$$H' = H + j\mathbf{S}^2 \tag{3}$$

$$H'|\Psi_{S=S_a}\rangle = E'_{S=S_a}|\Psi_{S=S_a}\rangle$$
$$= \{E_{S=S_a} + jS_a(S_a + 1)\}|\Psi_{S=S_a}\rangle \tag{4}$$

The energy gap between two spin states $|\Psi_{S=S_a}\rangle$ and $|\Psi_{S=S_b}\rangle$ under the shifted Hamiltonian H' is computed as

$$\Delta E' = E'_{S=S_b} - E'_{S=S_a}$$
$$= E_{S=S_b} - E_{S=S_a} + j\{S_b(S_b + 1) - S_a(S_a + 1)\} \tag{5}$$

If we can find the j parameter of which the two spin states have the same eigenvalue $E'_{S=S_a} = E'_{S=S_b}$, the left-hand side of eq 5 becomes zero and the energy gap between the two spin states under the original Hamiltonian H can be computed from the j value and spin quantum numbers S_a and S_b. Denoting the j value of which the two spin states give the same eigenvalue E' as j_{opt}, the spin state energy gap ΔE is calculated as in eq 6.

$$\Delta E = E_{S=S_b} - E_{S=S_a}$$
$$= -j_{\text{opt}}\{S_b(S_b + 1) - S_a(S_a + 1)\} \tag{6}$$

When two spin states have the same eigenvalue E' under the shifted Hamiltonian H', the wave function $|\Psi_0\rangle$ in the superposition of the two spin states as in eq 7 is also an eigenfunction of H'. Thus, the problem to calculate the spin state energy gap can be rewritten as the problem of finding the j parameter for which $|\Psi_0\rangle$ in eq 7 becomes an eigenfunction of H'.

$$|\Psi_0\rangle = c_a|\Psi_{S=S_a}\rangle + c_b|\Psi_{S=S_b}\rangle \tag{7}$$

If $|\Psi_0\rangle$ is an eigenfunction of H', the time evolution of $|\Psi_0\rangle$ under H' merely induces a phase shift without changing the structure of $|\Psi_0\rangle$. The deviation of $|\Psi_0\rangle$ from the eigenfunction of H' can be estimated from the square overlap $|\langle\Psi_0|U(H';j,t)|\Psi_0\rangle|^2$, where $U(H';j,t)$ is given in eq 8.

$$U(H'; j, t) = \exp\{-i(H + j\mathbf{S}^2)t\} \tag{8}$$

The square overlap $|\langle\Psi_0|U(H';j,t)|\Psi_0\rangle|^2$ can be efficiently evaluated by using a SWAP test.[34] The SWAP test consists of two Hadamard gates and a controlled-SWAP gate, which interchanges the quantum states of $|\varphi\rangle$ and $|\psi\rangle$ when the control qubit is in the $|1\rangle$ state, and the measurement of a qubit used as the control. The probability to obtain the $|0\rangle$ state in the measurement of the control qubit is calculated as eq 9, which is proportional to the square overlap of the two quantum states $|\varphi\rangle$ and $|\psi\rangle$.

$$P(0) = (1 + |\langle\varphi|\psi\rangle|^2)/2 \tag{9}$$

The quantum circuit for the direct calculations of spin state energy gaps proposed in ref 27 is given in Figure 1. Definitions of quantum gates are summarized in Supporting Information. Assuming eq 7, the probability to obtain the $|0\rangle$ state in the measurement of the first qubit in Figure 1, $P(0)$, is calculated as follows:[27]

$$P(0) = \frac{1}{2}[1 + |c_a|^4 + |c_b|^4 + 2|c_a|^2|c_b|^2 \cos(\Delta E't)] \tag{10}$$

Here, $\Delta E'$ is the energy gap between two spin states under the shifted Hamiltonian as defined in eq 5. By sweeping j and executing the quantum circuit in Figure 1, the probability $P(0)$ becomes a maximum at $\Delta E' = 0$. The optimization of the j parameter that gives the maximum $P(0)$ can be done by using
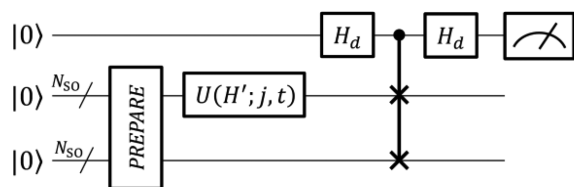
Figure 1. Quantum circuit for the direct calculations of spin state energy gaps proposed in ref 27. A PREPARE gate generates an approximate wave function $|\Psi_0\rangle$ on quantum register initialized to the $|0\rangle$ state, and $U(H'';j,t) = \exp\{-i(H + jS^2)t\}$.

