

Quantum Algorithm for Full Configuration Interaction Calculations without Controlled Time Evolutions

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<p>Highlights</p>	<p>◇ 量子コンピュータを用いれば、精密な量子化学計算を分子サイズに対して従来のコンピュータよりも指数関数的に少ない計算ステップで実行できることが理論的に示されている。</p> <p>◇ 量子コンピュータでの精密量子化学計算手法である量子位相推定は、量子ゲートの並列処理がしにくい、隣り合わない2量子ビットにかかる量子ゲートが多いなどの問題を抱えている。</p> <p>◇ 先行開発した量子位相差推定アルゴリズムを応用し、従来法よりも量子コンピュータ実機に実装しやすい新規量子化学計算量子アルゴリズムを開発。</p>
<p>Description</p>	<p>【概要】</p> <p>研究チームは、原子・分子の全エネルギーを計算する新規量子アルゴリズムを開発しました。今回開発した量子アルゴリズムは従来法よりも量子ゲートの並列実行性に優れ、量子コンピュータ実機への実装が格段に容易になることが期待されます。</p> <p>【今後の展開と応用】</p> <p>今回開発した量子位相差推定による全エネルギー計算手法は量子ゲートの並列処理がしやすくなるだけでなく、物理的に隣り合わない2つの量子ビットに作用する2量子ビットゲートの数も劇的に減らすことができ、従来法よりも量子コンピュータ実機への実装が容易になります。将来、本手法が量子コンピュータによる精密量子化学計算の代名詞となるかもしれません。</p> <p>‘高精度量子化学計算の新技术！量子コンピュータで原子・分子の全エネルギーを計算する新しい手法を提案！’. 大阪市立大学.</p> <p>https://www.osaka-cu.ac.jp/ja/news/2021/211112-1 (参照 2021-11-12)</p>

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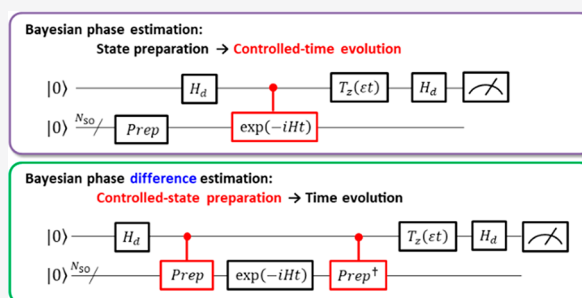


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Supporting Information

ABSTRACT: A quantum phase estimation algorithm allows us to perform full configuration interaction (full-CI) calculations on quantum computers with polynomial costs against the system size under study, but it requires quantum simulation of the time evolution of the wave function conditional on an ancillary qubit, which makes the algorithm implementation on real quantum devices difficult. Here, we discuss an application of the Bayesian phase difference estimation algorithm that is free from controlled time evolution operations to the full-CI calculations.



Accurately solving a Schrödinger equation is one of the ultimate goals in chemistry and physics, and it opens the way toward predictive quantum chemistry. It allows us not only to deeply understand nature but also to design new materials with novel functionalities from the first principle's point of view, bringing a paradigm shift in scientific research and development. The full configuration interaction (full-CI) method gives numerically the best possible wave function for the space spanned by a given basis set, providing us the benchmarking results to which other approximate approaches can refer from the methodological point of view, and it is a practical goal of quantum chemical calculations. However, the computational cost of full-CI calculations grows exponentially against the increase of the basis set and of the number of electrons relevant to the system size under study, and it can afford to deal with only small molecules;^{1,2} also it has been noted that putatively with the exception of strongly correlated systems and materials, there is no actual need to carry out full-CI calculations for chemical subjects of practical interest.

The appearance of quantum computers can change this scenario. As Feynman pointed out, quantum mechanical systems can be efficiently simulated by using a computer built of quantum mechanical elements that obey quantum mechanical laws.³ Indeed, Aspuru-Guzik and co-workers in 2005 proposed a quantum algorithm for full-CI calculations by utilizing a quantum phase estimation (QPE) algorithm,⁴ and proof-of-principle experiments of the full-CI/STO-3G of H_2 by using photonic⁵ and NMR⁶ quantum computers were reported in 2010. Although the quantum circuit for QPE-based full-CI calculations is so deep that only small molecules like H_2 and HeH^+ can be handled by the noisy intermediate-scale quantum devices currently available,^{5–8} it is believed to be a powerful tool when fault-tolerant quantum computing is realized,

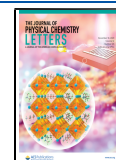
because an exponential speedup against classical algorithms is guaranteed.

