

Quantum Chemistry on Quantum Computers

#3 Quantum Phase Estimation

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Quantum phase estimation

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Quantum Algorithm Providing Exponential Speed Increase for Finding Eigenvalues and Eigenvectors

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(Received 27 July 1998)

We describe a new polynomial time quantum algorithm that uses the quantum fast Fourier transform to find eigenvalues and eigenvectors of a local Hamiltonian, and that can be applied in cases (commonly found in *ab initio* physics and chemistry problems) for which all known classical algorithms require exponential time. Applications of the algorithm to specific problems are considered, and we find that classically intractable and interesting problems from atomic physics may be solved with between 50 and 100 quantum bits.

PACS numbers: 03.67.Lx, 31.15.Ar

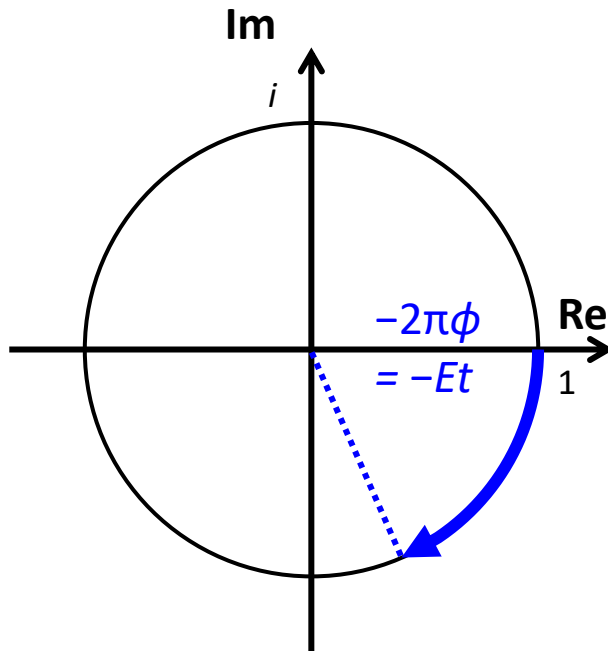
Basic idea of QPE for quantum chemistry

$$\underline{\exp(-iHt)}|\Psi\rangle = \underline{\exp(-iEt)}|\Psi\rangle = \underline{\exp(-i2\pi\phi)}|\Psi\rangle$$

Time evolution of
wave function



Phase shift depending on energy



$$Et = 2\pi\phi$$

By determining the phase shift caused by the time evolution, we can extract the energy eigenvalue of the system!

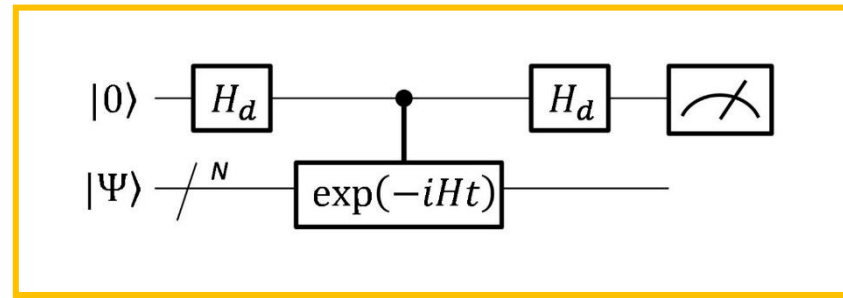
Basic idea of QPE for quantum chemistry

Quantum Fourier transformation (QFT)

$$\begin{aligned} U|j\rangle &= \frac{1}{\sqrt{2^n}} \sum_{k=0}^{2^n-1} e^{2\pi i j k / 2^n} |k\rangle \\ &= \frac{1}{\sqrt{2^n}} (|0\rangle + e^{2\pi i 0 \cdot j_n} |1\rangle) (|0\rangle + e^{2\pi i 0 \cdot j_{n-1} j_n} |1\rangle) \cdots (|0\rangle + e^{2\pi i 0 \cdot j_1 j_2 \cdots j_n} |1\rangle) \end{aligned}$$

- 1) Generate the quantum state corresponding to r.h.s. of equation
- 2) Apply **inverse QFT** to obtain the quantum state in l.h.s. of equation
- 3) Measure the quantum state to obtain j

One-qubit QPE



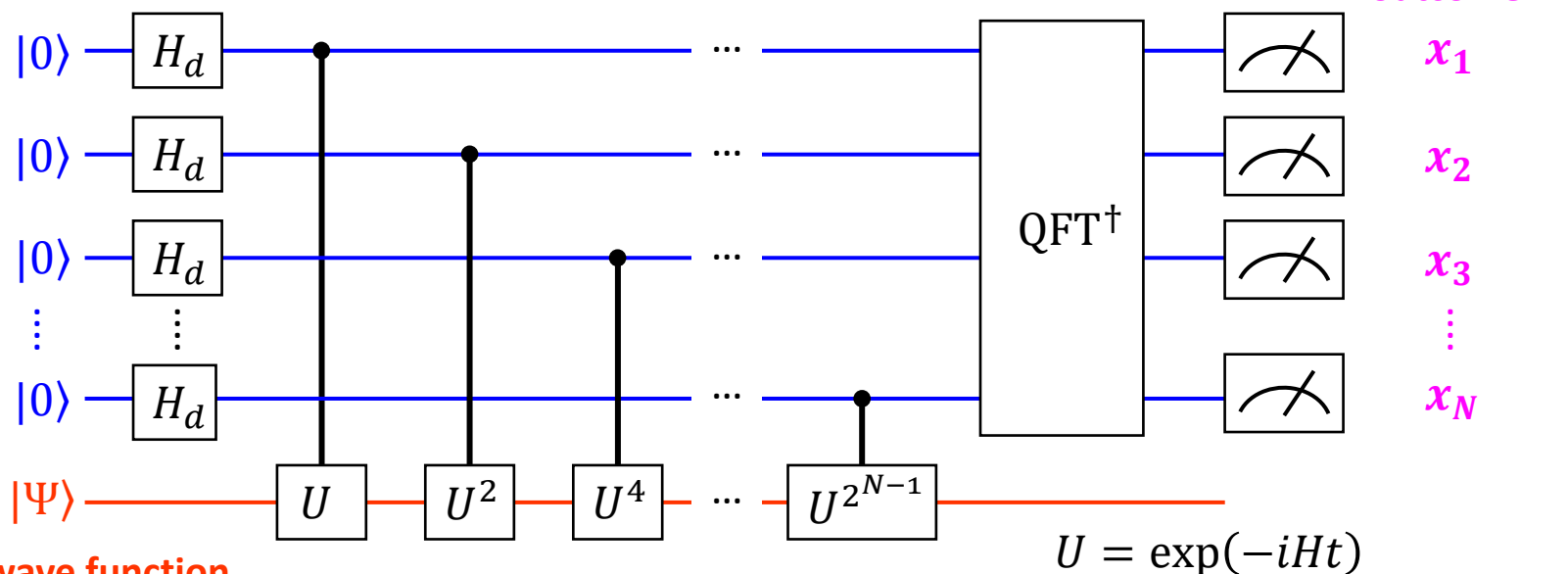
$$e^{-iHt}|\Psi\rangle = e^{-iEt}|\Psi\rangle$$

$$\begin{aligned} |0\rangle \otimes |\Psi\rangle &\xrightarrow{H \otimes I} \frac{1}{\sqrt{2}} (|0\rangle + |1\rangle) \otimes |\Psi\rangle \\ &\xrightarrow{c-U} \frac{1}{\sqrt{2}} (|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes e^{-iHt}|\Psi\rangle) = \frac{1}{\sqrt{2}} (|0\rangle + e^{-iEt}|1\rangle) \otimes |\Psi\rangle \\ &\xrightarrow{H \otimes I} \left(\frac{1 + e^{-iEt}}{2} |0\rangle + \frac{1 - e^{-iEt}}{2} |1\rangle \right) \otimes |\Psi\rangle \\ &= \left(\frac{1 + e^{-i2\pi\phi}}{2} |0\rangle + \frac{1 - e^{-i2\pi\phi}}{2} |1\rangle \right) \otimes |\Psi\rangle \end{aligned}$$

