Quantum Algorithm for Optimal Molecular Geometries Based on Probabilistic Imaginary-Time Evolution

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Various ITE approaches on quantum computers

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Variational ITE (VITE)

Circuit parameters $\boldsymbol{\theta}(\tau)$ for unitaries are updated by solving $[\mathrm{Re}\, A(\tau)]\dot{\boldsymbol{\theta}}(\tau) = -\mathrm{Re}\, \boldsymbol{C}'(\tau)$

McLachlan, Mol. Phys. **8**, 39 (1964)
Jones et al., Phys. Rev. A **99**, 062304 (2019)
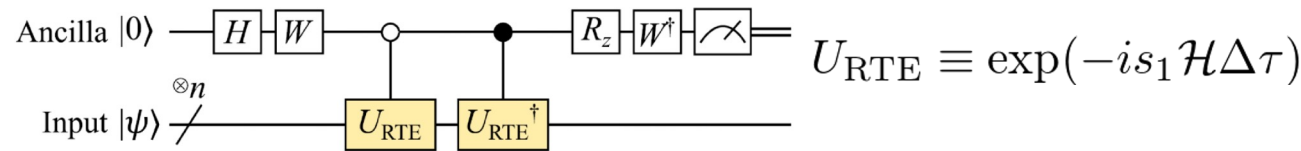
Quantum ITE (QITE)

Determine coeffs in Hermitian oprs $\hat{A}_n[m] = \sum_{i_1 \cdots i_D, l_1 \cdots l_D} a^{(n)}_{i_1 \cdots i_D, l_1 \cdots l_D}[m] \hat{\sigma}_{i_1, l_1(m)} \otimes \cdots \otimes \hat{\sigma}_{i_D, l_D}$ for approximate unitaries.

Motta et al., Nat. Phys. **16**, 205 (2020)
cf. Nishi, Kosugi, and Matsushita, npj Quant. Inf. **7**, 85 (2021)

Probabilistic ITE (PITE)

Implements the nonunitary opr $\mathcal{M} = m_0 e^{-\mathcal{H}\Delta\tau}$ by using real-time evolution (RTE) gates:

$U_{\mathrm{RTE}} \equiv \exp(-i s_1 \mathcal{H} \Delta\tau)$

Kosugi, Nishiya, Nishi, and Matsushita,
Phys. Rev. Res. **4**, 033121 (2022)

$$|\psi\rangle \otimes |0\rangle \longmapsto \underline{m_0(1 - \mathcal{H}\Delta\tau)|\psi\rangle} \otimes |0\rangle + \left(\sqrt{1 - m_0^2} + \frac{m_0^2}{\sqrt{1 - m_0^2}} \mathcal{H}\Delta\tau \right) |\psi\rangle \otimes |1\rangle + \mathcal{O}(\Delta\tau^2)$$

Success state

$\approx M|\psi\rangle$

Failure state

😀Every impl of RTE can be transferred to PITE.
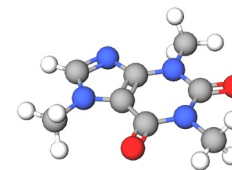
Finite-temperature calc is also possible.

PITE for first-quantized systems

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Hamiltonian

Hamiltonian of n_e electrons

$$\mathcal{H} = \underbrace{\sum_{\ell=0}^{n_e-1} \frac{\hat{\boldsymbol{p}}_\ell^2}{2m_e}}_{\equiv \hat{T}} + \underbrace{\frac{1}{2} \sum_{\substack{\ell,\ell'=0 \\ (\ell \neq \ell')}}^{n_e-1} v(|\hat{\boldsymbol{r}}_\ell - \hat{\boldsymbol{r}}_{\ell'}|)}_{\equiv \hat{V}_{ee}} + \underbrace{\sum_{\ell=0}^{n_e-1} v_{\text{ext}}(\hat{\boldsymbol{r}}_\ell)}_{\equiv \hat{V}_{\text{ext}}}$$

cf. Kassal et al., PNAS **105**, 18681 (2008)
for real-time dynamics

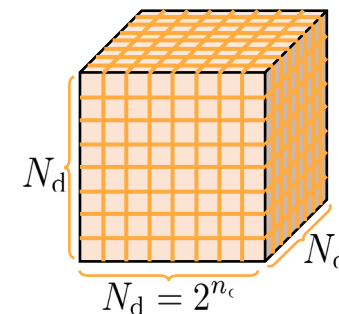## Encoding of wave functions

Many-electron wave function in pos repr

$$|\psi\rangle = \Delta V^{n_e/2} \sum_{\boldsymbol{k}_0, \ldots, \boldsymbol{k}_{n_e-1}} \psi(\boldsymbol{r}^{(\boldsymbol{k}_0)}, \ldots, \boldsymbol{r}^{(\boldsymbol{k}_{n_e-1})})|\boldsymbol{k}_0\rangle \otimes \cdots \otimes |\boldsymbol{k}_{n_e-1}\rangle$$