Various theoretical attempts to improve the QPE-based methods have been reported so far, for example, improvement of computational space and Toffoli gate complexities using qubitization,^{9–11} truncated Taylor series,^{12,13} linear combination of unitary¹⁴ and tensor hypercontraction,¹⁵ quantum circuit optimizations,¹⁶ construction of approximated wave functions beyond Hartree–Fock (HF) level,^{17–19} and so on. Here, we focus on the modification of the QPE algorithm itself. In the QPE-based methods, time evolution of a wave function is simulated conditionally on an ancillary qubit, and the phase shift caused by the time evolution is read out by inverse quantum Fourier transformation^{20–22} or Bayesian inference.^{23,24} The controlled time evolution simulation requires many controlled R_z gates, whose fidelity is often lower than the single qubit R_z gates used for unconditional time evolutions. The presence of many controlled R_z gates also hinders parallel execution of quantum gates and compression of quantum circuits. Here, we take advantage of the Bayesian phase difference estimation (BPDE), recently proposed by us,²⁵ to perform full-CI calculations without controlled time evolution operations. The BPDE algorithm allows us to directly compute the energy difference of two electronic states by conditional preparation of the quantum superposition of the two electronic states and following an unconditional time evolution. In

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applying the BPDE algorithm to full-CI calculations, we construct the quantum superposition of vacuum and target electronic states. In other words, we compute the full-CI energy of an N -electron system as the N -electron ionization energy. To execute quantum chemical calculations on quantum computers, Fermionic wave functions should be mapped onto qubits by utilizing Fermion–qubit transformation techniques such as Jordan–Wigner transformation (JWT),⁴ Bravyi–Kitaev transformation (BKT),²⁶ and parity basis (PB).²⁶ Importantly, if the JWT, BKT, or PB is adopted for the transformation, the quantum state initialized to the $|00\dots0\rangle$ corresponds to the vacuum state having no electron. Note that the time evolution of the vacuum state under an electronic Hamiltonian causes no effects including that on the phase shift.

The quantum circuits for the full-CI calculations with Bayesian phase estimation (BPE)²³ and BPDE²⁵ are illustrated in Figure 1a,b, respectively. The definition of quantum gates is

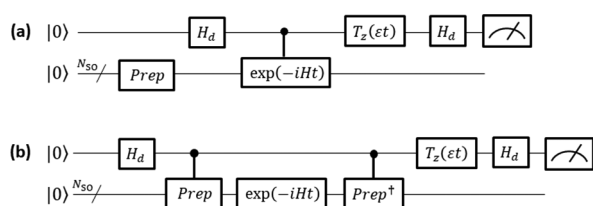


Figure 1. Quantum circuits for the full-CI calculations using (a) Bayesian phase estimation and (b) Bayesian phase difference estimation algorithms.

given in Supporting Information. The *Prep* gate in Figure 1 generates an approximated wave function of the target electronic state defined in eq 1 from the quantum state initialized to the $|00\dots0\rangle$. The probability to obtain the $|0\rangle$ state in the measurement of the first qubit, $P(0)$, is calculated as in eq 2.

$$|\Phi\rangle = \sum_j c_j |\Psi_j\rangle \quad (1)$$

$$P(0) = [1 + \sum_j |c_j|^2 \cos\{(E_j - \varepsilon)t\}]/2 \quad (2)$$

Here, $|\Psi_j\rangle$ represents the j th eigenfunction of the Hamiltonian, and c_j is the corresponding expansion coefficient. In an ideal case, if $|\Phi\rangle$ is the p th eigenfunction of the Hamiltonian, the probability $P(0)$ becomes maximum when $\varepsilon = E_p$. Even if $|\Phi\rangle$ is described by a linear combination of many eigenfunctions, $P(0)$ has the upward peak at $\varepsilon \approx E_p$, as long as the expansion coefficient of the target electronic state, c_p , is sufficiently large. In BPE, the phase rotation angle ε is optimized by Bayesian inference to maximize $P(0)$. The controlled time evolution is used to extract the phase difference between the wave functions before and after the time evolution.

By contrast, in the BPDE-based implementation given in Figure 1b, the controlled operations appear in the state preparation and inverse state preparation, instead of the time evolution. Again, $P(0)$ is calculated as in eq 2, and thus the full-CI energy can be obtained by optimizing the phase rotation angle ε giving maximum $P(0)$. The BPDE-based implementation is more preferable than the conventional BPE if the quantum circuit for the *Prep* gate is shallower than that for the time evolution operation.