$\phi = 0.0$ in binary	\longrightarrow	$e^{-i2\pi\phi} = e^0 = 1$	$\xrightarrow{\text{Quantum state before measurement}}$	$ 0\rangle \otimes \Psi\rangle$
$\phi = 0.1$ in binary	\longrightarrow	$e^{-i2\pi\phi} = e^{-i\pi} = -1$	\longrightarrow	$ 1\rangle \otimes \Psi\rangle$

N-qubit QPE

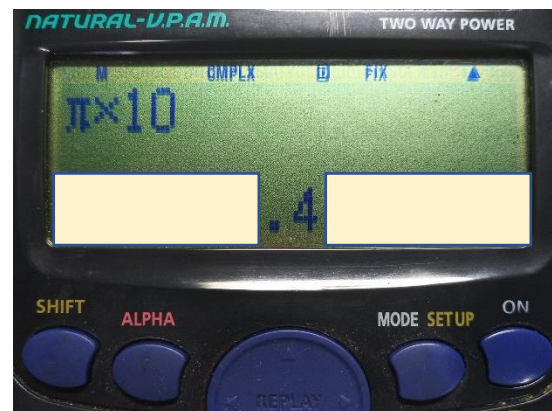
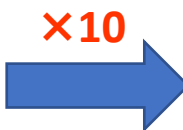
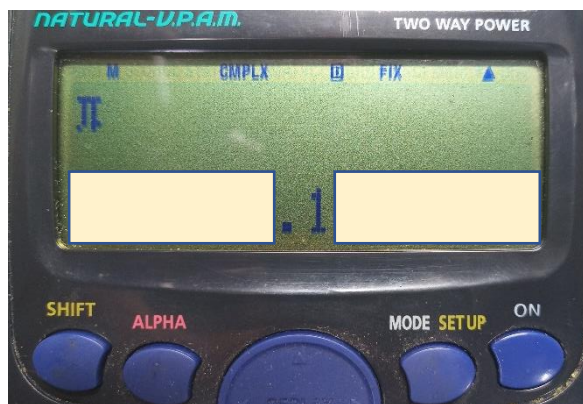
N-qubits for energy readout



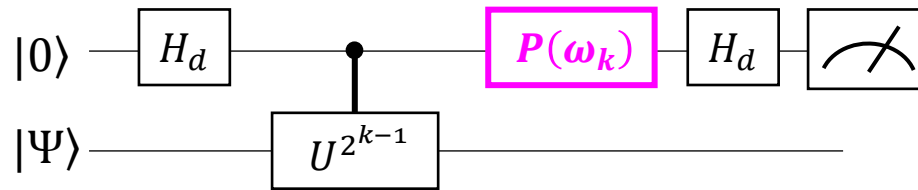
Qubits for wave function storage

$$Et = 2\pi\phi$$

$$\phi = 0.x_1x_2x_3 \cdots x_N$$

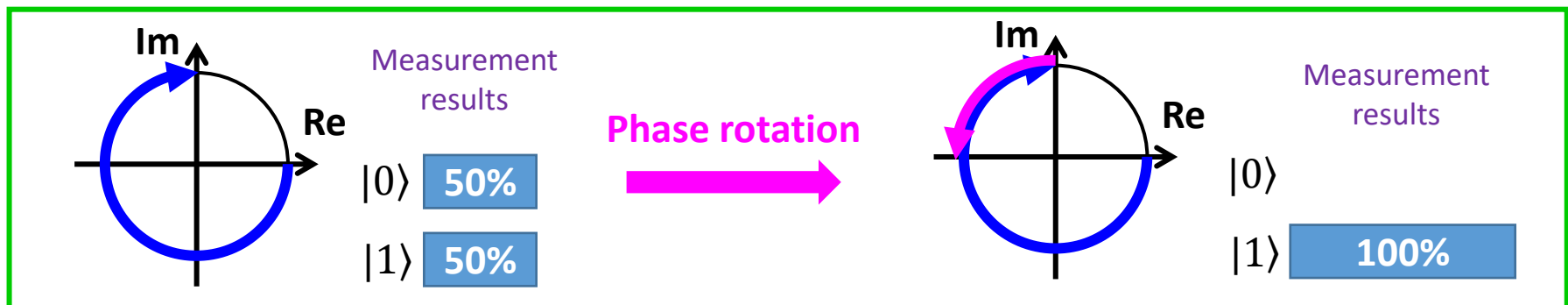


Iterative QPE

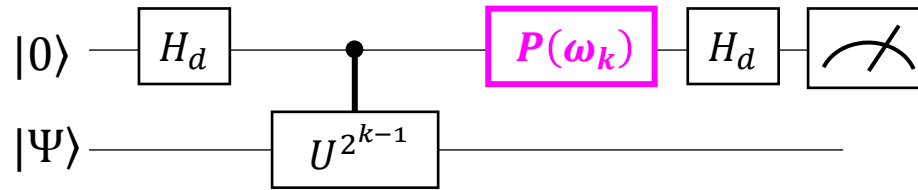


$$P(\theta) = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{pmatrix}$$

- I. Evaluate the least important digit (e.g., 10th digit of fraction binary) with $\omega_{10} = 0$
- II. Evaluate the next least important digit (e.g., 9th) with
 - $\omega_9 = 0$ if the 10th digit of fraction binary is 0
 - $\omega_9 = \pi/2$ if the 10th digit of fraction binary is 1
- III. Evaluate the next least important digit (e.g., 8th) with
 - $\omega_8 = 0$ if the 9th and 10th digits of fraction binary are 00
 - $\omega_8 = \pi/4$ if the 9th and 10th digits of fraction binary are 01
 - $\omega_8 = \pi/2$ if the 9th and 10th digits of fraction binary are 10
 - $\omega_8 = 3\pi/4$ if the 9th and 10th digits of fraction binary are 11
 and so on.



