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Geometric optimization based on first-quantized Hamiltonian using imaginary-time evolution on a quantum computer

arXiv:2210.09883

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Background

One of the important tasks: geometric structure optimization of molecules and crystals

Quantum computer → It is expected to accelerate the geometric structure optimization

Methodologies developed so far:

Force-field based optimization method

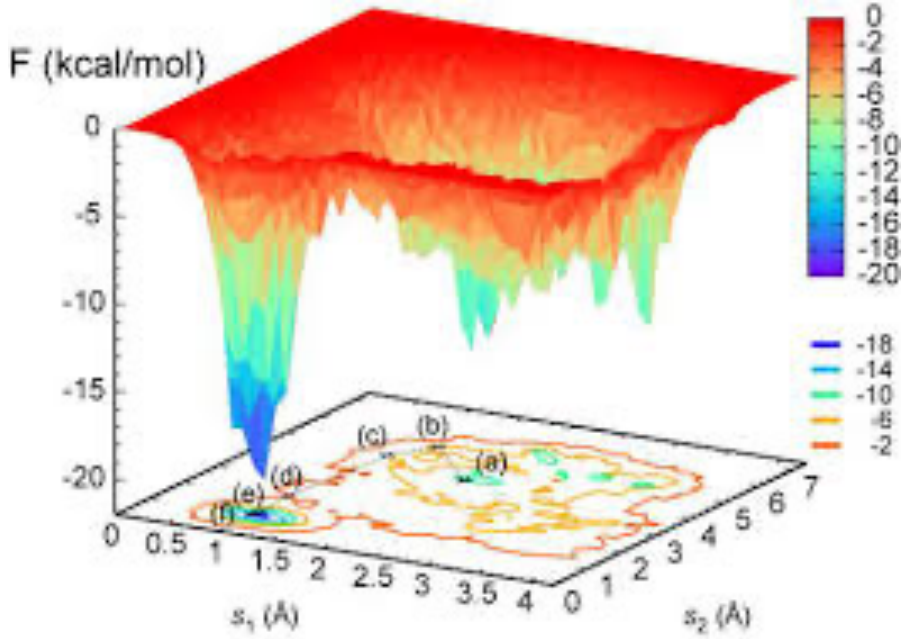
QPE: Kassal and Aspuru-Guzik, JCP **131**, 224102 (2009).

VQE: Delgado et al., PRA **104**, 052402 (2021).

Protein folding using Quantum annealer

Perdomo-Ortiz et al., Sci. Rep. **2**, 571 (2012).

Born-Oppenheimer surface



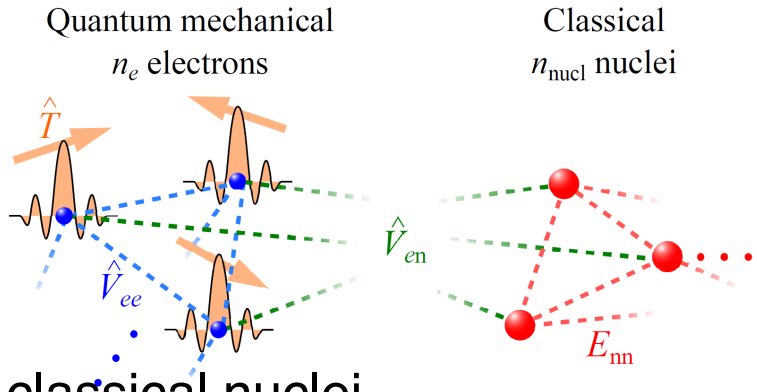
Propose a quantum algorithm of exhaustive search from candidate geometries on the Born-Oppenheimer surface

Hamiltonian for electrons and nuclei

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

$$+ \underbrace{\sum_{\nu=0}^{n_{\mathrm{nucl}}-1} -\frac{1}{2M_\nu}\nabla_\nu^2}_{\equiv \hat{T}_n} + \underbrace{\frac{1}{2}\sum_{\nu=0}^{n_{\mathrm{nucl}}-1}\sum_{\nu'=0}^{n_{\mathrm{nucl}}-1} Z_\nu Z_{\nu'} v(|\boldsymbol{R}_\nu - \boldsymbol{R}_{\nu'}|)}_{\equiv E_{\mathrm{nn}}} + \underbrace{\sum_{\ell=0}^{n_e-1} v_{\mathrm{ext}}(\hat{\boldsymbol{r}}_\ell)}_{\equiv \hat{V}_{\mathrm{ext}}}$$

Ignore nuclear kinetic part → Treat nuclei as classical particles (point charge)



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

By solving the Hamiltonian, we get the nuclear positions $\{\boldsymbol{R}_\nu\}_\nu$ so that the total energy is the lowest.