The *Prep* gate should have the ability to prepare the wave function having sufficiently large overlap with the target electronic state. For typical closed shell singlet molecules around their equilibrium geometry, the HF wave function, $|\Psi_{\text{HF}}\rangle$, is generally a good approximation of the ground state wave function. In the JWT, $|\Psi_{\text{HF}}\rangle$ can be prepared by N_e Pauli- X gates, where N_e is the number of electrons. One can also prepare a spin symmetry-adapted configuration state function (CSF)^{17,18} or a multiconfigurational wave function¹⁹ with shallow quantum circuits. The quantum circuit for the *Prep* gate is usually very short, and thus the number of two-qubit gates can be drastically reduced by adopting the BPDE-based approach.

To demonstrate the efficiency of the BPDE-based full-CI calculations, we developed a numerical quantum circuit simulation program using Python with OpenFermion²⁷ and Cirq²⁸ libraries. Detailed computational conditions are given in Supporting Information.

We focused on the potential energy curves of four valence electronic states (S_0 , S_1 , S_2 , and T_1) of the H_2 molecule with the 6-31G basis set. The wave functions of these electronic states can be well approximated by using eqs 3–6.

$$|\Phi(S_0)\rangle = \sqrt{1-y/2}|2000\rangle - \sqrt{y/2}|0200\rangle \quad (3)$$

$$|\Phi(S_1)\rangle = (\alpha\beta 00) - |\beta\alpha 00\rangle/\sqrt{2} \quad (4)$$

$$|\Phi(S_2)\rangle = \sqrt{y/2}|2000\rangle + \sqrt{1-y/2}|0200\rangle \quad (5)$$

$$|\Phi(T_1)\rangle = |\alpha\alpha 00\rangle \quad (6)$$

Here, 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 molecular orbitals, respectively. y in eqs 3 and 5 is a diradical character, which denotes a measure of the open shell electronic configuration.^{19,29,30} It can be calculated from the occupation number of the lowest unoccupied natural orbital (n_{LUNO}) constructed from the spin-projected broken-symmetry (BS)-UHF wave functions, using eq 7.²⁹

$$y = 1 - \frac{2(1 - n_{\text{LUNO}})}{1 + (1 - n_{\text{LUNO}})^2} \quad (7)$$

The quantum circuits of the controlled *Prep* gates are illustrated in Figure 2. The rotational angle θ in Figure 2a should be $-2 \arccos(\sqrt{1-y/2})$ and $2 \arccos(\sqrt{y/2})$ for the S_0 and S_2 states, respectively. The results of the BPDE quantum circuit simulations are plotted in Figure 3a, and the deviations from the full-CI energy are given in Figure 3b–e. All the BPDE simulations converged after 4–5 Bayesian optimization cycles, and the length of total evolution time is about 180–280 atomic units. The numerical simulations revealed that BPDE reproduces the full-CI energy within 3 kcal mol⁻¹ of errors with ca. 0.05 kcal mol⁻¹ of standard deviations. However, the plots in Figure 3b–e indicate the presence of somewhat systematic errors. The deviations mainly originate from Trotter decomposition errors, and they can be reduced by adopting shorter time length for the single Trotter slice. Current simulations use the time for a single Trotter slice $t/N = 0.5$ atomic unit. By adopting five times finer Trotter decomposition, the $\Delta E(\text{BPDE} - \text{full-CI})$ values become less than 0.2 kcal mol⁻¹ for all the states and geometries (see Figure S7 in Supporting Information). Note that the computational cost is inversely proportional to the Trotter time steps t/N . We also

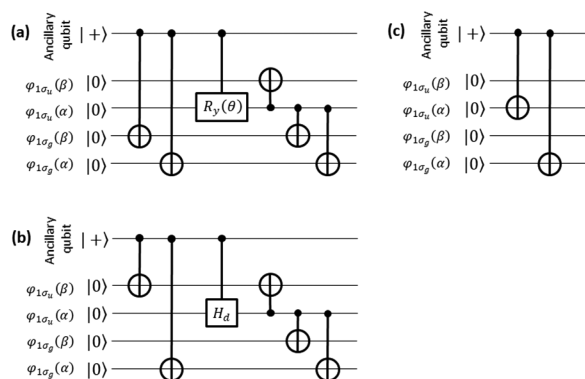


Figure 2. Quantum circuits of the controlled-*Prep* gates used for the full-CI calculations of the (a) S_0 and S_2 , (b) S_1 , and (c) T_1 states. The rotational angle θ is $-2 \arccos(\sqrt{1 - y/2})$ and $2 \arccos(\sqrt{y/2})$ for the S_0 and S_2 states, respectively. Qubits storing the occupation number of $\varphi_{2\sigma_g}$ and $\varphi_{2\sigma_u}$ orbitals are omitted for clarity.