Iterative QPE



$$P(\theta) = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{pmatrix}$$

$$U|\Psi\rangle = e^{-2\pi i\phi}|\Psi\rangle \quad \phi = 0.10\textcolor{red}{1} \text{ in binary (5/8 in decimal)}$$

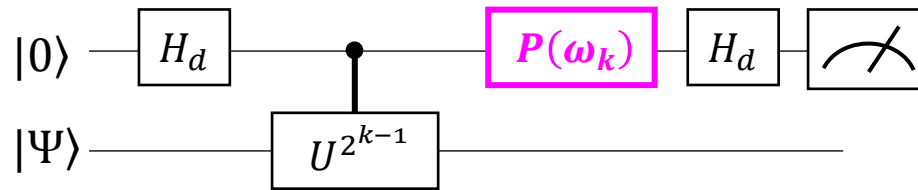
1) Perform IQPE circuit with $k = 3$ and $\omega_k = 0$

$$\begin{aligned} |0\rangle \otimes |\Psi\rangle &\xrightarrow{H \otimes I} \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \otimes |\Psi\rangle \\ &\xrightarrow{c-U^4} \frac{1}{\sqrt{2}}(|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes e^{-8\pi i \cdot (\frac{5}{8})}|\Psi\rangle) = \frac{1}{\sqrt{2}}(|0\rangle \otimes |\Psi\rangle - |1\rangle \otimes |\Psi\rangle) \\ &\xrightarrow{H \otimes I} |1\rangle \otimes |\Psi\rangle \end{aligned}$$

2) Perform IQPE circuit with $k = 2$ and $\omega_k = \pi/2$

$$\begin{aligned} |0\rangle \otimes |\Psi\rangle &\xrightarrow{H \otimes I} \xrightarrow{c-U^2} \frac{1}{\sqrt{2}}(|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes e^{-4\pi i \cdot (\frac{5}{8})}|\Psi\rangle) \\ &\xrightarrow{\textcolor{violet}{P}(\pi/2)} \frac{1}{\sqrt{2}}(|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes e^{-\frac{5\pi i}{2} + \frac{\textcolor{violet}{\pi}i}{2}}|\Psi\rangle) = \frac{1}{\sqrt{2}}(|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes |\Psi\rangle) \\ &\xrightarrow{H \otimes I} |0\rangle \otimes |\Psi\rangle \end{aligned}$$

Iterative QPE



$$P(\theta) = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{pmatrix}$$

$$U|\Psi\rangle = e^{-2\pi i\phi}|\Psi\rangle \quad \phi = 0.101 \text{ in binary (5/8 in decimal)}$$

3) Perform IQPE circuit with $k = 1$ and $\omega_k = \pi/4$

$$\begin{aligned} |0\rangle \otimes |\Psi\rangle &\xrightarrow{H \otimes I} \xrightarrow{C-U} \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes e^{-2\pi i \cdot (\frac{5}{8})} |\Psi\rangle \right) \\ &\xrightarrow{P(\pi/4)} \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |\Psi\rangle + |1\rangle \otimes e^{-\frac{5\pi i}{4} + \frac{\pi i}{4}} |\Psi\rangle \right) = \frac{1}{\sqrt{2}} (|0\rangle \otimes |\Psi\rangle - |1\rangle \otimes |\Psi\rangle) \\ &\xrightarrow{H \otimes I} |1\rangle \otimes |\Psi\rangle \end{aligned}$$

[Measurement results]

Step 1 ... 1

Step 2 ... 0

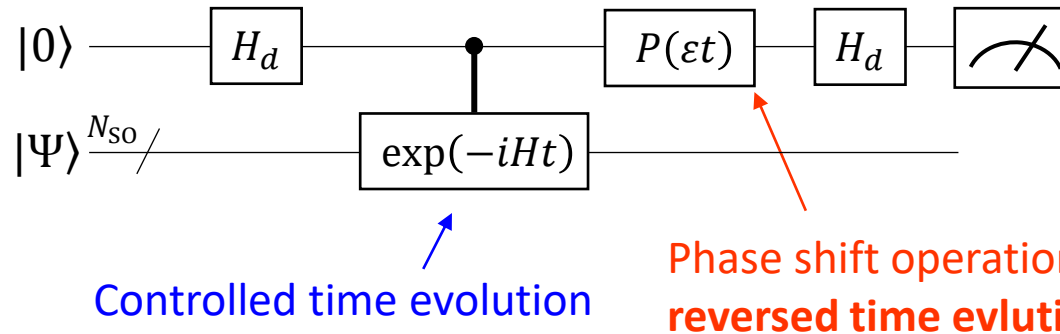
Step 3 ... 1



[Eigenphase]

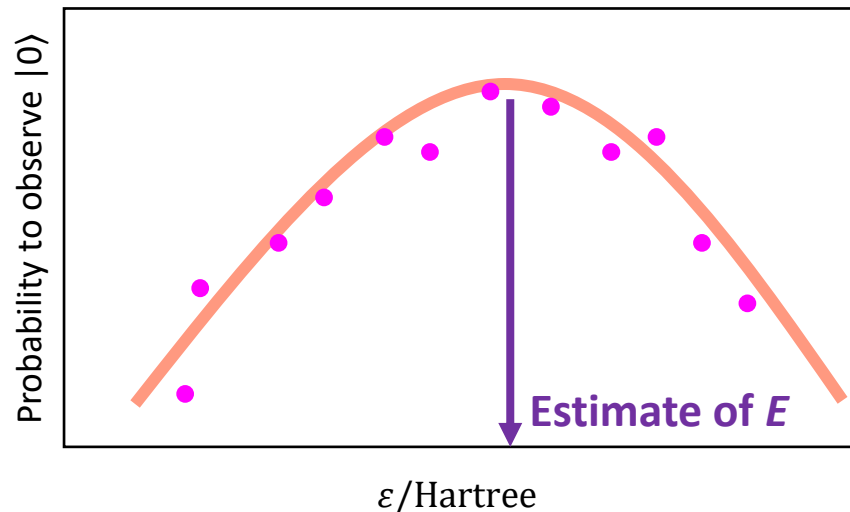
$$\phi = 0.101$$

Bayesian QPE



$$P(\theta) = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{pmatrix}$$

Probability to observe the $|0\rangle$ state: $P(0) = \frac{1 + \cos\{(E - \varepsilon)t\}}{2} \rightarrow P(0) = 1$ if $E = \varepsilon$



N. Wiebe, C. Granade, *Phys. Rev. Lett.* **2016**, 117, 010503.

S. Paesani, et al., *Phys. Rev. Lett.* **2017**, 118, 100503.

Relationship between evolution time and energy precision

$$Et = 2\pi\phi$$

$$t = 1 \rightarrow E = 2\pi\phi$$

N -qubit QPE \rightarrow We can determine the eigenphase with an accuracy $1/2^N$

Number of ancillary qubits	Evolution time t	Energy precision/Hartree
1	1	π
N	1	$\pi/2^{N-1}$
1	2^{N-1}	$\pi/2^{N-1}$