Encoding nuclear positions on a quantum computer

Encode the geometric candidates by using n_{qn} qubits.

Sum over possible geometries

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

Many-electron state

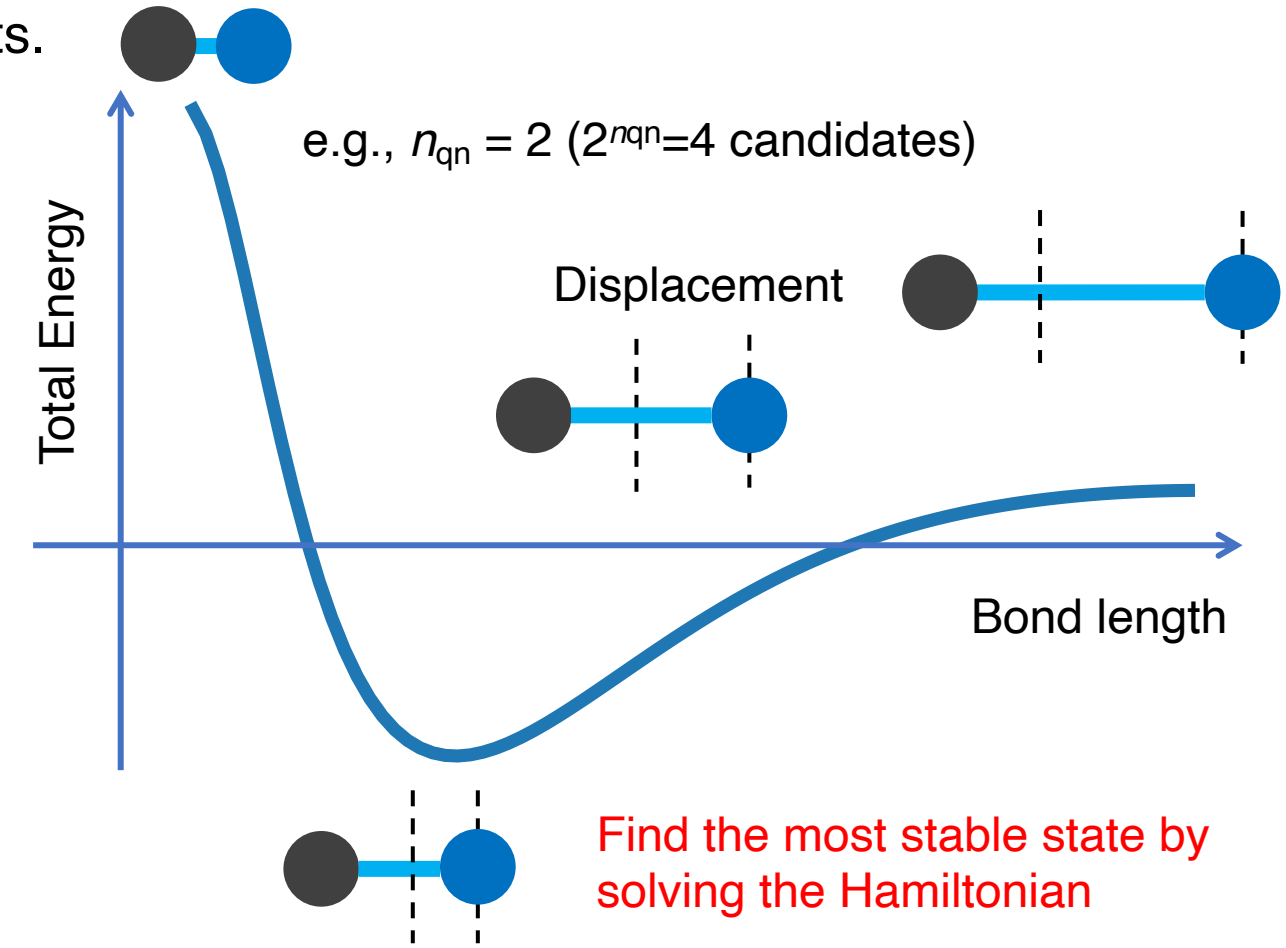
Nuclear positions

e.g., n_{qn}=2 (2^{nqn}=4 candidates)

$$|\Psi\rangle = \sqrt{w_{00}}|\psi[00]\rangle \otimes |00\rangle + \sqrt{w_{01}}|\psi[01]\rangle \otimes |01\rangle$$

$$+ \sqrt{w_{10}}|\psi[10]\rangle \otimes |10\rangle + \sqrt{w_{11}}|\psi[11]\rangle \otimes |11\rangle$$