$N \equiv 2^{nq}$

$\Delta x \equiv L/N$: grid step

L: cell size

$|\boldsymbol{k}\rangle$: Position eigenstate of an electron

N_d

N_d

$N_d = 2^{n_c}$

Implementation of RTE

1st-order Suzuki-Trotter $e^{-i\mathcal{H}\Delta t} \approx e^{-i\hat{T}\Delta t} e^{-i(\hat{V}_{ee}+\hat{V}_{\text{ext}})\Delta t}$
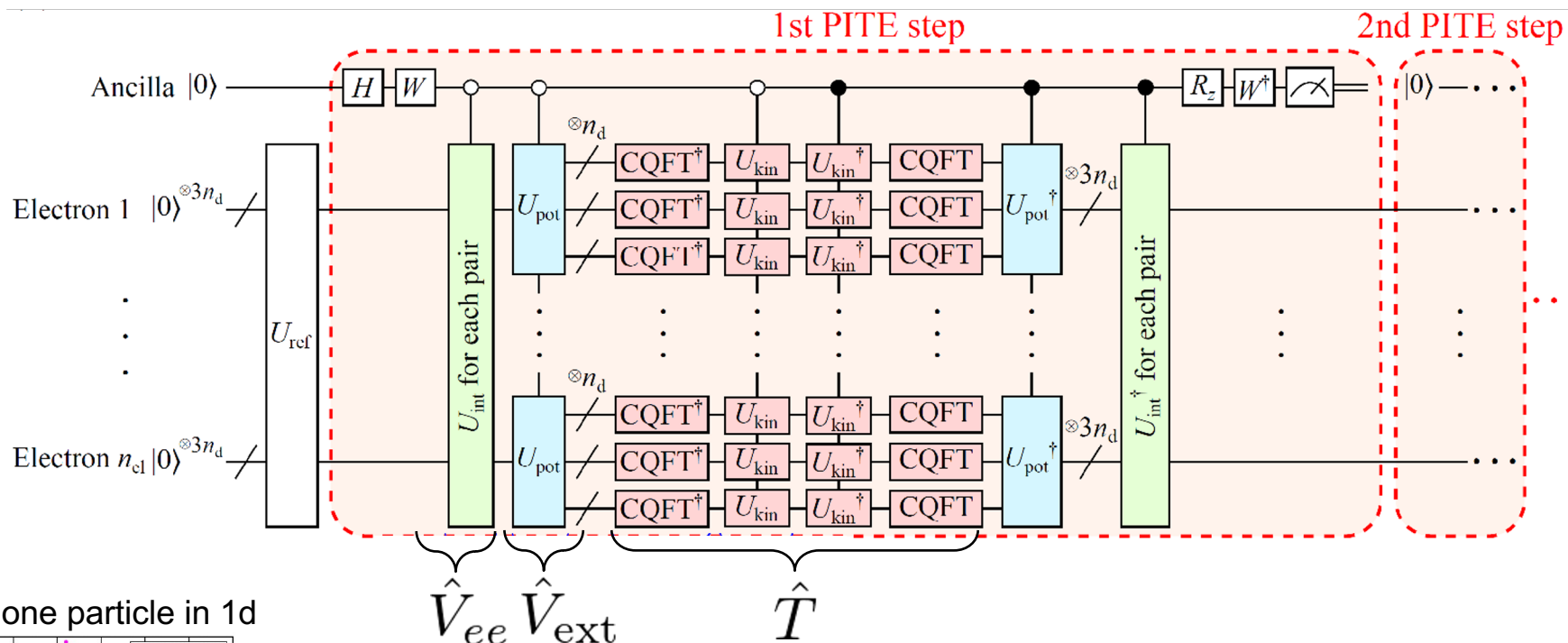
For example, from phase gate for 2 electrons $U_{\text{int}}(\Delta t)|\boldsymbol{r}\rangle \otimes |\boldsymbol{r}'\rangle \equiv \exp(-iv(|\boldsymbol{r}-\boldsymbol{r}'|)\Delta t)|\boldsymbol{r}\rangle \otimes |\boldsymbol{r}'\rangle$
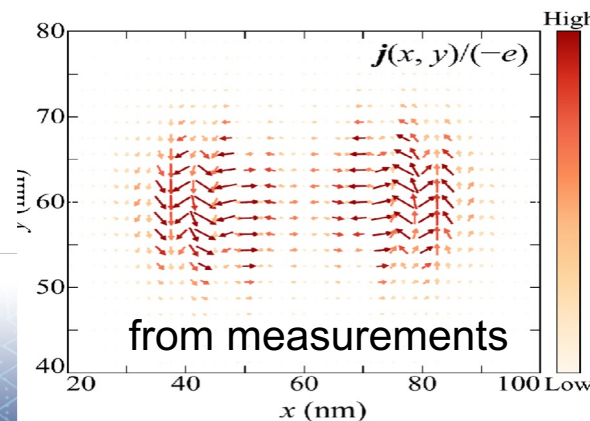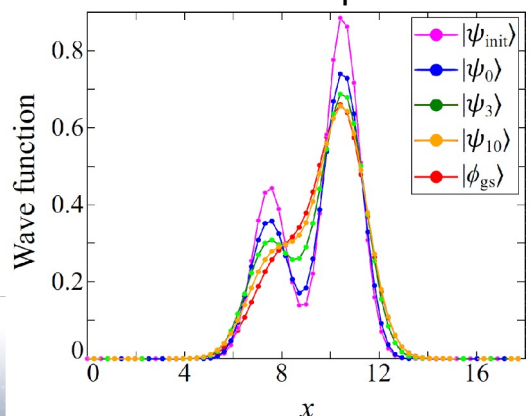
we can construct *e-e* part of RTE opr: $e^{-i\hat{V}_{ee}\Delta t} = \prod_{\ell < \ell'} \overbrace{U_{\text{int}}(\Delta t)}^{\text{On } \ell\text{th and } \ell'\text{th electrons}}$

