

Quantum chemistry on quantum computers: quantum simulations of the time evolution of wave functions under the S^2 operator and determination of the spin quantum number S

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| 概要 | <p>量子コンピュータを用いて分子の量子化学計算を行ったときに、量子計算が正しく実行され、求めようと思っていた電子状態が計算で得られたかを簡単に検証することができる新しい量子アルゴリズムの開発に成功しました。</p> <p>この研究成果により、酵素タンパク質の化学反応解析や、単分子メモリデバイスに適した分子の理論設計など、実際の化学研究に量子コンピュータを役立てるための道筋が初めて示されました。</p> |

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Description

【研究背景】

近年、スーパーコンピュータを含めた従来のコンピュータ（古典コンピュータという）を凌駕する性能を持つ量子コンピュータの研究が国内外で盛んに行われています。特に、原子や分子の微視的性質を支配する Schrödinger 方程式を正確に解き、エネルギーを正確に求める問題（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注目を集めています。原子・分子のエネルギーの超精密計算は、古典コンピュータを使うと計算時間が分子サイズに対して指数関数的に増加するのに対し、量子コンピュータを用いることで計算時間の指数爆発を抑えることができ、現実時間内に計算が可能なが示されています。現在、量子コンピュータを用いて原子・分子のエネルギーをより高速に求めるための手法や分子の安定構造を探索する手法、分子の吸光・発光波長を計算する手法など、様々な理論手法の開発研究が世界各地で活発に行われています。

単分子メモリデバイスなどへの応用が期待されている単分子磁石や酵素タンパク質の酵素活性を担う金属クラスターなどは、その機能や分子物性が非常に注目されている分子系ですが、これらの分子は、エネルギーが最も低い電子状態の近くに数多くの電子状態が存在しており、どの電子状態が量子化学計算で求めたかを明らかにすることが重要です。量子コンピュータを用いてこれらの分子のエネルギー計算を実行したとき、求めようと思っていた電子状態が量子計算で得られたかを検証する手段がなければ、量子コンピュータを使った機能分子設計など、実際の化学研究へと応用することができません。特に、化学結合を作らず、反応性や機能性に重要な役割を果たす不対電子と呼ばれる電子を持つ分子系のエネルギー計算を量子コンピュータで実行したとき、得られた電子状態がどのような電子構造を持っているかを簡便に決定できる手法はこれまで報告されていませんでした。

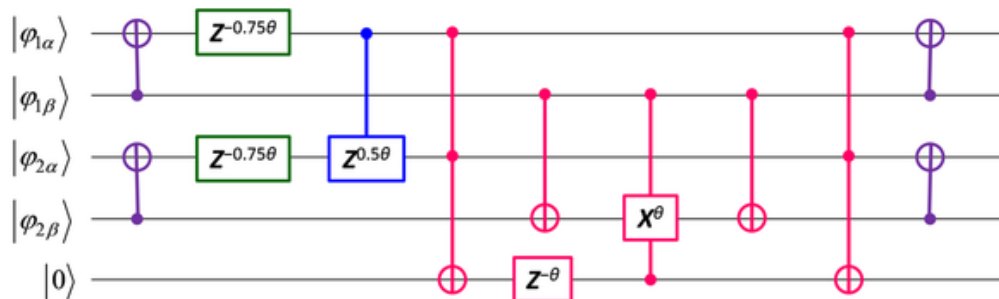
【研究内容】

共有結合解離で生成するジラジカルや単分子メモリデバイスなどへの応用が期待されている単分子磁石、酵素タンパク質の酵素活性を担う金属クラスターの多くは分子内に不対電子と呼ばれる電子対を作っていない電子を持ち、開殻分子と呼ばれます。不対電子は分子内で上向きスピン (a スピン) 状態、下向きスピン (b スピン) 状態という 2 種類の状態のどちらかをとります。分子内に複数の不対電子をもつ開殻分子では、不対電子間に量子力学的な相互作用が働くため、2 つの電子スピンの平行に並ぶか反平行に並ぶかによってエネルギーが変わります。2 つの電子スピンの平行に並ぶと分子は三重項状態 ($S = 1$) に、反平行に並ぶと一重項状態 ($S = 0$) にあるとして区別されます。この時の鍵となる物理量が、スピン量子数 S と呼ばれるものです。開殻分子ではエネルギーが最も低い状態である基底状態のエネルギー的近傍にスピン量子数の異なる電子状態が数多く存在しているため、基底状態のスピン量子数を決定することが非常に重要な課題となります。量子コンピュータを使うことで基底状態の