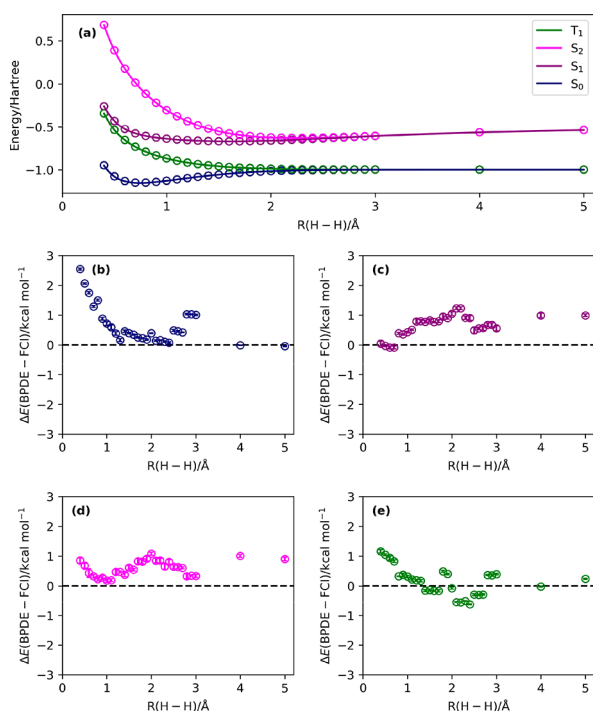


Figure 3. Numerical quantum circuit simulation results of the potential energy curves of the H_2 molecule. (a) Total energies. Solid lines denote the full-CI energies, and open circles represent the BPDE results. (b–e) Energy deviations from the full-CI values in the (b) S_0 , (c) S_1 , (d) S_2 , and (e) T_1 states. Error bars denote the standard deviations.

examined noisy quantum circuit simulations of the S_0 state of the H_2 molecule with Pauli error channels. The noisy quantum circuit simulations gave larger standard deviations (0.15 kcal mol⁻¹ on average), but the ΔE values are almost the same between the noiseless and noisy simulations (Figure S8 in Supporting Information), exemplifying the robustness of the BPDE algorithm.

Note that the number of Bayesian optimization cycles depends on the total energy and thus the system size, although it becomes less dependent on the system size for the direct calculation of energy gaps using the BPDE algorithm.²⁵ Therefore, the two-step approach to calculate the total energy

of the electronic ground state using the BPDE-based method described here and subsequently perform the direct calculation of the excitation energies with the BPDE algorithm can be more preferable to obtain the potential energy curves of excited states from the viewpoint of computational cost reduction.

We also applied the BPDE-based method to the energy diagram of the *cis*–*trans*–*iso* isomerization reaction of the diazene (N_2H_2) molecule at the CAS-CI(10e,8o)/6-311G-(d,p) level. The two major reaction pathways of the *cis*–*trans* isomerization, namely, in-plane inversion and out-of-plane torsion, have been well investigated.^{31–34} Sophisticated quantum chemical calculations predicted that the transition state of the in-plane inversion (TS1 in Figure 4) has slightly

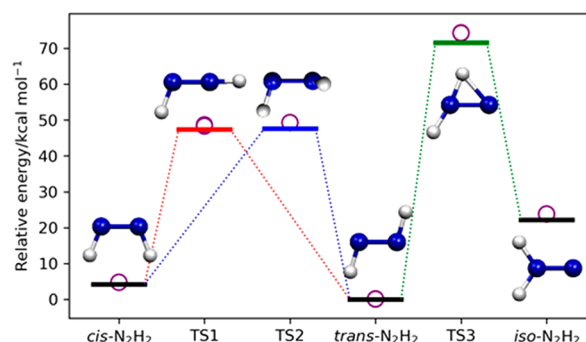


Figure 4. Potential energy profiles of the *cis*–*trans*–*iso* isomerization reaction of diazene, N_2H_2 . Solid lines denote the CAS-CI energies, and purple circles represent the numerical simulation results.