Nonvariational energy minimization for a molecular system

Simulation for one particle in 1d

Introduction of an ext. magnetic field is possible.

from measurements

First-quantized eigensolver (FQE) based on PITE

Comparison with 2nd-quantized formalism

Typical simulation cells satisfy $L^3 \propto n_e$, we have $n_q \propto \log n_e$ for each electron.

Classical and quantum cost for performing a PITE calculation is estimated as follows:

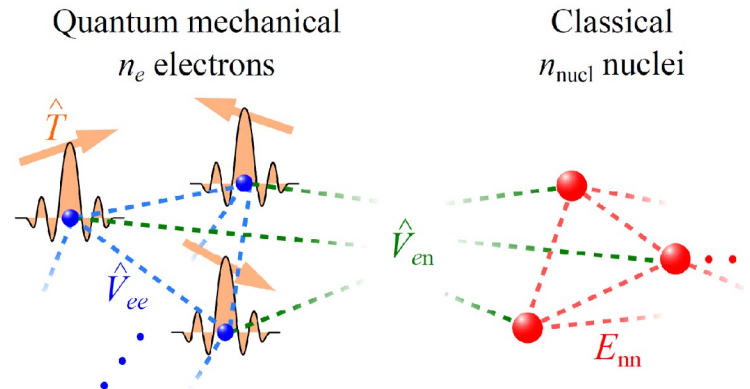|		1st-quantized	2nd-quantized
Classical	# of oprs for obtaining MOs	None	$O(n_e^4)$ for two-electron integrals (and $O(n_e^3)$ for diagonalization)
	# of oprs for constructing Hamiltonian	None	$O(n_e^5)$ (U_{abcd} for AOs -> U_{pqrs} for MOs)
Quantum	# of qubits for a many-electron state	$O(n_e \log n_e)$	$O(n_e)$
	# of oprs at each PITE step	$O(n_e^2 (\log n_e)^{p'})$ p': degree of polynomial for e-e interactions	$O(n_e^4)$ ($c_p^\dagger c_q^\dagger c_r c_s$ terms)

😀 Better scaling of 1st-quantized formalism both for classical and quantum oprs

Geometry optimization based on PITE

We treat the target molecule as quantum mechanical electrons and classical nuclei.

$$\mathcal{H}\left(\{\boldsymbol{R}_\nu\}_\nu\right) = \underbrace{\sum_{\ell=0}^{n_e-1} -\frac{1}{2m_e}\nabla_\ell^2}_{\equiv\hat{T}} + \underbrace{\frac{1}{2}\sum_{\ell=0}^{n_e-1}\sum_{\ell'=0}^{n_e-1} v\left(|\hat{\boldsymbol{r}}_\ell - \hat{\boldsymbol{r}}_{\ell'}|\right)}_{\equiv\hat{V}_{ee}} + \underbrace{\sum_{\ell=0}^{n_e-1}\sum_{\nu=0}^{n_{\mathrm{nucl}}-1} -Z_\nu v\left(|\hat{\boldsymbol{r}}_\ell - \boldsymbol{R}_\nu|\right)}_{\equiv\hat{V}_{en}}$$

$$+ \underbrace{\frac{1}{2}\sum_{\nu=0}^{n_{\mathrm{nucl}}-1}\sum_{\nu'=0}^{n_{\mathrm{nucl}}-1} Z_\nu Z_{\nu'} v\left(|\boldsymbol{R}_\nu - \boldsymbol{R}_{\nu'}|\right)}_{\equiv E_{\mathrm{nn}}} + \underbrace{\sum_{\ell=0}^{n_e-1} v_{\mathrm{ext}}\left(\hat{\boldsymbol{r}}_\ell\right)}_{\equiv\hat{V}_{\mathrm{ext}}}$$