Bayesian inference. Bayesian inference is an optimization algorithm based on Bayes' theorem and it allows us to calculate the posterior probability (updated probability by considering new evidence) of the hypothesis from the prior probability and a likelihood function. In quantum computing, it has been adopted for QPE[32,33] and Hamiltonian learning.[35−37] Bayesian optimization is robust against noises[32,35] and is, thus, very suitable for parameter optimization tasks in hybrid quantum algorithms.

A computation scheme of the BxB algorithm is summarized as follows: (1) Define a prior distribution by a Gaussian function. (2) Set the time evolution length t from a variance σ^2 of the prior distribution. (3) Draw m samples in the range of $\mu - \sigma^2$ to $\mu + \sigma^2$ with a constant interval and execute the quantum circuit in Figure 1 R times with given t and j to calculate a likelihood function $P(0|j;t)$. Here, μ is the mean of the prior distribution. (4) Fitting the obtained likelihood function by a Gaussian function and calculate a posterior distribution $P(j|0;t)$ using eq 11. (5) If the variance of the posterior distribution is smaller than the threshold, the algorithm returns the mean of the posterior distribution as the estimate of the j value, and otherwise, the algorithm returns to step 2 with the posterior distribution as the prior distribution of the next iteration. Because Bayesian optimization is executed on classical computers, the BxB belongs to the quantum−classical hybrid algorithm as same as VQE. However, the BxB has different features from VQE. For example, the BxB is free from the barren plateaus problem[38] because it optimizes a single parameter j.[27]

$$P(j|0;\ t) = \frac{P(0|j;\ t)P(j)}{\int P(0|j;\ t)P(j)\mathrm{d}j} \quad (11)$$

A PREPARE gate in Figure 1 generates the approximate wave function $|\Psi_0\rangle$ in superposition of different spin states on the quantum registers initialized to the $|0\cdots0\rangle$ state. In the previous study on the direct calculations of an exchange coupling parameter J, the PREPARE gate generates the broken-symmetry wave function $|\Psi_{BS}\rangle$ defined in eq 12 for biradical systems by using N_{elec} of Pauli-X gates, where N_{elec} is the number of electrons. In eq 12, 2, α, β, and 0 stand for doubly occupied, singly occupied by a spin-α electron, singly occupied by a spin-β electron, and unoccupied orbitals, respectively.

$$|\Psi_{BS}\rangle = |22\cdots2\alpha\beta0\cdots0\rangle \quad (12)$$

The quantum circuit depicted in Figure 1 needs $(2 \times N_{SO} + 1)$ of qubits for implementation, where N_{SO} denotes the number of spin orbitals. This is about twice of the number of qubits required for iterative QPE which requires $(N_{SO} + 1)$ of qubits to implement.[39] However, as we demonstrate below, the number of qubits can be reduced by modifying the quantum circuit. Note that the approach for the qubit reduction was pointed out in our

preceding paper,[27] but here we provide a mathematical proof of this approach.

The quantum algorithm for the direct calculation of spin state energy gaps is based on the SWAP test.[33] By executing the SWAP test, the probability to obtain the $|0\rangle$ state is calculated as eq 9. In our quantum algorithm, we used $|\varphi\rangle = |\Psi_0\rangle$ and $|\psi\rangle = U(H';j,t)|\Psi_0\rangle$ to calculate the square overlap $|\langle\Psi_0|U(H';j,t)|\Psi_0\rangle|^2$, where $U(H';j,t)$ is the time evolution operator under the shifted Hamiltonian H' as given in eq 8.