lower energy than that of the out-of-plane torsion (TS2).^{32–34} From the viewpoint of transition energies, the two reaction pathways are competitive or the in-plane inversion is slightly favorable, but classical trajectory simulations revealed that the in-plane inversion is forbidden because of a centrifugal barrier, and the out-of-plane torsion is only the pathway of the isomerization reaction.^{34–36} Potential energy curves of these two reaction pathways were investigated at the HF level using variational quantum eigensolver (VQE)³⁷ with a superconducting quantum processor.³⁸ However, it should be emphasized that in TS2 the $N=N$ π bond is broken and it exhibits a strong diradical character. The wave function of the lowest electronic state of TS2 cannot be well approximated at the HF level, and the post-HF calculation is essential to describe its electronic structure correctly. Numerical VQE simulations for low-lying electronic states and transition amplitudes in the *cis*–*trans* isomerization reaction pathway were also reported.³⁹

The diradical character y 's were calculated to be 0.0233, 0.0373, 0.9950, and 0.1665 for *iso*- N_2H_2 , TS1, TS2, and TS3, respectively. The BS-UHF calculations converged to the closed shell RHF state in the *cis*- and *trans*-isomers. In the simulations for the *cis*-, *trans*-, and *iso*-species, we used the controlled *Prep* gate that generates the RHF wave function. For the calculations of TS1, TS2, and TS3, we applied a quantum circuit similar to that in Figure 2a with $\theta = -2 \arccos(\sqrt{1 - y/2})$ to prepare the two-configurational wave function. The results of the numerical simulations and the CAS-CI energies are plotted in Figure 4. The Bayesian optimization converged after 16 or 17 iterations. The energy differences between the BPDE simulations and the CAS-CI are

0.536, 0.124, 1.588, 1.058, 1.703, and 2.680 kcal mol⁻¹ for *cis*-N₂H₂, *trans*-N₂H₂, *iso*-N₂H₂, TS1, TS2, and TS3, respectively, and the standard deviation is 0.05 kcal mol⁻¹ on average. If we used the finer Trotter time steps, $t/N = 0.1$ atomic unit, the $\Delta E(\text{BPDE} - \text{full-CI})$ became 0.187, 0.013, 0.093, 0.160, 0.118, and 1.983 kcal mol⁻¹ for *cis*-N₂H₂, *trans*-N₂H₂, *iso*-N₂H₂, TS1, TS2, and TS3, respectively. Only TS3 exhibits a large error in the simulations with the finer Trotter decompositions. This trend can be explained by the quality of the approximated wave function $|\Phi\rangle$. The square overlaps $|\langle\Phi|\Psi_{\text{CAS-CI}}\rangle|^2$ were calculated to be 0.9466, 0.9499, 0.9655, 0.9435, 0.9796, and 0.8753 for *cis*-N₂H₂, *trans*-N₂H₂, *iso*-N₂H₂, TS1, TS2, and TS3, respectively. In TS3, contributions from electronic states other than the target state are not negligible, which shifts the ε value giving maximum $P(0)$ in eq 2 from the value of E_0 . Replacing the controlled *Prep* gate by more sophisticated wave function preparation techniques such as adiabatic state preparation (ASP)^{6,40} is necessary to acquire the energy of TS3 accurately. For such applications, the ASP should start from the quantum superposition of the vacuum state and the eigenfunction of a starting Hamiltonian as in eq 8 and execute normal (unconditioned) ASP.

$$|\Phi_{\text{ASP},\text{ini}}\rangle = \frac{1}{\sqrt{2}}(|0\rangle \otimes |\text{vac}\rangle + |1\rangle \otimes |\Psi_{0,\text{ini}}\rangle) \quad (8)$$

In summary, we have examined a new quantum algorithm for full-CI calculations based on the BPDE algorithm. The proposed quantum algorithm is free from controlled-time evolution, making parallelization of quantum gates and implementation on real quantum devices easier. The proposed algorithm is easily connectable to ASP. Our algorithm could pave the way for more practical full-CI calculations on fault-tolerant quantum computers.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c03214>.

Definitions of quantum gates, computational conditions for quantum chemical calculations and numerical quantum circuit simulations, Trotter decomposition error analysis, and quantum circuit simulations with Pauli error channels (PDF)

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Notes

The authors declare no competing financial interest.

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