エネルギーを超高速に求めることができますが、求まった電子状態のスピン量子数を明らかにしなければ電子状態を解明したことにはなりません。しかし、量子コンピュータ上で任意の波動関数のスピン量子数を決定することができる量子アルゴリズムはこれまで報告されていませんでしたが、今回初めて発見されました。

量子コンピュータを用いた量子化学計算では、分子の電子状態を支配するハミルトニアンのもとで波動関数がどのように時間発展するかを量子コンピュータ上でシミュレートして、ハミルトニアンの固有値であるエネルギーを量子位相推定と呼ばれる手法で読み出します。同研究グループはこの量子位相推定アルゴリズムに着目し、ハミルトニアンの代わりに分子のスピン状態を特徴づける S^2 演算子という演算子のもとで波動関数がどのように時間発展するかを量子コンピュータ上でシミュレートすることで S^2 演算子の固有値を読み出し、スピン量子数 S を決定する新規手法を開発しました。同研究グループは、 S^2 演算子のもとでの波動関数の時間発展を量子コンピュータ上で効率的にシミュレートするために、波動関数の情報を量子コンピュータに保存するための新規手法として「一般化スピン座標マッピング法」と呼ばれる手法を提案しました。この手法は以前に同研究グループが、量子コンピュータを用いた開殻分子の full-CI 計算に適した近似波動関数を効率的に生成するために提案した「スピン座標マッピング法」(K. Sugisaki et al, J. Phys. Chem. A2016, 120, 6459-6466.)を一般化したもので、 S^2 演算子のようなスピン演算子を効率的にシミュレートすることができます。

一般化スピン座標マッピング法を用い、 S^2 演算子のもとでの波動関数の時間発展を計算する量子論理回路（量子サーキット）の例を図に示します。従来用いられてきたマッピング法で同様の量子論理回路を構築すると、必要な量子ゲートの数は 100 を超えるため、一般化スピン座標マッピング法を用いることで量子ゲートの数を 10 分の 1 程度に削減できることが明らかになりました。また、量子論理回路の数値シミュレーションから、非常に高い精度で波動関数の時間発展が計算でき、任意の波動関数のスピン量子数を決定できることが示されました。



図：一般化スピン座標マッピング法を用い、 S^2 演算子のもとでの波動関数の時間発展量子シミュレーションを実行するための量子論理回路の例。横線は量子ビットを、カラーで描かれた図形は量子ゲートを表す。

【今後の展開と応用について】

本研究により、分子内に複数の不対電子を持つ分子系について量子コンピュータを用いた量子化学計算を実行したとき、得られた電子状態がどのような電子スピン構造を持っているかを明らかにするための手法が初めて示されました。これにより、新規機能材料開発や化学反応機構解明など、量子コンピュータを実際の化学研究に応用するための道筋が示されました。

本研究で用いた S^2 演算子のもとでの波動関数の時間発展量子シミュレーションは、スピン量子数 S を決定することができるだけでなく、量子コンピュータによる開殻分子の量子化学計算の高速化や新規量子アルゴリズム構築へと応用できる可能性が示されており、今後の量子コンピューティング理論の発展、特に量子アルゴリズムの開発への大きな寄与が期待されます。

“量子コンピュータを化学研究に役立てるための鍵となる手法を開発！” 大阪市立大学.
<https://www.osaka-cu.ac.jp/ja/news/2019/190704>. (参照 2019-07-04)



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Quantum chemistry on quantum computers: quantum simulations of the time evolution of wave functions under the S^2 operator and determination of the spin quantum number S^\dagger

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Quantum computers have an enormous impact on quantum chemical calculations. Approaches to calculate the energies of atoms and molecules on quantum computers by utilizing quantum phase estimation (QPE) and the variational quantum eigensolver (VQE) have been well documented, and dozens of methodological improvements to decrease computational costs and to mitigate errors have been reported until recently. However, the possible methodological implementation of observables on quantum computers such as calculating the spin quantum numbers of arbitrary wave functions, which is a crucial issue in quantum chemistry, has been discussed less. Here, we propose a quantum circuit to simulate the time evolution of wave functions under an S^2 operator, $\exp(-iS^2t)|\Psi\rangle$, and integrate it into the QPE circuit enabling us to determine the spin quantum number of the arbitrary wave functions. We demonstrate that the spin quantum numbers of up to three spins can be determined by only one qubit measurement in QPE.