Importantly, $U(H';j,t)$ can be decomposed as in eq 13 without any approximation, because $[H,S^2] = 0$.

$$\begin{aligned} U(H';\ j,\ t) &= \exp(-ijS^2t)\exp(-iHt)\\ &= U(jS^2;\ t)U(H;\ t)\\ &= U^\dagger(-jS^2;\ t)U(H;\ t) \end{aligned} \quad (13)$$

By substituting eq 13 for the equation of the square overlap we want to evaluate, the following equation can be derived.

$$|\langle\Psi_0|U(H';\ j,\ t)|\Psi_0\rangle|^2 = |\langle\Psi_0|U^\dagger(-jS^2;\ t)U(H;\ t)|\Psi_0\rangle|^2 \quad (14)$$

From eq 14, we can perform the SWAP test with $|\varphi\rangle = U(-jS^2;t)|\Psi_0\rangle$ and $|\psi\rangle = U(H;t)|\Psi_0\rangle$. This decomposition is very useful not only for the case that quantum circuit depth becomes shallower but also for the case that the quantum simulation of the $U(-jS^2;t)$ operator becomes simpler. The $U(-jS^2;t)$ operator only affects the quantum state of the qubits storing the occupation number of singly occupied molecular orbitals. The approximate wave function $|\Psi_0\rangle$ used in the direct spin state energy gap calculation is a single Slater determinant in the previous application for an exchange coupling parameter J calculations,[27] and $|\Psi_0\rangle$ is a linear combination of two Slater determinants in the present study for ionization energy calculations, as discussed below. We can easily classify the molecular orbitals to open shell and closed shell natures. To adopt this strategy, we sorted molecular orbitals into three regions; doubly occupied region (DOR), singly occupied region (SOR), and unoccupied region (UOR) by the occupation numbers of two spin states. The molecular orbital is labeled as DOR, SOR, and UOR, if the molecular orbital is doubly occupied in both spin states, singly occupied in $|\Psi_{S=S_a}\rangle$ or $|\Psi_{S=S_b}\rangle$ in eq 7, and unoccupied in both spin states, respectively. N_{DOR}, N_{SOR}, and N_{UOR} is the number of qubits used for mapping the molecular orbitals in DOR, SOR, and UOR, respectively. The qubits in DOR and UOR can be excluded from the SWAP test, because the contribution from these qubits to $P(0)$ does not depend on j. As a result, the number of qubits used for the SWAP test can be reduced from $(2 \times N_{SO} + 1)$ to $(2 \times N_{SOR} + 1)$, and the total number of qubits required for implementation is also reduced from $(2 \times N_{SO} + 1)$ to $(N_{SO} + N_{SOR} + 1)$. It should be noted that direct calculations of vertical ionization energies can also be possible by using the number operator of electron $\mathbf{N}_{elec}$ defined in eq 15 instead of the S^2 operator in the shifted Hamiltonian H' in eq 3, but in this case, the qubit reduction scheme discussed here cannot be applied.

$$\mathbf{N}_{elec} = \sum_p a_p^\dagger a_p \quad (15)$$

The modified quantum circuit for the direct calculations of spin state energy gaps is illustrated in Figure 2. Importantly, the computational cost of the quantum simulation of the time
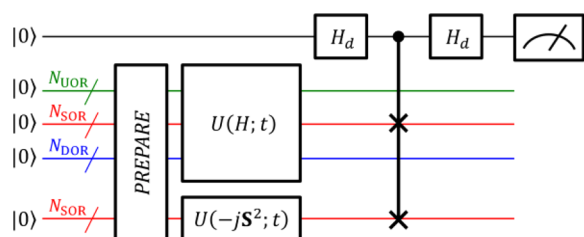
Figure 2. Modified quantum circuit for the direct calculations of spin state energy gaps used in this work. N_{DOR}, N_{SOR}, and N_{UOR} stand for the number of spin orbitals in doubly occupied region, singly occupied region, and unoccupied region, respectively. $U(H;t) = \exp(-iHt)$ and $U(-j\mathbf{S}^2;t) = \exp\{-i(-j\mathbf{S}^2t)\}$.

evolution operator $U(-j\mathbf{S}^2;t)$ is decreased drastically. For example, when the SOR contains only one molecular orbital, the time evolution operator $U(-j\mathbf{S}^2;t)$ can be realized by two CNOT gates and one phase shift gate by using a generalized spin coordinate mapping (GSCM) proposed by us,[17,18] regardless of the evolution time length.

We applied the quantum algorithm to the direct calculations of ionization energies, by using the wave function $|\Psi_0\rangle$ defined in eq 16.