Quantum mechanical n_e electrons

Classical n_{nucl} nuclei

What we have to do is to determine the nuclear positions $\{\boldsymbol{R}_\nu\}_\nu$ so that the total energy is the lowest.

There is no need for knowing the energies of the candidate geometries for finding the optimal one.
We should know only which geometry has the unknown lowest energy.

Many candidates for optimal nuclear positions

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We encode the candidates by using n_{qn} qubits per direction for each nucleus.
Nuclear-position opr:

$$\hat{R}_{\nu x}|j_{\nu x}\rangle_{n_{qn}} \equiv \left(R_{\nu 0x} + j_{\nu x}\frac{\Delta R_{\nu x \max}}{N_{qn}} \right) |j_{\nu x}\rangle_{n_{qn}} \quad (j_{\nu x} = 0, 1, \ldots, N_{qn} - 1)$$

Original position   Displacement

We use the nuclear qubits not for wave functions of nuclei, but for classical data of nuclear positions.
Each geometry is specified by $3n_{qn}n_{\mathrm{nucl}}$ integers.

The qubits in our approach encode a state looking like:

$$|\Psi\rangle = \sum_{\boldsymbol{J}} \sqrt{w_{\boldsymbol{J}}}|\psi[\boldsymbol{J}]\rangle \otimes |\boldsymbol{J}\rangle_{3n_{\mathrm{nucl}}n_{qn}}$$

Summation over possible geoms   Many-electron state   Nuclear positions

We perform an ITE calculation for this superposition of all candidate geometries.
This approach finds the optimal geometry, for which the total energy is the lowest.
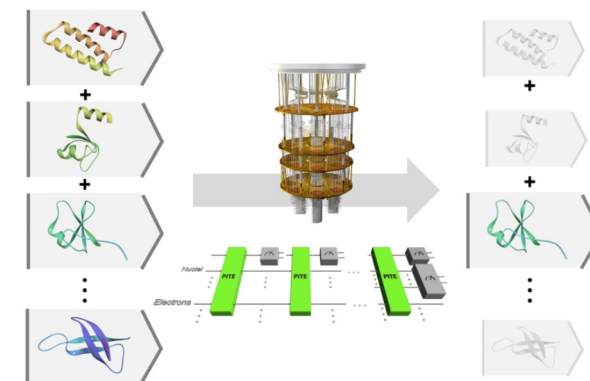
Circuit for PITE steps
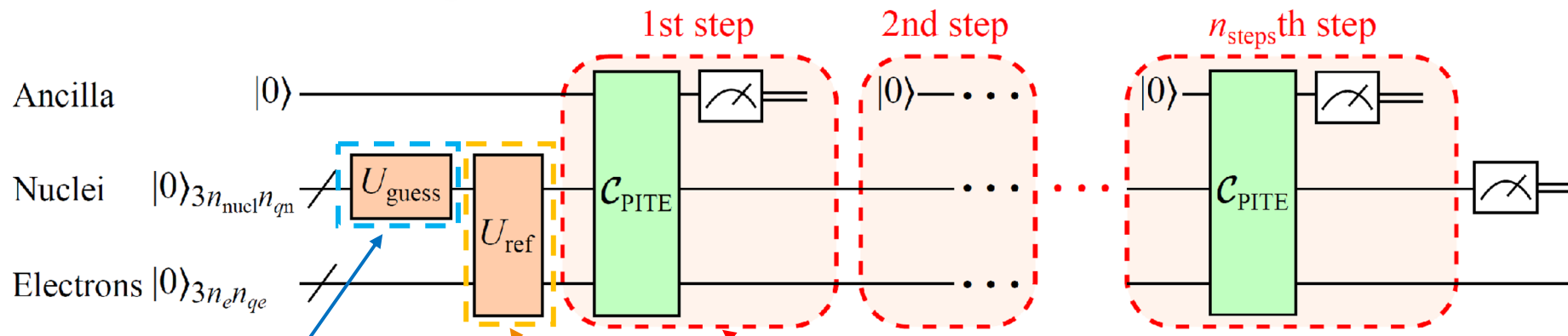
For giving initial weights to candidates

For generating reference electronic states

For energy minimization

Resultant state $|\Psi\rangle = \sum_{\boldsymbol{J}} \sqrt{w_{\boldsymbol{J}}} |\psi[\boldsymbol{J}]\rangle \otimes |\boldsymbol{J}\rangle_{3n_{\mathrm{nucl}}n_{qn}}$

😀Geoms having lower energies will be observed with higher probs.