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1. Introduction

Quantum computing is the focus of current interest in modern society. Although currently available quantum computing devices are noisy and of intermediate scale, quantum computers consisting of more than 100 qubits are expected to appear soon. This reminds us that we are close to “quantum supremacy”,¹ in which quantum computing devices solve problems that are practically intractable for classical computers. Among the diverse topics in quantum computing, the electronic structure calculations of atoms and molecules are one of the most studied realms.^{2–28} Sophisticated quantum chemical calculations on quantum computers can bring a paradigm shift in chemistry and related fields such as nitrogen fixation processes, drug

designs, elucidation of catalytic mechanisms of enzymes, and so on.

The ideas to use computers built of quantum mechanical elements to simulate quantum mechanics were proposed by Feynman in the early 1980s.²⁹ An approach to calculate full-CI energy was proposed by Aspuru-Guzik and coworkers in 2005² by using quantum phase estimation (QPE).³⁰ In the QPE-based full-CI calculations, the time evolutions of the wave function $|\Psi\rangle$ using a Hamiltonian are simulated and an energy eigenvalue E is extracted as a phase ϕ , as given in eqn (1), using inverse quantum Fourier transformation.³¹

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

In 2014, a quantum–classical hybrid system known as a variational quantum eigensolver (VQE) was proposed to solve the unitary coupled cluster (UCC) ansatz.^{19,20} The VQE has attracted attention as the computation model in noisy intermediate-scale quantum (NISQ)³² devices, because coherence times required for the simulations are much lower than the QPE-based approaches.^{19–26}

Despite the rapid progress in the methodologies to calculate molecular energies on quantum computers, approaches to calculate physical quantities other than energies have been less documented. In fact, to our knowledge, there is no theoretical proposal to determine spin quantum numbers of arbitrary wave

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[†] Electronic supplementary information (ESI) available: Definitions of quantum gates, quantum circuit simulations for the time evolution of wave functions under the S^2 operator, and quantum circuit simulations for the quantum phase estimation to determine the S^2 eigenvalue. See DOI: 10.1039/c9cp02546d

[‡] Deceased on March 23, 2019.



functions on quantum computers. The determination of spin quantum numbers is an important task, especially for the study of open shell systems. Open shell molecules have many low-lying electronic states with different spin multiplicities and characterization of the spin properties of their electronic ground state is one of the most fundamental issues in quantum chemistry. Molecules and materials having open shell electronic structures play an important role in chemistry and related fields: molecules undergoing covalent bond cleavages, molecular magnets and molecular spin devices, transition metal complexes in active centers of enzymes, *etc.*, and thus the study of open shell electronic structures is crucial in current chemistry and condensed matter physics. The current computational quantum chemistry is based on many approximations and the calculations often fail to predict chemical properties for larger systems. For systems with few electrons/spins, the Lanczos methods or exact diagonalization technique for many body interactions can afford more accurate and reliable energies,³³ but the application of such an approach on classical computers is difficult for larger systems due to the exponential scaling of the computational time against the system size. Noticeably, molecular spin quantum technologies and quantum-assisted biomolecular or organic molecular modellings are the topics of ongoing interest in this field. For example, electron spin-mediated nuclear quantum simulations with switchable interaction were studied by using a vanadyl-based two-qubit system,³⁴ adiabatic quantum computations using molecular spins were implemented to execute prime factorization,³⁵ and three-electron spin qubits were exemplified to provide a realistic path forward to solid state quantum information processing.³⁶

Here, we propose a quantum circuit that allows us to efficiently simulate the time evolution of wave functions under the \mathbf{S}^2 operator to calculate the \mathbf{S}^2 eigenvalues of arbitrary wave functions by using QPE.