To achieve chemical precision (energy error less than 1 kcal/mol), we need

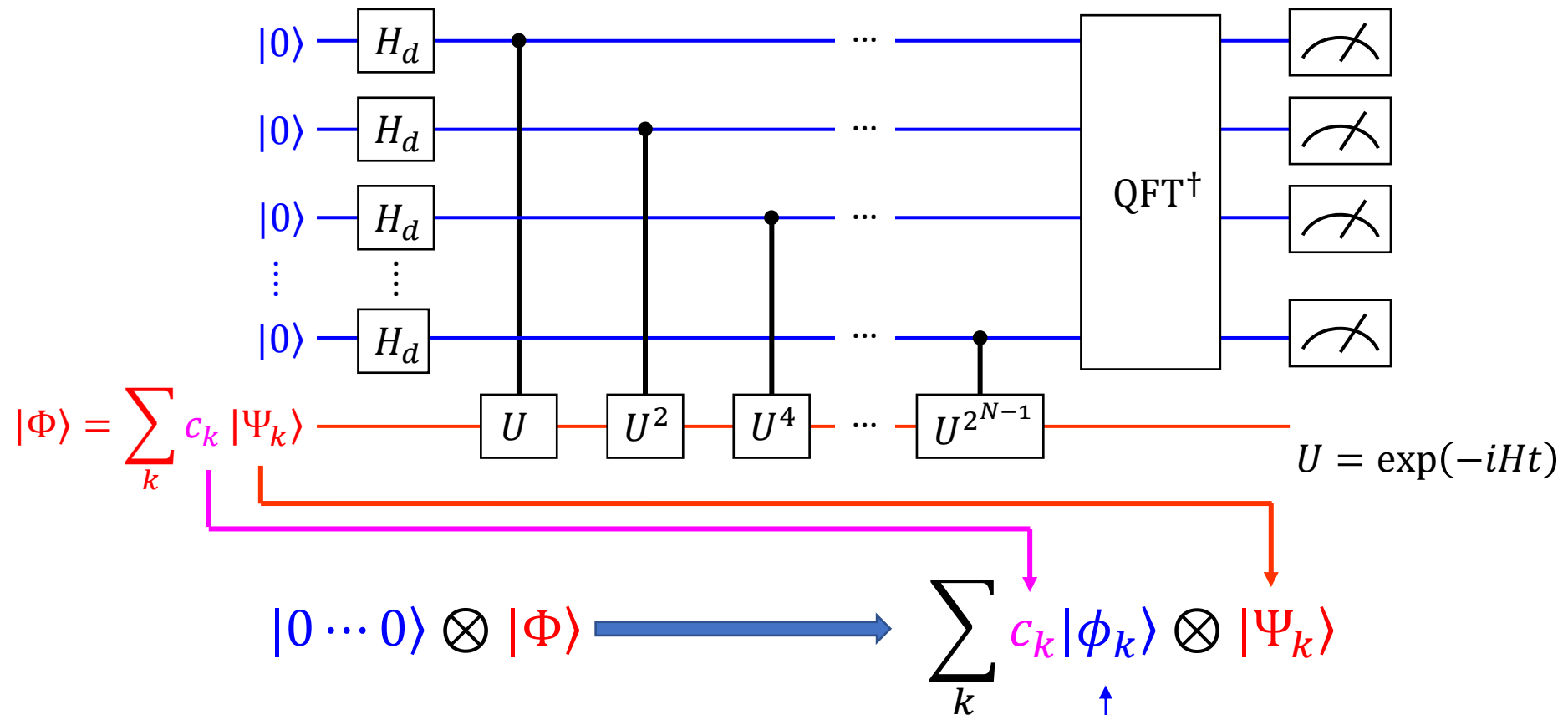
12-qubit QPE with $t = 1$

or

Iterative QPE (1 ancillary qubit) with $t \sim 2,048$

Shorter than $t \sim 2,048$ for Bayesian QPE
(empirically, $t = 300\text{--}400$)

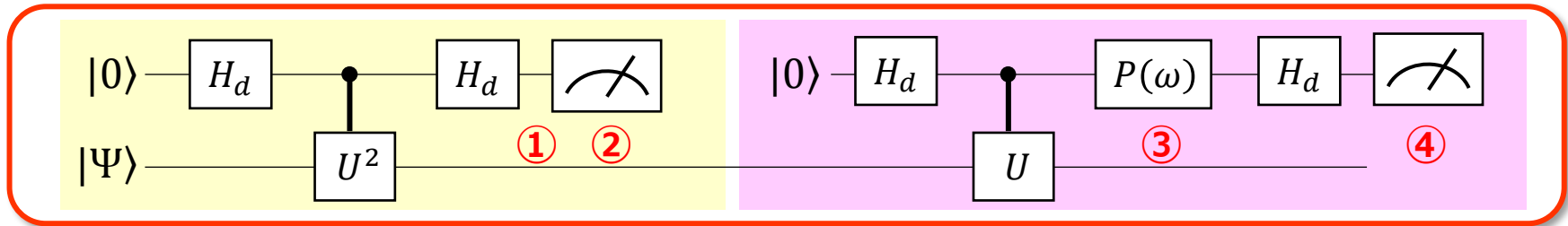
N-qubit QPE with an approximated wave function



Which electronic state can be obtained in QPE is proportional to the **square overlap between the approximated and full-CI wave functions!**

Iterative QPE with an approximated wave function

$$|\Phi\rangle = c_0|\Psi_0\rangle + c_1|\Psi_1\rangle + c_2|\Psi_2\rangle, \quad U|\Psi_i\rangle = e^{-2\pi\phi_i}|\Psi_i\rangle, \quad \begin{aligned} \phi_0 &= 0.01 \\ \phi_1 &= 0.10 \text{ in binary} \\ \phi_2 &= 0.11 \end{aligned}$$



Quantum state at ①: $c_0|1\rangle \otimes |\Psi_0\rangle + c_1|0\rangle \otimes |\Psi_1\rangle + c_2|1\rangle \otimes |\Psi_2\rangle$

Measurement at ②:

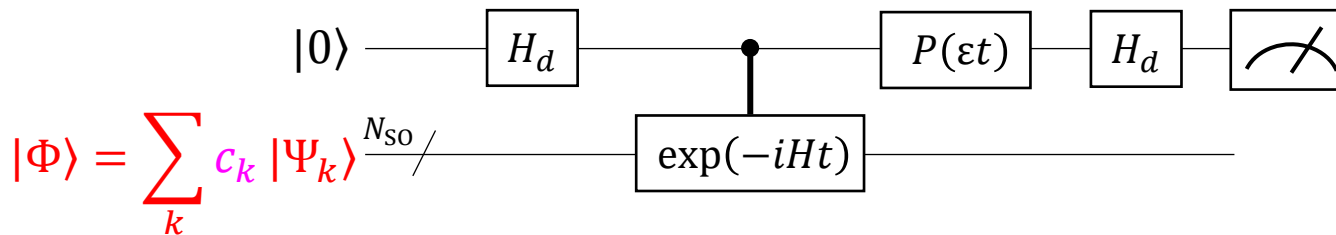
Measurement outcome	Probability	Quantum state after measurement
0	c_1^2	$ 0\rangle \otimes \Psi_1\rangle$
1	$c_0^2 + c_2^2$	$ 1\rangle \otimes \left\{ \sqrt{\frac{c_0^2}{c_0^2 + c_2^2}} \Psi_0\rangle + \sqrt{\frac{c_2^2}{c_0^2 + c_2^2}} \Psi_2\rangle \right\}$

If the measurement outcome at ② is 0 \rightarrow Use $\omega = 0$ in ③, measurement at ④ gives 1

If the measurement outcome at ② is 1 \rightarrow Use $\omega = \pi/2$ in ③,

Measurement outcome	Probability	Quantum state after measurement
0	$c_0^2/(c_0^2 + c_2^2)$	$ 0\rangle \otimes \Psi_0\rangle$
1	$c_2^2/(c_0^2 + c_2^2)$	$ 1\rangle \otimes \Psi_2\rangle$