Computational time for finding the lowest-energy state among N_{cand} candidates is

$$\mathcal{O}\left(n_e^2 \mathrm{poly}(\log n_e) N_{\mathrm{cand}} \log N_{\mathrm{cand}}\right)$$

PITE with quantum amplitude amplification (QAA) -> quadratic speedup

$$\mathcal{O}\left(n_e^2 \mathrm{poly}(\log n_e) \sqrt{N_{\mathrm{cand}}} \log N_{\mathrm{cand}}\right)$$

Nishi et al. in poster session
See also Nishi et al., arXiv:2212.13816

Numerical simulations for a LiH model system

Setup

2 electrons and 2 atoms in 1d space, $Z_{\rm H} = Z_{\rm Li} = 1$ (Li 1s electrons frozen)

All interactions are soft-Coulomb type:
$$v_{\rm soft}(r; \lambda) \equiv \frac{1}{\sqrt{\lambda^2 + r^2}}$$
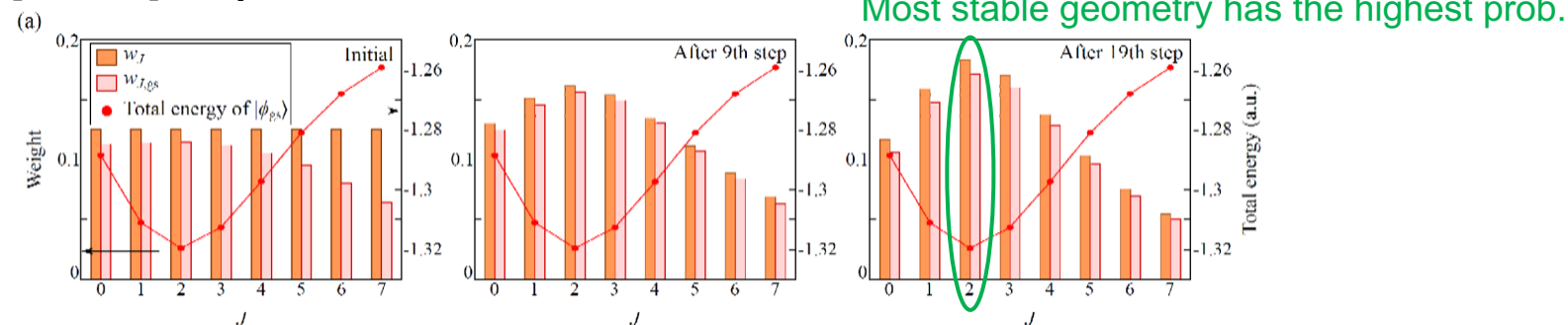
$n_{qe} = 6$ for spatial discretization
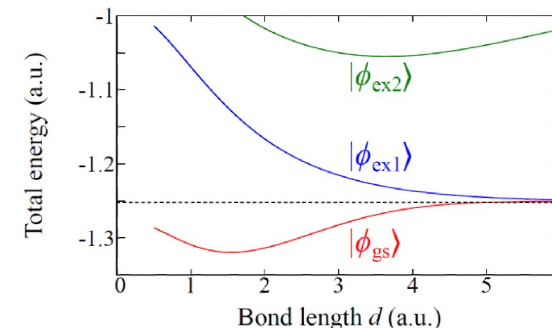
Geometry optimization

By using $n_{q\rm n} = 3$ qubits, we tried $2^{n_{q\rm n}} = 8$ candidate bond lengths for optimization: $d_J = 0.55 + 0.5J$ ($J = 0, \ldots, 7$)

Starting from a symmetric state (spin triplet)

$$\Psi_{\rm s}(x_0, x_1) \propto \exp\left(-\frac{(x_0 - X_{\rm m})^2 + (x_1 - X_{\rm m})^2}{w^2}\right)$$

$X_{\rm m}$: bond center

Most stable geometry has the highest prob.