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}}(|\Psi_{HF}\rangle - a_i|\Psi_{HF}\rangle) \tag{16}$$

Here, $|\Psi_{HF}\rangle$ is a Hartree−Fock wave function of the neutral state and a_i denotes an annihilation operator acting on the electron to be ionized. Thus, $a_i|\Psi_{HF}\rangle$ is an approximated wave function of the ionized state under the Koopmans' theorem.[40] By using the Jordan−Wigner transformation (JWT) as the wave function mapping,[41] the wave function given in eq 16 can easily be prepared. Figure 3 illustrates the quantum circuit to generate the
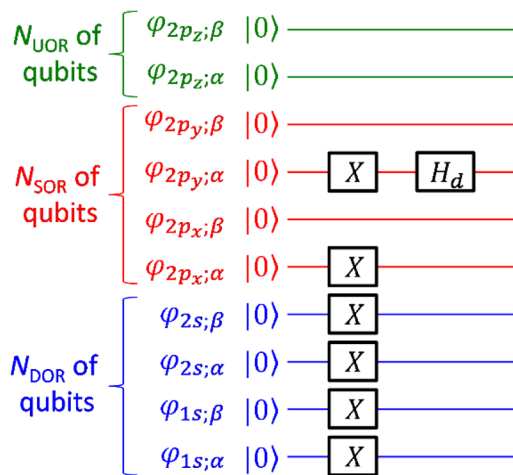

Figure 3. Quantum circuit to generate the approximate wave function $|\Psi_0\rangle$ defined in eq 16 of a carbon atom.

approximate wave function of a carbon atom with (1s,2s,2p) active space, which corresponds to the PREPARE gate in Figures 1 and 2. In Figure 3, the Pauli-X gates generate the Hartree−Fock configuration of the neutral state in JWT. Following Hadamard gate (H_d) applied to the qubit storing the occupation number of the spin orbital that ionization occurs generates the superposition of neutral and cationic wave functions in eq 16.

To demonstrate the quantum algorithm, we performed numerical quantum circuit simulations for ionization of atoms

(He, Li, Be, B, C, and N) and small molecules (HF, BF, CF, CO, O_2, NO, CN, F_2, H_2O, and NH_3). The numerical simulations were carried out by using our own Python program developed with OpenFermion[42] and Cirq[43] libraries. We used the active space approximation and computed the ionization energies at the CAS-CI/6-311G(d,p) level. In the quantum simulations of time evolution with $U(H;t)$ and $U(-j\mathbf{S}^2;t)$, we adopted second-order Trotter decomposition, and the time length for single Trotter step is set to be 0.5 atomic unit. Detailed computational conditions for quantum chemical calculations and the numerical simulations of quantum circuits are given in Supporting Information.

The numerical simulation results are summarized in Table 1. We examined two types of an initial estimate of the ionization energy, the ionization energies at the Koopmans' theorem (IE(Koopmans) = −E(HOMO)) and those at the ΔSCF level (IE(ΔSCF) = E(cation) − E(neutral)). The same ionization energies were obtained from both the initial estimates. The standard deviations are less than 0.01 eV in all the calculations. All quantum simulations were converged after 8−9 Bayesian updates. The evolution time length required to acquire the ionization energy within 0.01 eV of precision is at most $t \sim 250$ au We also executed the numerical simulations using the quantum circuit given in Figure 1 that uses all qubits for the SWAP test, obtaining the same results.

Table 1 clearly shows that our quantum algorithm is capable of reproducing the ionization energy at the CAS-CI/6-311G(d,p) level within 0.1 eV of difference. The deviation from the CAS-CI value is rationally explained by the Trotter decomposition errors. In fact, the deviation becomes small by increasing the Trotter slices (see Supporting Information for details). It should be noted that effect of Trotter decomposition error on the calculated spin state energy gap is larger in the ionization energy calculation than in the exchange coupling parameter J. This is because in the exchange coupling parameter J calculations high-spin and low-spin states have the same number of electrons and their electronic configurations are similar, and therefore a large amount of Trotter errors can be canceled out when computing the energy difference. By contrast, in the ionization energy calculation, neutral and cationic states have different numbers of electrons and thus Trotter error cancellation is not sufficient. We also performed the ionization energy calculation of a carbon atom by using the naïve approach based on two separate iterative QPE simulations of the neutral and cationic states, giving IE(IQPE) = 11.437 eV. The deviation from the CAS-CI value is smaller in our quantum algorithm than in IQPE, revealing the usefulness of our approach (see Supporting Information for details).