2. Theory

The spin quantum number S of wave functions can be determined using the eigenvalue of the \mathbf{S}^2 operator as defined in eqn (2)–(4).³⁷

$$\mathbf{S}^2|\Psi(S)\rangle = S(S+1)|\Psi(S)\rangle \quad (2)$$

$$\mathbf{S}^2 = \sum_p \mathbf{S}(p)^2 + \sum_{p \neq q} \mathbf{S}(p) \cdot \mathbf{S}(q) \quad (3)$$

$$\mathbf{S}(p) \cdot \mathbf{S}(q) = \mathbf{S}_Z(p)\mathbf{S}_Z(q) + \frac{1}{2}[\mathbf{S}_+(p)\mathbf{S}_-(q) + \mathbf{S}_-(p)\mathbf{S}_+(q)] \quad (4)$$

Here, the summation in eqn (3) runs over unpaired electrons. In the quantum chemical calculations on classical computers, equations to calculate the \mathbf{S}^2 expectation values for spin-unrestricted Hartree–Fock (UHF) and electron correlated wave functions have been reported.^{38,39} On the other hand, in the quantum chemical calculations on quantum computers, analogous to calculating full-CI energies using QPE, we can readout the \mathbf{S}^2 eigenvalue as the phase φ by applying QPE if we

can simulate the time evolution of wave functions under the \mathbf{S}^2 operator as given in eqn (5) on quantum computers.

$$\exp(-i\mathbf{S}^2 t)|\Psi\rangle = \exp[-i\{S(S+1)\}t]|\Psi\rangle = \exp(-i2\pi\varphi)|\Psi\rangle \quad (5)$$

It should be emphasized that the \mathbf{S}^2 operator can be used not only for the calculation of the spin quantum numbers, but also it is applicable to accelerating quantum simulations and to implementing new algorithms. For example, we can speed up adiabatic state preparations² of spin-singlet states by using the \mathbf{S}^2 operator as a penalty function, $H(t) = (1-t)H_{\text{HF}} + tH_{\text{full-CI}} + \mathbf{S}^2$ ($0 \leq t \leq 1$). The \mathbf{S}^2 operator shifts the energy eigenvalue for spin multiplet states depending on the spin quantum number, and therefore the Hamiltonian with the \mathbf{S}^2 operator has inherently larger energy gaps between singlet and spin-multiplet states. Importantly, the addition of the \mathbf{S}^2 operator does not change the structure of eigenfunctions because the \mathbf{S}^2 operator commutes with H . It should be noted that the idea to use the \mathbf{S}^2 operator as the cost function in the quantum simulations was proposed to avoid kinks in the computations of potential energy surfaces using the VQE.^{21,22} Spin annihilations based on the Löwdin projection operator⁴⁰ and adiabatic spin purifications by using a time-dependent Hamiltonian $H(t) = H + t\mathbf{S}^2$ are promising applications relevant to the \mathbf{S}^2 operator.

To simulate the time evolution in eqn (5) on quantum computers, we have to define the \mathbf{S}^2 operator in the second quantized form and transform it to strings of Pauli operators by using the Jordan–Wigner transformation (JWT) or other wave function mapping techniques.^{2,41–43} In JWT, each qubit represents the occupation number of a particular spin orbital: $|1\rangle$ if the spin orbital is occupied, otherwise $|0\rangle$. The first and second terms in eqn (4) can be rewritten as in eqn (6) and (7), respectively, by using creation (a^\dagger) and annihilation (a) operators.

$$\mathbf{S}_Z(p)\mathbf{S}_Z(q) = \frac{1}{4}(a_{pz}^\dagger a_{pz} a_{qz}^\dagger a_{qz} + a_{p\beta}^\dagger a_{p\beta} a_{q\beta}^\dagger a_{q\beta}) - \frac{1}{4}(a_{pz}^\dagger a_{pz} a_{q\beta}^\dagger a_{q\beta} + a_{p\beta}^\dagger a_{p\beta} a_{qz}^\dagger a_{qz}) \quad (6)$$

$$\frac{1}{2}[\mathbf{S}_+(p)\mathbf{S}_-(q) + \mathbf{S}_-(p)\mathbf{S}_+(q)] = \frac{1}{2}(a_{pz}^\dagger a_{p\beta} a_{q\beta}^\dagger a_{qz} + a_{p\beta}^\dagger a_{p\beta} a_{qz}^\dagger a_{qz}) \quad (7)$$