Starting from an antisymmetric state (spin singlet)

$$\Psi_{\rm a}(x_0, x_1) \propto \frac{x_0 - x_1}{w} \Psi_{\rm s}(x_0, x_1)$$

No energy minimum within this range

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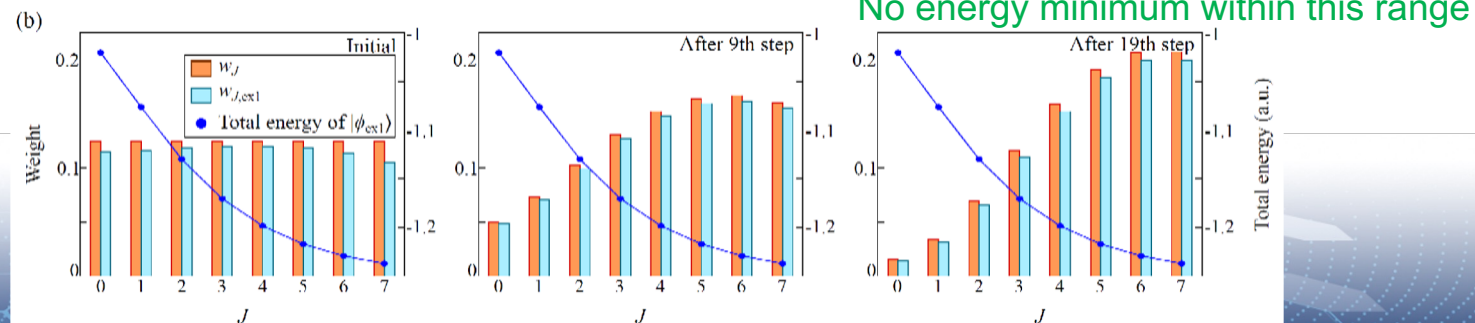
Setup

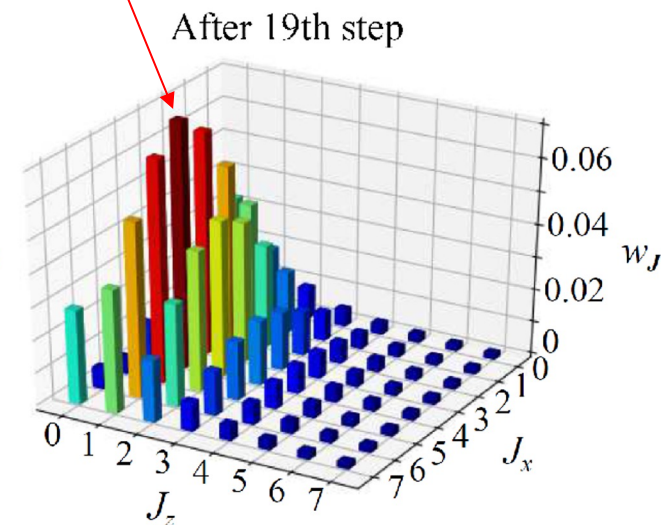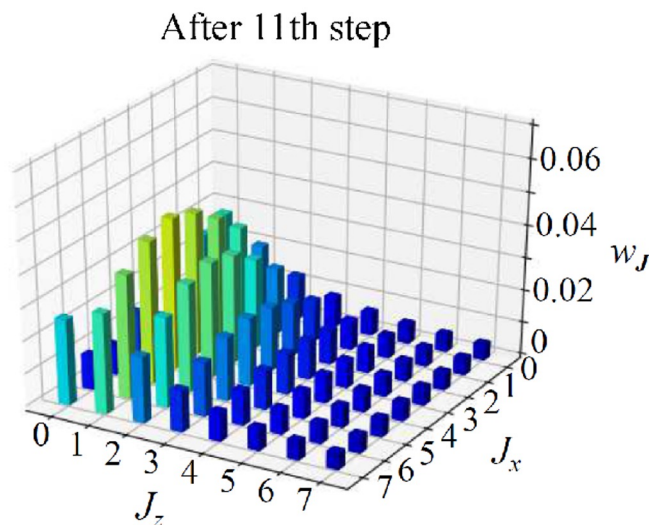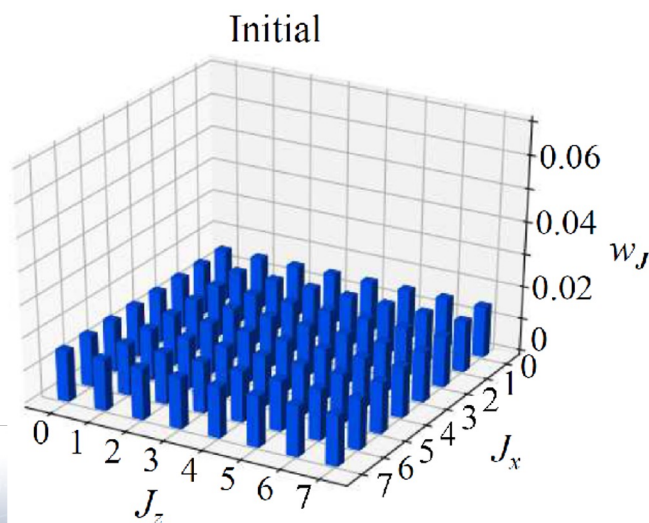Ar atom above a benzene molecule