Note that all the results in Table 1 are obtained from noiseless quantum circuit simulations. Noisy quantum circuit simulations of C atom were also executed with a Pauli error model, in which one of the Pauli operators (X, Y, Z, and I) is randomly applied with a probability η, η, η, and $(1 − 3\eta)$, respectively. Details of the noisy quantum circuit simulations are given in Supporting Information. The ionization energy with $\eta = 0.01$ is 11.319 ± 0.013 eV and Bayesian optimization converged after 9 iterations. This result also supports the robustness of our quantum algorithm. More detailed analyses of the effect of noises are a future task.

In summary, we proposed a modified quantum circuit for the direct calculations of spin state energy gaps executable with a fewer number of qubits and lower computational costs against originally proposed one, and applied it to the direct calculations

Table 1. Numerical Quantum Circuit Simulation Results of the Ionization Energy (IE) of Atoms and Small Molecules

systems	N_{SO}[a]	neutral state electron configuration[b]	IE(Koopmans) (eV)	IE(ΔSCF) (eV)	IE(CAS-CI) (eV)	IE(Sim) (eV)	IE(Exptl)[44,45] (eV)
He	4	$|20\rangle$	24.950	23.450	23.899	23.892	24.58741
Li	10	$|2\boldsymbol{\alpha}000\rangle$	2.158	5.341	5.340	5.330	5.39172
Be	10	$|22000\rangle$	8.406	8.044	8.924	8.883	9.32263
B	10	$|22\boldsymbol{\alpha}00\rangle$	2.275	7.934	8.098	8.085	8.29803 ± 0.00002
C	10	$|22\boldsymbol{\alpha\alpha}0\rangle$	3.469	10.800	11.342	11.322	11.26030
N	10	$|22\boldsymbol{\alpha\alpha\alpha}\rangle$	4.830	13.984	14.900	14.842	14.53414
HF	10	$|22220\rangle$	17.345	14.370	16.922	16.918	16.03 ± 0.04
BF	10	$|22200\rangle$	10.991	9.984	11.251	11.228	11.12 ± 0.01
CF	10	$|222\boldsymbol{\alpha}0\rangle$	2.884	9.527	9.825	9.814	9.11 ± 0.01
CO	12	$|222000\rangle$	15.040	13.415	14.819	14.775	14.014 ± 0.0003
O$_2$	12	$|222\boldsymbol{\alpha\alpha}0\rangle$	5.796	13.250	12.702	12.667	12.0697 ± 0.0002
NO	12	$|222\boldsymbol{\alpha}00\rangle$	14.762	10.065	9.879	9.883	9.2642 ± 0.00002
CN	12	$|22\boldsymbol{\alpha}000\rangle$	13.306	12.289	14.379	14.325	13.598
F$_2$	12	$|222220\rangle$	18.202	16.742	16.501	16.473	15.697 ± 0.003
H$_2$O	12	$|222200\rangle$	13.600	10.971	13.272	13.270	12.621 ± 0.002
NH$_3$	14	$|2222000\rangle$	11.513	9.374	11.351	11.341	10.070 ± 0.020

[a]The number of spin orbitals included in the active space, which corresponds to the number of qubits required to store the wave function $|\Psi_0\rangle$.
[b]Written in boldface specifies the electron to be ionized.

of vertical ionization energies. Our quantum algorithm can afford to compute ionization energies of atoms and molecules at the CAS-CI level within 0.1 eV of deviation, regardless of the electronic spin structure of the neutral state, that is, whether it is closed shelled or open shelled. The number of Bayesian optimization cycle does not depend on the system size, and it quickly converges to the optimal value. The proposed quantum algorithm does not require controlled-time evolution operations and evolution time is much shorter than that needed in QPE-based full-CI calculations. Our quantum algorithm is easier to implement than QPE, and it has the potential for opening the door to solve real-world chemistry problems on fault-tolerant quantum computers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00283.

Definitions of quantum gates, computational conditions for ionization energy calculations, numerical quantum circuit simulations, Trotter decomposition error analysis, ionization energy calculations based on iterative quantum phase estimation, and noisy quantum circuit simulations (PDF)

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Notes

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