Therefore, $\mathbf{S}_Z(p)\mathbf{S}_Z(q)$ and $[\mathbf{S}_+(p)\mathbf{S}_-(q) + \mathbf{S}_-(p)\mathbf{S}_+(q)]$ terms are expressed as the product of number operators n_p ($n_p = a_p^\dagger a_p$) and two-electron excitation operators, respectively, in the second quantized form. By using the JWT and quantum circuit designs proposed by Whitfield and coworkers,⁵ the quantum circuits to simulate the time evolution in eqn (5) can be constructed. For the H_2 molecule with the minimal basis set (two molecular orbitals), the quantum circuit to simulate eqn (5) can be composed of 76 one-qubit and 54 two-qubit gates in the upper bound (72 one- and 48 two-qubit gates for the $[\mathbf{S}_+(p)\mathbf{S}_-(q) + \mathbf{S}_-(p)\mathbf{S}_+(q)]$ term, 4 one- and 2 two-qubit gates for the $\mathbf{S}(p)^2$ term, and 4 two-qubit gates for the $\mathbf{S}_Z(p)\mathbf{S}_Z(q)$ term), without



Trotter decompositions. For general molecules, the number of quantum gates scales to N_{MO}^2 , where N_{MO} is the number of molecular orbitals.

The reason why more than 100 quantum gates are required for the quantum simulations of $\exp(-i\mathbf{S}^2t)|\Psi\rangle$ in two molecular orbital systems is the fact that the $[\mathbf{S}_+(p)\mathbf{S}_-(q) + \mathbf{S}_-(p)\mathbf{S}_+(q)]$ term is expressed by two-electron excitation operators in the second quantized form. However, as discussed below, the number of required quantum gates can be drastically reduced by introducing a new wave function mapping method for the spin operators S .

In our previous publications, we introduced a spin coordinate mapping (SCM) to construct spin symmetry-adapted configuration state functions (CSFs) on quantum computers.^{15,16} In the SCM scheme, the qubit represents the spin degree of freedom of an unpaired electron in the singly occupied molecular orbital (SOMO), namely $|0\rangle$ for $|\alpha\rangle$ and $|1\rangle$ for $|\beta\rangle$. The SCM is convenient for the manipulations of spin degree of freedom, *e.g.*, the $[\mathbf{S}_-(p) + \mathbf{S}_+(p)]$ operation becomes a NOT operation, although it corresponds to one-electron excitations in JWT. However, the originally proposed SCM is available only for SOMOs, and here we extend the SCM for general occupations and propose generalized spin coordinate mapping (GSCM).

The correspondence between JWT and GSCM is given in Table 1. As discussed above, in the JWT, qubits store the occupation number of spin orbitals. In Table 1, the first and second qubits correspond to α and β spin orbitals, respectively. In the GSCM, the first qubit specifies whether the molecular orbital is singly occupied or not, and the second qubit represents the occupation number of the β spin orbital. It should be noted that the GSCM has a similarity to the Bravyi-Kitaev transformation (BKT) for wave function mapping in which information on both occupation and parity is stored non-locally.⁴¹ Interconversions between JWT and GSCM are achieved by applying controlled-NOT (CNOT) gates; applying a NOT operation to the first qubit if the second qubit is the $|1\rangle$ state.

To simulate $\exp(-i\mathbf{S}^2t)|\Psi\rangle$ on quantum computers using the GSCM, we rewrite the \mathbf{S}^2 operator using permutation operators \mathbf{P}_{pq} and number operators of unpaired electrons $n_p^{\text{spin}} = |n_{p\alpha} - n_{p\beta}|$, where $n_{p\alpha}$ and $n_{p\beta}$ are number operators acting on the α - and β -spin orbitals, respectively, of the p -th molecular orbital:³⁷

$$\mathbf{S}^2 = \sum_p^N \frac{3}{4} n_p^{\text{spin}} + \frac{1}{2} \sum_{p \neq q}^N \left(-\frac{1}{2} n_p^{\text{spin}} n_q^{\text{spin}} + \mathbf{P}_{pq} \right) \quad (8)$$

Table 1 Correspondence table of Jordan–Wigner transformation (JWT) and generalized spin coordination mapping (GSCM)

| Electron occupancy of molecular orbitals | JWT | GSCM |
|---------------------------------------------|--------------|--------------|
| Unoccupied | $ 00\rangle$ | $ 00\rangle$ |
| Singly occupied by spin- α electrons | $ 10\rangle$ | $ 10\rangle$ |
| Singly occupied by spin- β electrons | $ 01\rangle$ | $ 11\rangle$ |
| Doubly occupied | $ 11\rangle$ | $ 01\rangle$ |