Improved Lennard-Jones potential

Pirani et al, Chem. Phys. Lett. **394**, 37 (2004)
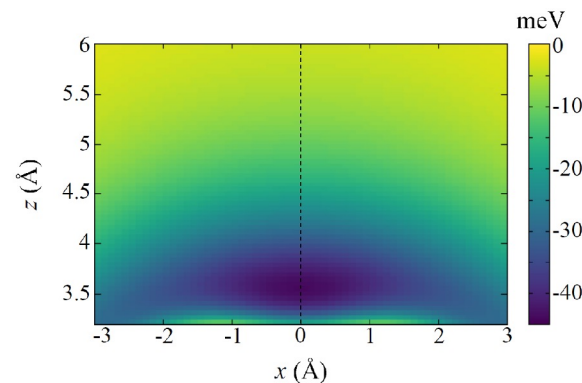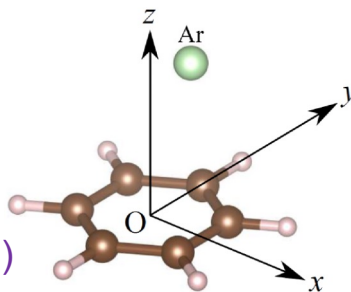
Geometry optimization using PITE

$n_{qn} = 3$ for each of x and z directions -> 64 candidates

Most stable geometry has the highest prob.


Initial | After 11th step | After 19th step

Geometry optimization based on variational calculations

Our scheme can also be adapted to vatiational imaginary-time evolution (VITE).

McLachlan, Mol. Phys. **8**, 39 (1964)
Jones et al., Phys. Rev. A **99**, 062304 (2019)

Geometry optimization of H_2^+ model system

By using $n_{qn} = 3$ qubits, we tried $2^{n_{qn}} = 8$ candidate bond lengths for optimization: $d_J = 0.5 + (7.5/8)J$ ($J = 0, \ldots, 7$)

Ansatz circuit ($d = 12$)

Most stable geometry

Summary
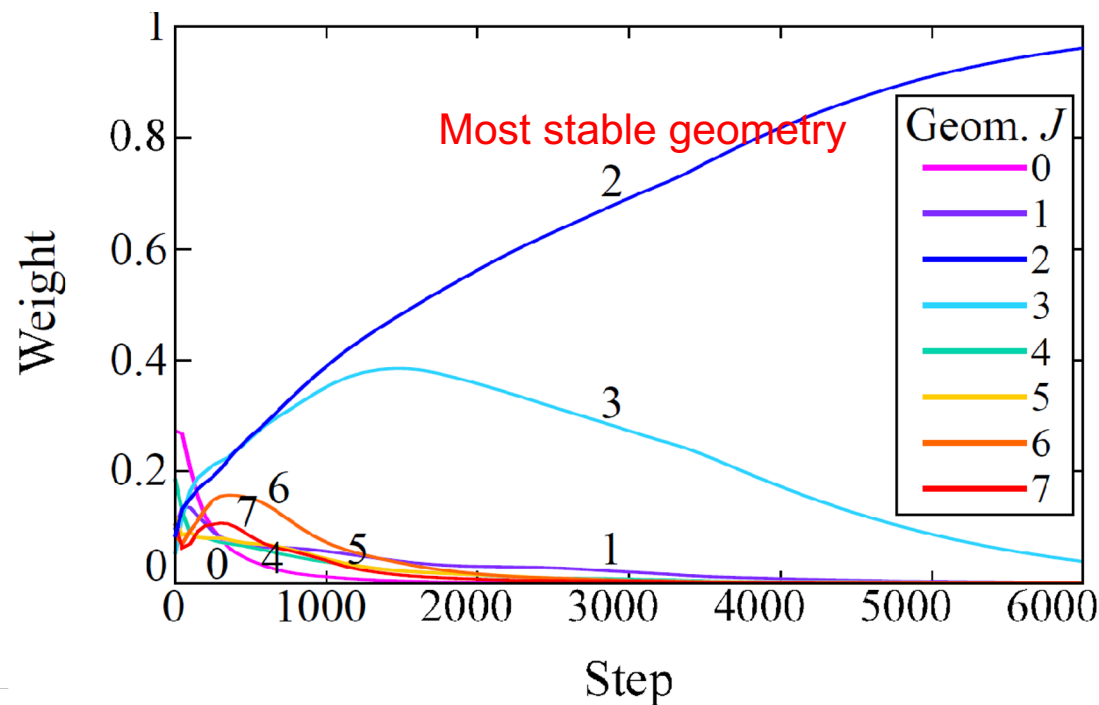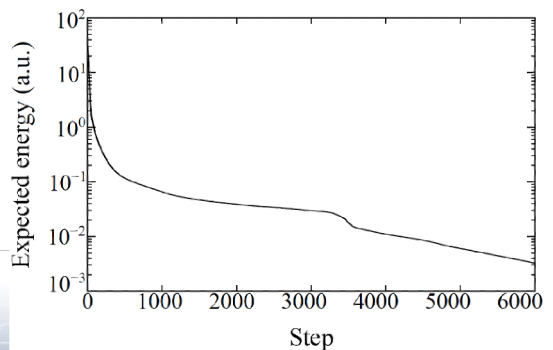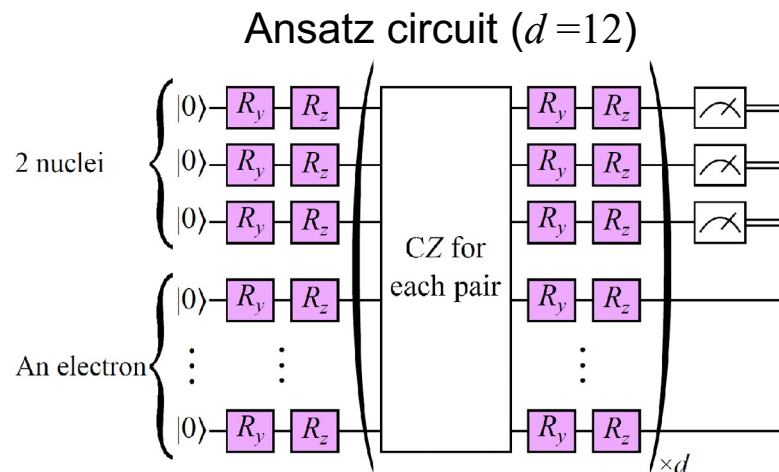
- PITE performs nonvariational energy minimization for a generic system using RTE oprs.