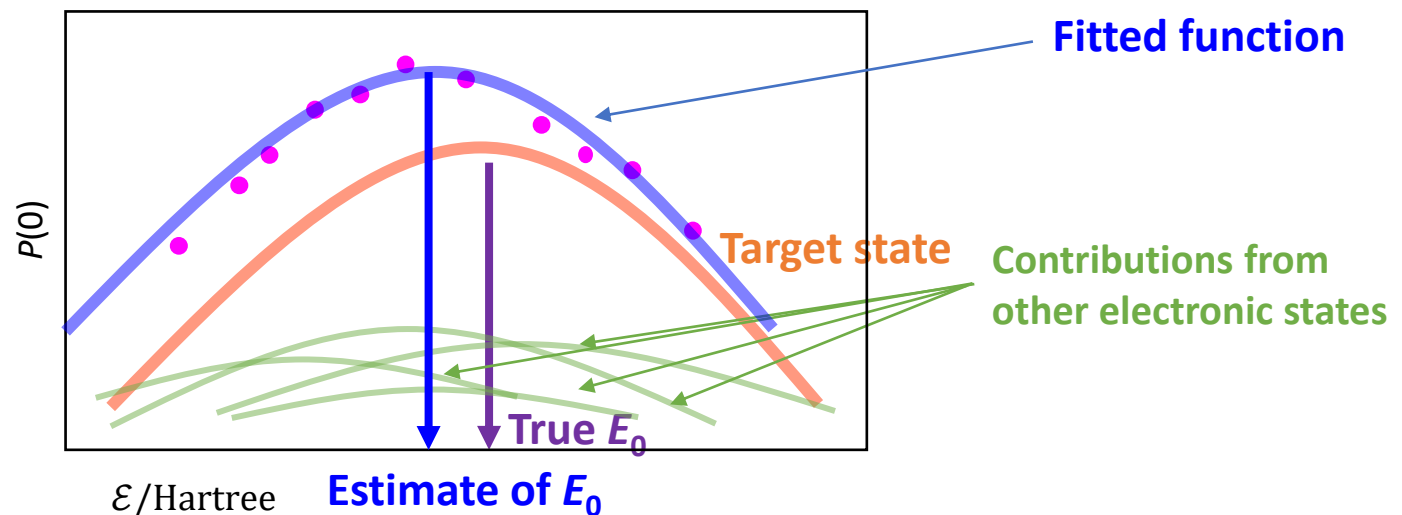
Bayesian QPE with an approximated wave function



Probability to obtain the $|0\rangle$ state in the measurement of the first qubit

$$P(0) = \frac{1}{2} \left[1 + \sum_k |c_k|^2 \cos\{(E_k - \varepsilon)t\} \right]$$

Linear combination of many cosine functions with different periods



Assumptions in QPE-based full-CI

■ Hartree–Fock wave function is a good approximation of the wave function of electronic ground state

This assumption is not always correct. A representative example is open shell molecules carrying unpaired electrons of spin- β .
Use spin symmetry adapted wave function is crucial

K. Sugisaki et al, *J. Phys. Chem. A* **2016**, 120, 6459–6466.

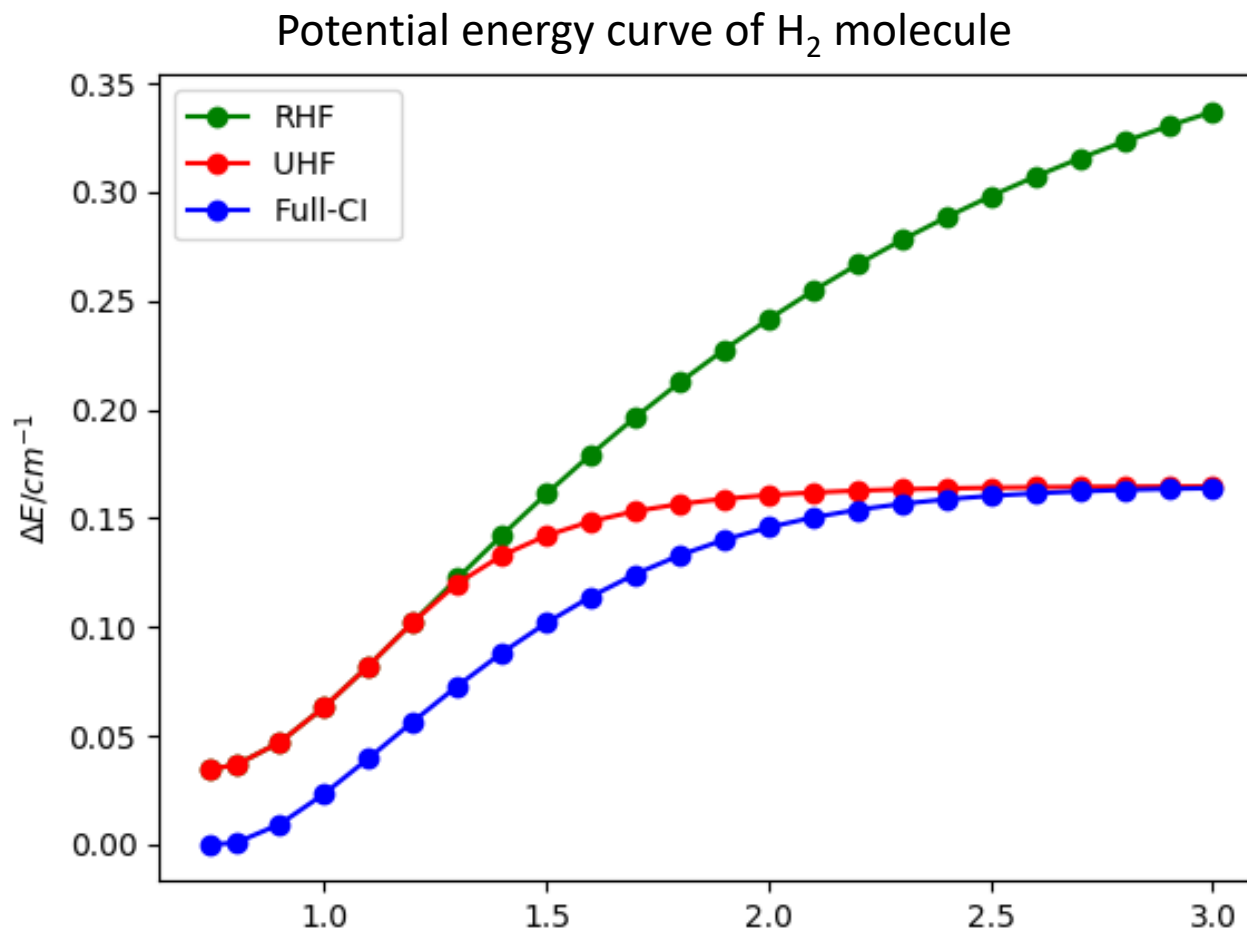
K. Sugisaki et al, *Chem. Phys. Lett.: X* **2019**, 1, 100002.

K. Sugisaki et al, *ACS Cent. Sci.* **2019**, 5, 167–175.

■ Hartree–Fock wave function is available

Sometimes Hartree–Fock calculations do not converge in large molecules like proteins. Application of QCC-on-QCs for such systems is still an open question

Preparation of “good” initial wave function



RHF method is not able to describe bond dissociation limit correctly.

Molecules undergoing bond dissociation are representatives of open shell systems.