Here, \mathbf{P}_{pq} interchanges spin coordinates of unpaired electrons in the p -th and q -th molecular orbitals, as in eqn (9).

$$\begin{aligned} \mathbf{P}_{pq} |\cdots \alpha_p \cdots \alpha_q \cdots\rangle &= |\cdots \alpha_p \cdots \alpha_q \cdots\rangle, \\ \mathbf{P}_{pq} |\cdots \beta_p \cdots \beta_q \cdots\rangle &= |\cdots \beta_p \cdots \beta_q \cdots\rangle, \\ \mathbf{P}_{pq} |\cdots \alpha_p \cdots \beta_q \cdots\rangle &= |\cdots \beta_p \cdots \alpha_q \cdots\rangle, \\ \mathbf{P}_{pq} |\cdots \beta_p \cdots \alpha_q \cdots\rangle &= |\cdots \alpha_p \cdots \beta_q \cdots\rangle. \end{aligned} \quad (9)$$

It is clear that n_p^{spin} can be simulated by the one-qubit operation in the GSCM, although it becomes two-qubit operations in the JWT. The time evolution operator arising from \mathbf{P}_{pq} operators, namely $\exp(-i\mathbf{P}_{pq}t)$, seems to be non-trivial at a glance, but it can be expanded as in eqn (10) by using the relationship $(\mathbf{P}_{pq})^2 = \mathbf{1}$ (identity operator).

$$\exp(-i\mathbf{P}_{pq}t) = \cos(t) - i\mathbf{P}_{pq} \sin(t) \quad (10)$$

A quantum circuit for the simulations of eqn (5) for two molecular orbital systems is illustrated in Fig. 1. Here, each horizontal line corresponds to the qubit and quantum gates depicted by circles and squares are used from left to right order. Definitions of quantum gates are given in the ESI.† The quantum circuit consists of five steps: (I) transformation of basis from the JWT to the GSCM, (II) time evolutions by the first term on the right hand side of eqn (8), (III) time evolutions by the first term in the parenthesis of eqn (8), (IV) time evolutions by \mathbf{P}_{pq} terms, and (V) back transformation of the basis from the GSCM to the JWT. Here, we introduced one ancillary qubit to simulate the \mathbf{P}_{pq} terms. Clearly, the number of quantum gates required for the simulations of $\exp(-i\mathbf{S}^2t)|\Psi\rangle$ is dramatically reduced by using the GSCM (3, 7, and 3 for one-, two-, and three-qubit operations, respectively). It should also be noted that Trotter decomposition is required only for the \mathbf{P}_{pq} terms, because $[n_p^{\text{spin}}, n_q^{\text{spin}}] = 0$ and $[n_p^{\text{spin}}, \mathbf{P}_{pq}] = 0$ but $[\mathbf{P}_{pq}, \mathbf{P}_{qr}] \neq 0$.

3. Results and discussion

The results of quantum circuit simulations of the time evolution $\exp(-i\mathbf{S}^2t)|\Psi\rangle$ for the two- and three-spin systems starting from $|\Psi\rangle = |\alpha\beta\rangle$ and $|\alpha\alpha\beta\rangle$ are depicted in Fig. 2 and 3, respectively, and several simulations starting from other initial

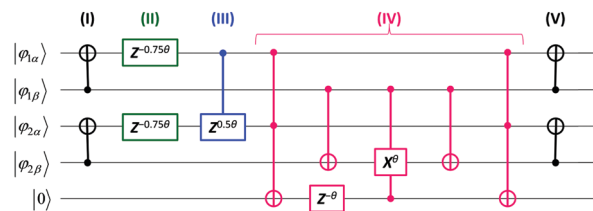


Fig. 1 A quantum circuit for the simulation of time evolution of the wave function under the \mathbf{S}^2 operator in two molecular orbital systems like the H_2 molecule in the minimal basis, using generalized spin coordinate mapping (GSCM). The circuit consists of five steps: (I) transformation of basis from JWT to GSCM, (II)–(IV) time evolutions caused by the \mathbf{S}^2 operators (see the text and eqn (8)), and (V) back transformation of the basis from GSCM to JWT. Rotation angle $\theta = t/\pi$, where t is the time to be evolved.