- When combined with first-quantized formalism, PITE for an electronic system exhibits better scaling than second-quantized formalism.

- By using ITE for a superposition of candidate geometries, exhaustive search for finding the optimal one is possible.

Kosugi, Nishiya, Nishi, and Matsushita,
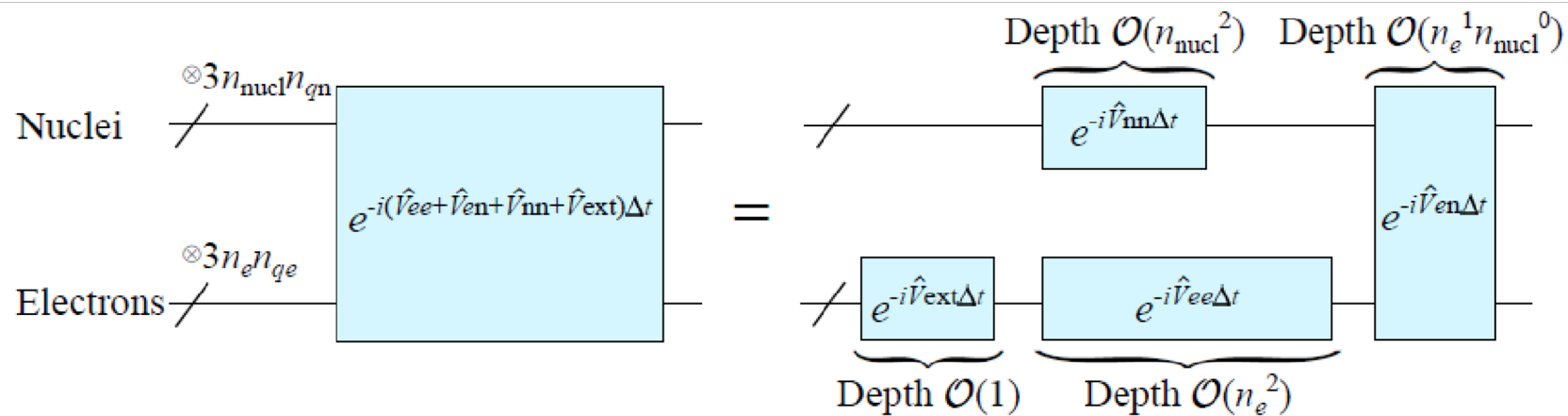Phys. Rev. Res. **4**, 033121 (2022)

Kosugi, Nishi, and Matsushita,
arXiv:2210.09883

Thank you.

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Position-dependent part in RTE

Efficient impl of *e-e* part for 4 electrons