Preparation of “good” initial wave function

Quantum Chemistry on Quantum Computers: A Method for Preparation of Multiconfigurational Wave Functions on Quantum Computers without Performing Post-Hartree–Fock Calculations

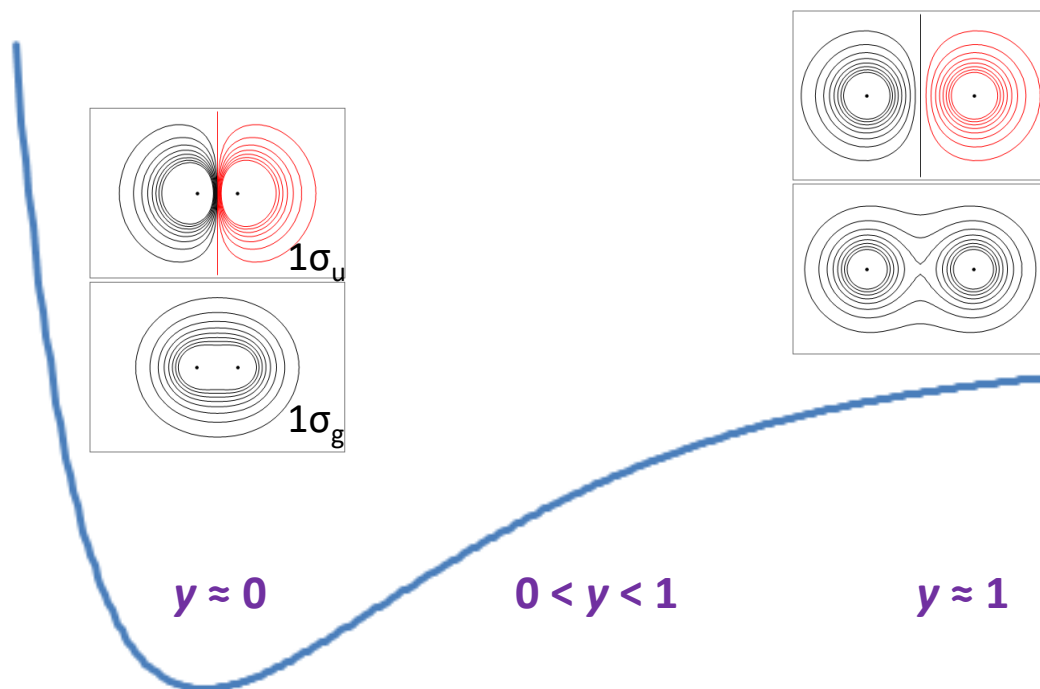
Kenji Sugisaki,^{*,†} Shigeaki Nakazawa,[†] Kazuo Toyota,[†] Kazunobu Sato,^{*,†} Daisuke Shiomi,[†] and Takeji Takui^{*,†,‡}

[†]Department of Chemistry and Molecular Materials Science, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

[‡]Research Support Department/University Research Administrator Center, University Administration Division, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

- Preparation of correlated wave functions beyond mean field approximation usually requires post-Hartree–Fock calculations.
- Approximated wave function preparations based on the CASSCF method have been discussed (e.g., L. Veis, J. Pittner, *J. Chem. Phys.* **2010**, *133*, 194106), but CASSCF itself becomes a bottleneck for large systems.

Preparation of “good” initial wave function



Diradical character y

$y \approx 0$

$0 < y < 1$

$y \approx 1$

$$y_i^{\text{PUHF}} = 1 - \frac{2(1 - n_{\text{LUNO}+i})}{1 + (1 - n_{\text{LUNO}+i})^2}$$

$$|\Psi\rangle \sim \sqrt{1 - \frac{y^2}{2}} |20\rangle - \sqrt{\frac{y^2}{2}} |02\rangle$$

HF config

HONO-LUNO
two-electron excited config

QPE experiments

☆ B. P. Lanyon et al, *Nat. Chem.* **2010**, 2, 106–111.

- Photonic quantum computer (use polarization of photons as the basis of qubits)
- Potential energy curves of the S_0 , S_1 , S_2 , and T_1 states of H_2 molecule
- STO-3G basis set
- One qubit for wave function storage by using symmetry
- Iterative QPE

☆ J. Du et al, *Phys. Rev. Lett.* **2010**, 104, 030502.

- NMR quantum computer (use ^{13}C and 1H nuclear spins of $CHCl_3$ as the qubits)
- H_2 molecule, full-CI/STO-3G
- One qubit for wave function storage by using symmetry
- Iterative QPE with an adiabatic state preparation

☆ Y. Wang et al, *ACS Nano* **2015**, 9, 7769–7774.

- NV center in diamond (use electron and ^{14}N nuclear spins as the qubits)
- Potential energy curves of the ground and the first excited states of HeH^+ molecule
- STO-3G basis set
- Iterative QPE

Quantum gate complexity

PHYSICAL REVIEW A **90**, 022305 (2014)



Gate-count estimates for performing quantum chemistry on small quantum computers

Dave Wecker,¹ Bela Bauer,² Bryan K. Clark,^{2,3,4} Matthew B. Hastings,^{1,2} and Matthias Troyer⁵

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²*Station Q, Microsoft Research, Santa Barbara, California 93106-6105, USA*

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⁵*Theoretische Physik, ETH Zurich, 8093 Zurich, Switzerland*

(Received 20 June 2014; published 6 August 2014)

	Upper bound	Empirical scaling
Number of Hamiltonian terms:	$O(N^4)$	$O(N^{3.8})$
Number of quantum gates/term:	$O(N)$	$O(N)$
1/Trotter time step:	$O(N^6)$	$O(N^4)$

Total time scaling is $O(N^{11})$ in upper bound, $O(N^9)$ in empirical.

Computational time estimations

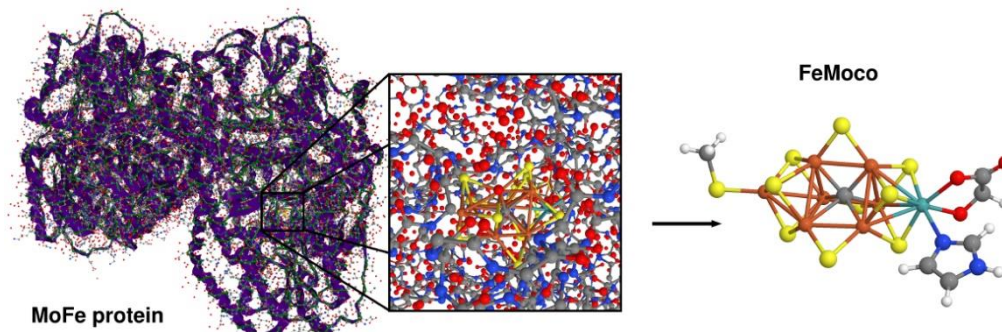
Elucidating reaction mechanisms on quantum computers

Markus Reiher^{a,1}, Nathan Wiebe^{b,1}, Krysta M. Svore^b, Dave Wecker^b, and Matthias Troyer^{b,c,2}

PNAS **2017**, *114*, 7555–7560.

Active site of nitrogenase

(Figure taken from *PNAS* 2017, 114, 7555)



Assume that gate operation time $\Delta t = 10$ ns, quantitatively accurate simulations (0.1 mHa) of (54e,54o) model system can be executed with

Logical qubits	T gates	Clifford gates	Time
111	1.1×10^{15}	1.7×10^{15}	130 days
135	3.5×10^{15}	5.7×10^{15}	15 days
1982	3.1×10^{16}	3.1×10^{16}	110 hours

Computational time estimations

PHYSICAL REVIEW X 8, 041015 (2018)

Encoding Electronic Spectra in Quantum Circuits with Linear T Complexity

Ryan Babbush,^{1,*} Craig Gidney,² Dominic W. Berry,³ Nathan Wiebe,⁴ Jarrod McClean,¹
Alexandru Paler,⁵ Austin Fowler,² and Hartmut Neven¹

- Two-dimensional array of nearest-neighbor coupled qubits
- Surface code error-detection cycle time of $1 \mu\text{s}$
- Gate error rates of $p = 10^{-3}$

Number of spin orbitals = number of logical qubits	Number of physical qubits	Execution time
54	1.7×10^6	51 minutes
128	2.9×10^6	10 hours
250	5.1×10^6	58 hours
1024	2.3×10^7	117 days

QPE summary 1

Wave function	Full-CI or CAS-CI
Energy	Eigenvalue
Principles of computation	Estimate the phase difference of wave functions before and after time evolution
Requirements	An approximated wave function having sufficiently large overlap with the target eigenfunction can be prepared efficiently
Quantum circuit	Deep
Computational cost scaling against the energy precision ε	$1/\varepsilon$
Exponential improvement of the computational cost scaling against the system size	Yes