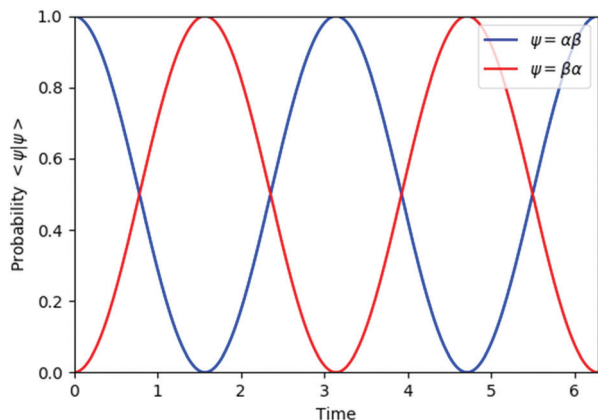


Fig. 2 Quantum circuit simulation results of the state probability of $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ after time evolution $\exp(-iS^2t)|\alpha\beta\rangle$.

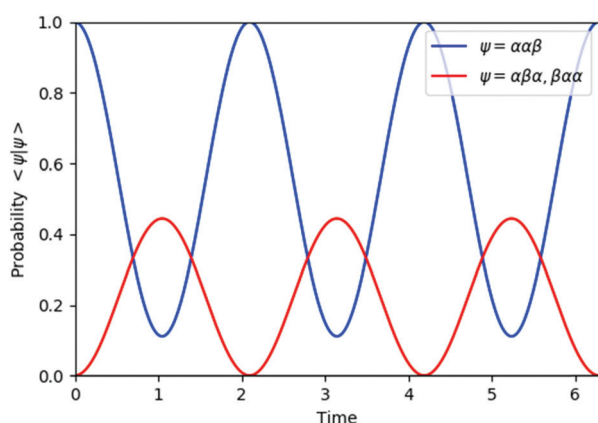


Fig. 3 Quantum circuit simulation results of the state probability of $|\alpha\alpha\beta\rangle$, $|\alpha\beta\alpha\rangle$, and $|\beta\alpha\alpha\rangle$ after time evolution $\exp(-iS^2t)|\alpha\alpha\beta\rangle$.

states are given in the ESI.† The simulation programs were developed by using OpenFermion⁴⁴ and Cirq⁴⁵ packages. The simulations were carried out with $t = 2\pi$ and 360 Trotter slices ($t = 2\pi/360$ for a single Trotter step) at the first order Trotterizations. The initial wave functions we used ($|\alpha\beta\rangle$ and $|\alpha\alpha\beta\rangle$) are not eigenfunctions of the S^2 operator but mixtures of two spin eigenfunctions, as given in eqn (11) and (12).

$$|\alpha\beta\rangle = \frac{1}{\sqrt{2}}\{|\Psi(S=1, M_S=0)\rangle + |\Psi(S=0, M_S=0)\rangle\} \quad (11)$$

$$|\alpha\alpha\beta\rangle = \frac{1}{\sqrt{3}}|\Psi(S=\frac{3}{2}, M_S=\frac{1}{2})\rangle + \frac{\sqrt{2}}{\sqrt{3}}|\Psi(S=\frac{1}{2}, M_S=\frac{1}{2})\rangle \quad (12)$$

The spin eigenfunctions with different spin quantum numbers evolve in a different manner, which causes interferences to lead state transformations from $|\alpha\beta\rangle$ to $|\beta\alpha\rangle$, and $|\alpha\alpha\beta\rangle$ to $|\alpha\beta\alpha\rangle$ and $|\beta\alpha\alpha\rangle$. The calculated overlaps between the wave functions obtained from the quantum circuit simulations and the wave functions under exact time evolutions are larger than 0.9999996 everywhere.

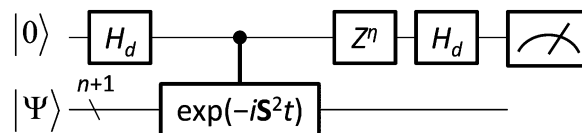


Fig. 4 A quantum circuit for one-qubit quantum phase estimation. For two- and three-electron systems, spin quantum numbers are calculated in a deterministic manner by setting $t = \pi/2$ and $\eta = 0$, and $t = \pi/3$ and $\eta = \pi/4$, respectively (see text for details).