Dissociation curve of two atoms

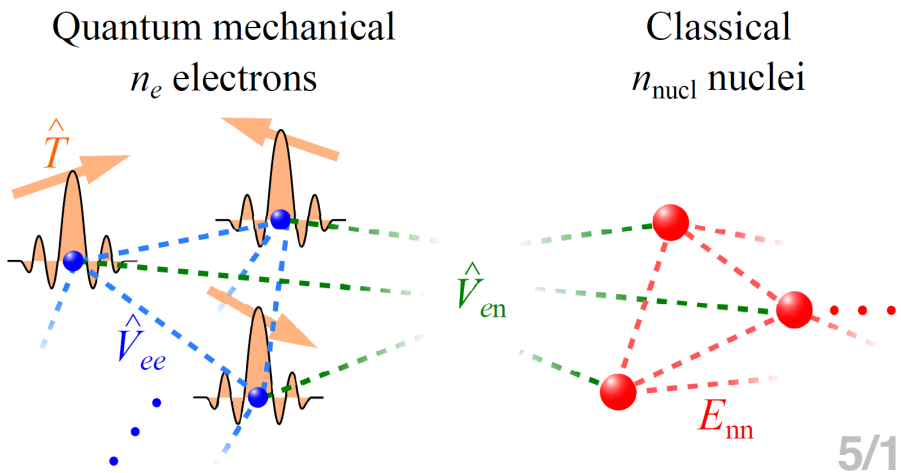


Find the most stable state by solving the Hamiltonian

We perform an ITE calculation for this superposition of all candidate geometries.

Features of this method

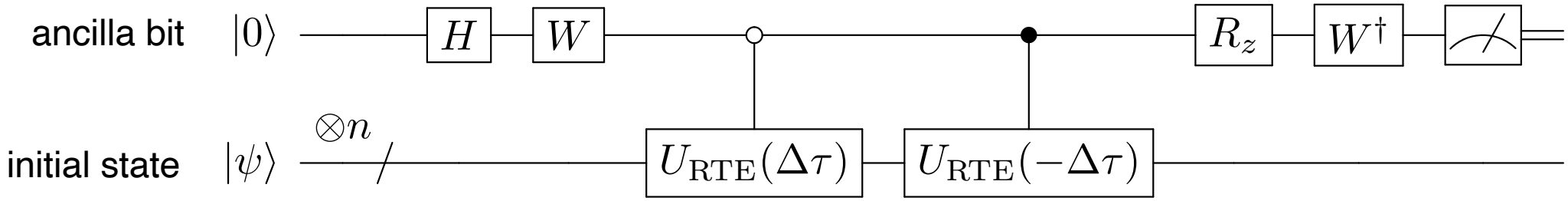
- ✓ We treat the target molecule as quantum mechanical electrons and classical nuclei.
- ✓ We find the most stable geometry by solving the Hamiltonian
- ✓ Our approach can be applied to any organic and inorganic materials
- ✓ There is no need for knowing the energies of the candidate geometries for finding the optimal one
- ✓ We don't need to calculate the gradients of the energies for the nuclei coordinates



Probabilistic Imaginary-Time Evolution (PITE) method

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

Approximate PITE circuit within first order of imaginary-time step $\Delta\tau$



Feature: Express ITE operator with real-time evolution operators (U_{RTE})

Input Output

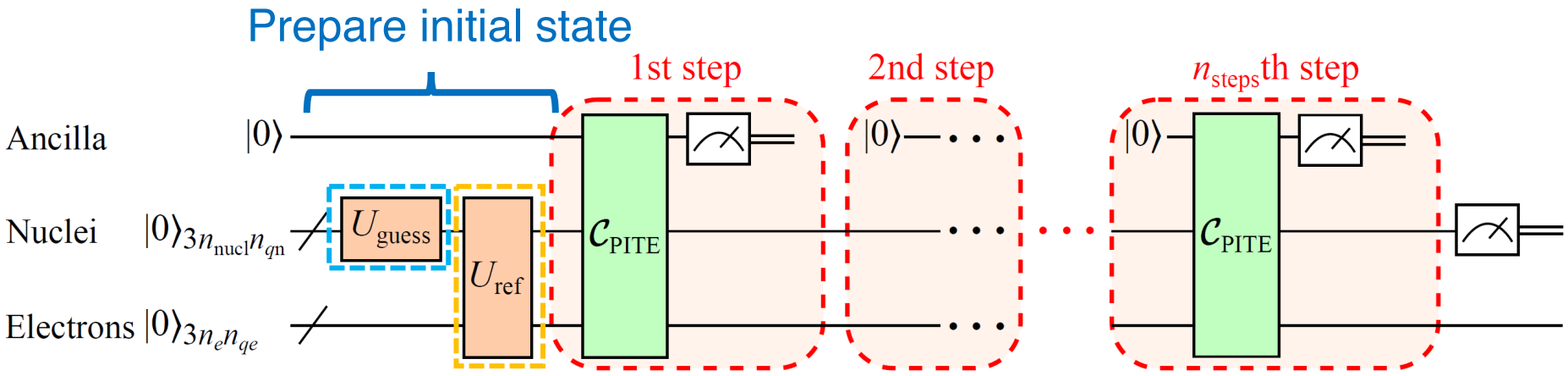
$$|\psi\rangle \otimes |0\rangle \longrightarrow \mathcal{M}|\psi\rangle \otimes |0\rangle + \sqrt{1-\mathcal{M}^2}|\psi\rangle \otimes |1\rangle$$