QPE summary 2

	<i>N</i> -qubit QPE	Iterative QPE	Bayesian QPE
Number of ancillary qubits	N	1	1
Projective?	Yes	Yes	No
Estimated resources to achieve chemical precision	$N = 12$ by setting $t = 1$ for $U = \exp(-iHt)$	$t \sim 2048$	$t \sim 150$
Number of circuit execution	1	Number of binary fractional digits	(1000–10000 shots to evaluate likelihood function) \times (Number of Bayesian updates)

Determination of the spin quantum number



PCCP

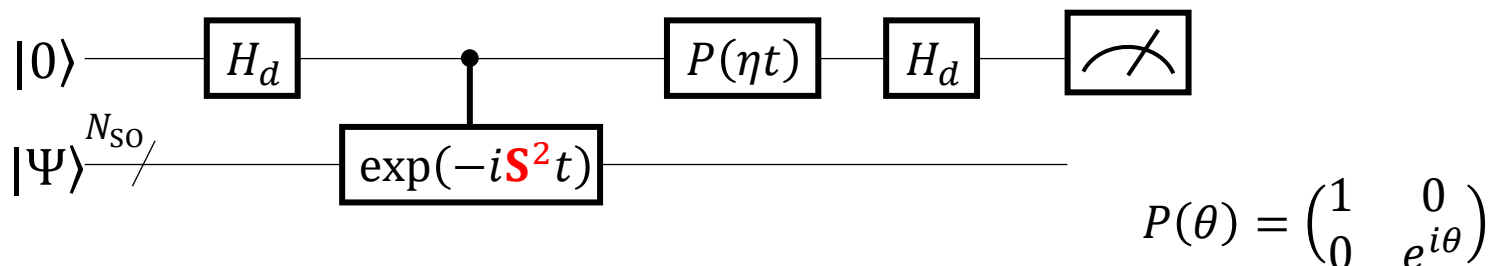
PAPER



Cite this: *Phys. Chem. Chem. Phys.*,
2019, 21, 15356

**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**

Kenji Sugisaki,^{ib}*^a Shigeaki Nakazawa,[‡]^a Kazuo Toyota,^a Kazunobu Sato,^{ib}*^a
Daisuke Shiomi^a and Takeji Takui^{ib}*^{ab}



Using the S^2 operator instead of the Hamiltonian H , we can determine spin quantum number S of the system

Probabilistic spin annihilation method

PCCP



COMMUNICATION



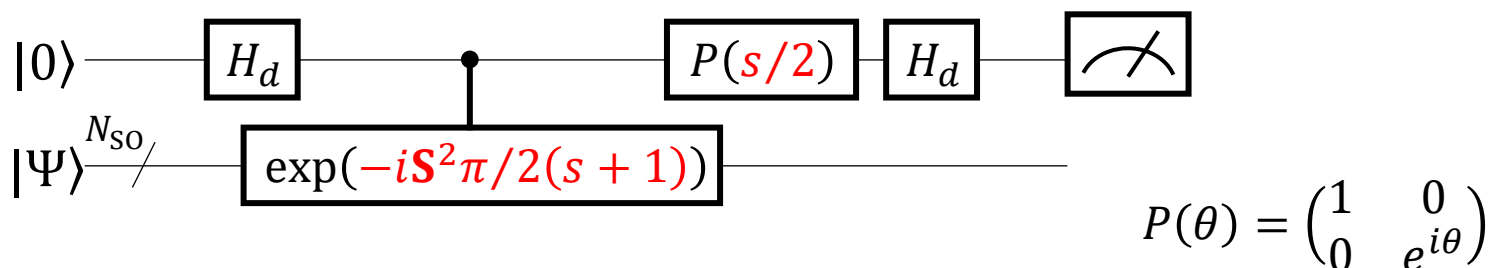
Cite this: *Phys. Chem. Chem. Phys.*, 2020, 22, 20990

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Accepted 4th September 2020

DOI: 10.1039/d0cp03745a

A probabilistic spin annihilation method for quantum chemical calculations on quantum computers†

Kenji Sugisaki,^{id} *^{ab} Kazuo Toyota,^a Kazunobu Sato,^{id} *^a Daisuke Shiomi^a and Takeji Takui^{id} *^{ac}



The QPE quantum circuit can be used as the probabilistic projection tool, if the eigenvalue of the target electronic state is known (like the S^2 operator)

Extension of QPE: Phase difference estimation algorithm

Why controlled-time evolution is required in QPE?

To extract the phase difference before and after the time evolution.

If we want to extract **the phase difference of two electronic states after the time evolution**, controlled-time evolution is not needed any more.

Conventional QPE

State preparation



Controlled-time evolution

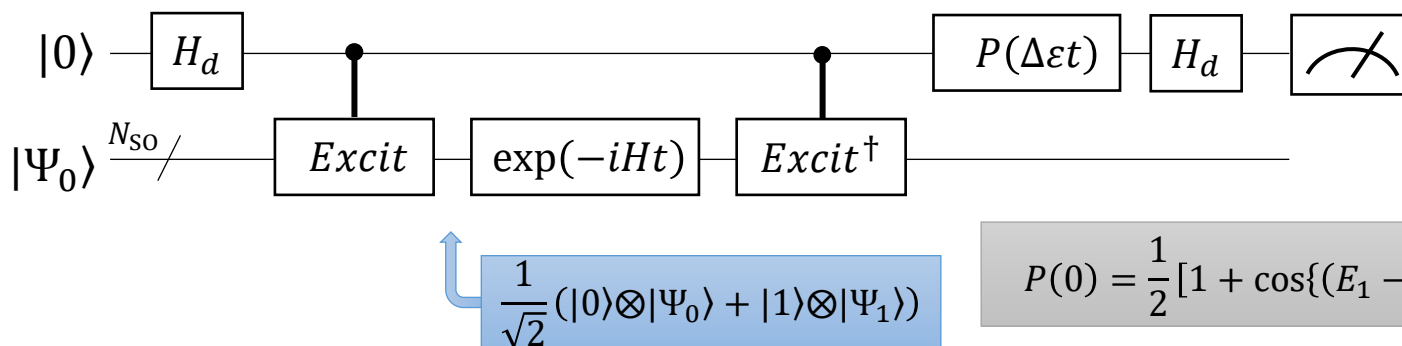
Quantum Phase **DIFFERENCE** Estimation

Controlled-state preparation

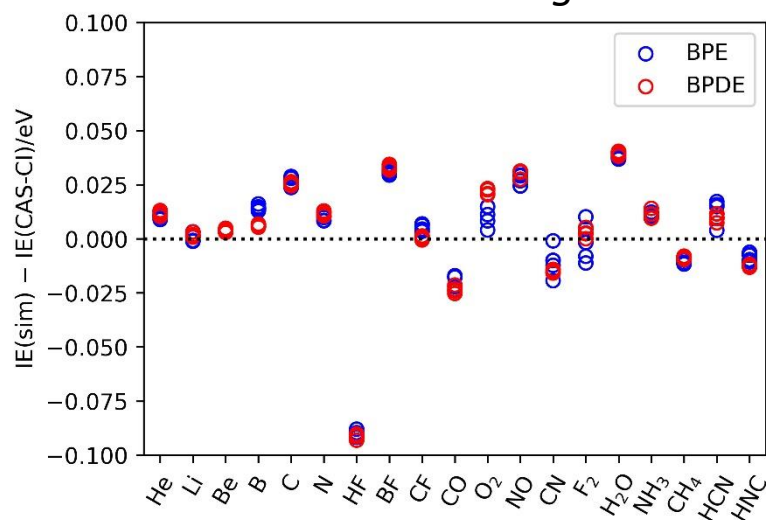


Time evolution

Bayesian phase difference estimation (BPDE)