By integrating the quantum circuit for $\exp(-iS^2t)|\Psi\rangle$ based on the GSCM into the QPE circuit, as illustrated in Fig. 4, we can determine the spin quantum number of the wave function $|\Psi\rangle$. For two-spin systems, the spin-triplet wave function evolves as $\exp(-iS^2t)|\Psi\rangle = \exp(-2it)|\Psi\rangle$ and therefore the measurement of the qubit for QPE always gives $|1\rangle$ after time evolution $t = \pi/2$, although the spin-singlet wave function does not evolve by S^2 operators and the measurement always gives $|0\rangle$, because the S^2 eigenvalue of spin-singlet states is 0. For three spin systems, the spin states $S = 3/2$ and $S = 1/2$ can be discriminated deterministically, by applying time evolution $\exp(-iS^2t)|\Psi\rangle$ with $t = \pi/3$ and following phase shift operation Z^η with $\eta = \pi/4$ to the qubit to be measured. Detailed discussions are given in the ESI.† For systems of more than three spins, measurements of two or more qubits are required to determine their spin quantum number, but estimations of the number of qubits and optimal time for evolutions are trivial, because the possible spin state is limited by the number of electrons and the eigenvalue of the S^2 operator is $S(S+1)$. The QPE simulation results for two-spin systems are given in Fig. 5. In the QPE simulations in Fig. 5 we gradually changed evolution time t from 0 to π , and plotted the probability to obtain the $|1\rangle$ state by using the spin-singlet wave function $|\Psi(S=0)\rangle = (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ and the spin-triplet wave function $|\Psi(S=1)\rangle = (|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$. The probability was calculated by repetitively performing the QPE quantum circuit simulations 10 000 times for each evolution time and counting how many times the $|1\rangle$ state was obtained. In the case of the spin-singlet state, the QPE always returns to the $|0\rangle$ state. By contrast, for the spin-triplet state, the probability to measure the $|1\rangle$ state depends on the evolution time, and after $\pi/2$ of time evolution, the probability becomes maximum as expected.

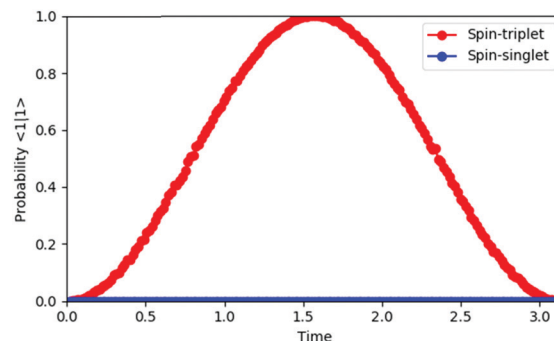


Fig. 5 Quantum circuit simulation results for the quantum phase estimation of two-electron systems.



We also performed quantum circuit simulations of QPE using a broken-symmetry wave function $|\Psi(\text{BS})\rangle = |\alpha\beta\rangle$ that corresponds to the 1 : 1 mixture of spin singlet and triplet wave functions (see eqn (11)). By running quantum circuit simulations 100 000 times for $t = \pi/2$, we obtained the $|1\rangle$ state 49 899 times, which is very close to the ideal probability 0.5. Similar results were obtained for the quantum circuit simulations of three-electron systems, as discussed in the ESI.†

4. Conclusions

In conclusion, we have developed a quantum circuit for the time evolution of wave functions under the S^2 operator, and we use it to determine the spin quantum number of wave functions by means of QPE, illustrating that the quantum circuit approach underlain by quantum algorithms affords extreme efficiency in evaluating observables, which is a seemingly intractable problem. By using the GSCM implemented for the manipulations of wave functions with spin operators, the number of quantum gates required for the simulation is drastically reduced compared with that using the JWT. The spin quantum number of wave functions can be determined from only one qubit readout in QPE for two- and three-spin systems. These results show that rapid computations of the spin quantum numbers S 's on quantum computers are possible, by applying the proposed quantum circuits. The approach developed here opens the door toward theoretical characterizations of the spin properties of open shell molecules in their electronic ground state, which is one of the most fundamental issues in open shell chemistry, by using quantum computers. Again, we emphasize that the S^2 operator can be used for more than just the calculations of the spin quantum number. Applications of the S^2 operator for other quantum chemical problems on quantum computers are underway and will be discussed in a forthcoming paper.

Conflicts of interest

There are no conflicts to declare.

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