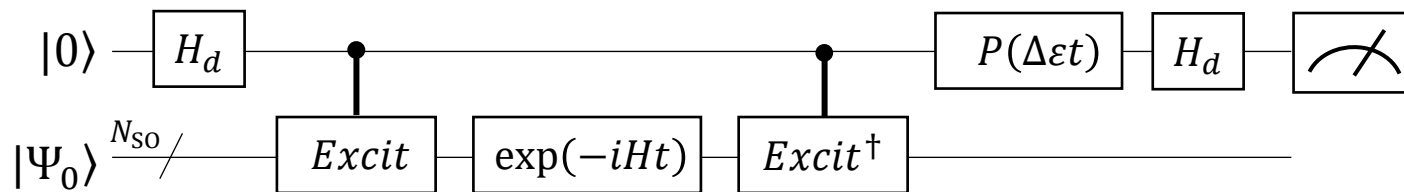


Ionization energies



Molecule	Excited state	Excitation energy/eV			
		BPE	BPDE	CAS-CI	Exptl.
CF ₂	1 ¹ B ₁	6.200	6.199	6.143	4.615
	1 ³ B ₁	3.060	3.062	2.999	2.458
CCl ₂	1 ¹ B ₁	3.188	3.186	3.191	2.139
	1 ³ B ₁	1.354	1.362	1.360	0.9(2)
CBr ₂	1 ¹ B ₁	2.745	2.747	2.755	1.871
	1 ³ B ₁	1.205	1.208	1.219	n.a.
SiF ₂	1 ¹ B ₁	6.622	6.622	6.643	5.469
	1 ³ B ₁	3.639	3.651	3.663	3.262
SiCl ₂	1 ¹ B ₁	4.689	4.686	4.689	3.721
	1 ³ B ₁	2.640	2.638	2.639	2.349
HCHO	1 ¹ A ₂	5.292	5.297	5.359	4.1
	1 ¹ B ₁	10.467	10.466	10.525	8.6-9.0
	2 ¹ A ₁	11.586	11.603	11.692	10.7

Bayesian phase difference estimation (BPDE)



Conventional QPE assumes that approximated wave function can be prepared efficiently.

We assume that *Prep* gates are available to calculate excitation energy using QPE.

$$Prep(g)|00 \cdots 0\rangle = |\Phi_g\rangle, \quad |\langle \Phi_g | \Psi_g \rangle|^2 \sim 1$$

$$Prep(e)|00 \cdots 0\rangle = |\Phi_e\rangle, \quad |\langle \Phi_e | \Psi_e \rangle|^2 \sim 1$$

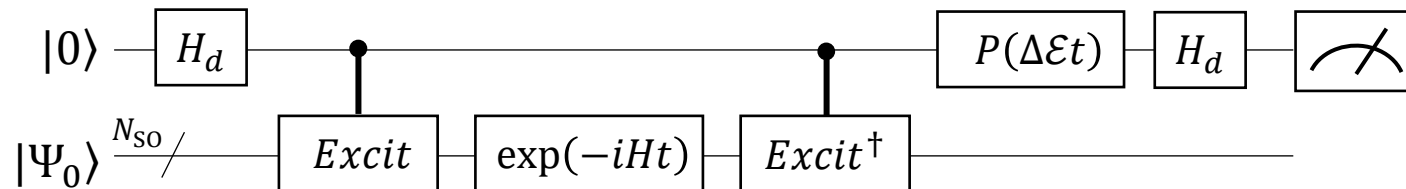
Excitation operator can be written by using *Prep* gates.

$$Excit = Prep(g)^\dagger Prep(e)$$

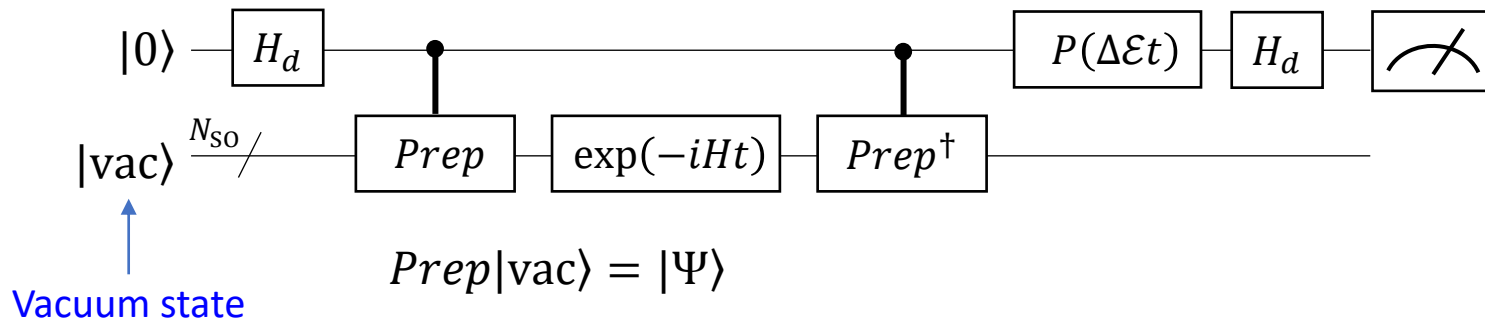
If *Excit* cannot be defined, it means that excitation energy calculation using conventional QPE is also impossible.

Full-CI with BPDE algorithm

Conventional BPDE



BPDE for Full-CI



- ✓ Calculate the full-CI energy of an N -electron system as the N -electron ionization energy.
- ✓ Do not need controlled-time evolution that is necessary for conventional QPE-based full-CI.

Full-CI with BPDE algorithm

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Letter

Quantum Algorithm for Full Configuration Interaction Calculations without Controlled Time Evolutions

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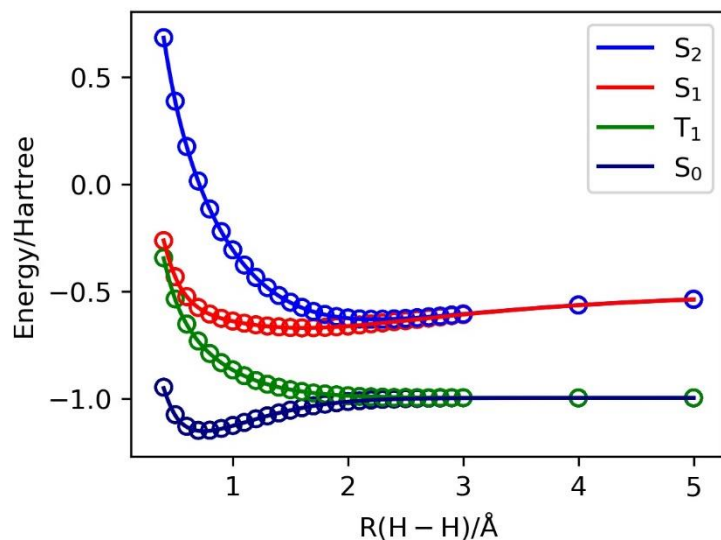


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H_2 , full-CI/6-31G



N_2H_2 , CASCI(10e,8o)/6-311G(d,p)