$$\mathcal{M} = \gamma e^{-\mathcal{H}\Delta\tau}$$

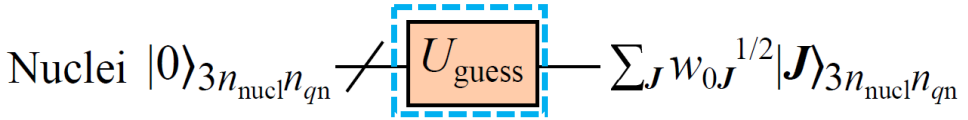
ancilla bit — success state — failure state

The approximate PITE circuit uses the Hamiltonian only as black boxes, so which can be applied to any types of Hamiltonian.

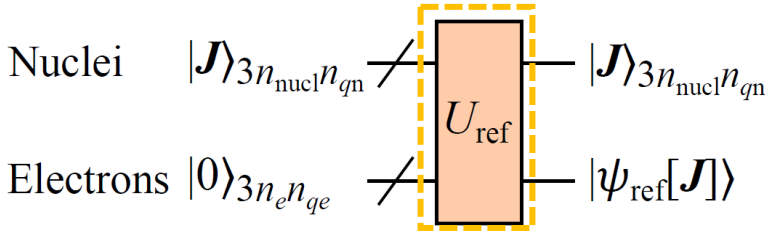
Circuit for PITE steps



Gate for giving initial weights to candidates
(If no information, equal weights are appropriate.)



Gate for generating reference electronic states



After sufficiently many steps, we measure a geometry |**J**> on nuclear register with the probability $w_{\boldsymbol{J}}$.

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

After sufficient PITE steps, the state with highest probability is the most stable geometry

Numerical results

(Example 1) Numerical simulations for a LiH model system

Structure optimization for nuclei coupled to electrons

(Example 2) Classical nuclei-only system as a special case

Structure optimization for only nuclei

(Example 3) Geometry optimization based on variational calculations

Structure optimization with variational method

(Example 1) Numerical simulations for a LiH model system

Setup

2 electrons and 2 atoms in 1d space,

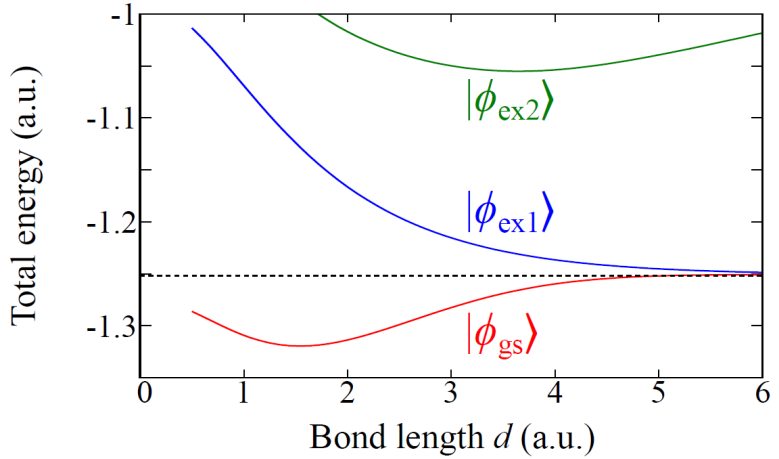
$Z_H = Z_{Li} = 1$ (Li 1s electrons frozen)

All interactions are soft-Coulomb type: $v_{\rm soft}(r;\lambda) \equiv \dfrac{1}{\sqrt{\lambda^2 + r^2}}$

Tempel et al, JCTC **5**, 770 (2009)

n_{qe} = 12 bits for n_e = 2 electrons
n_{qn} = 3 bits for nuclei

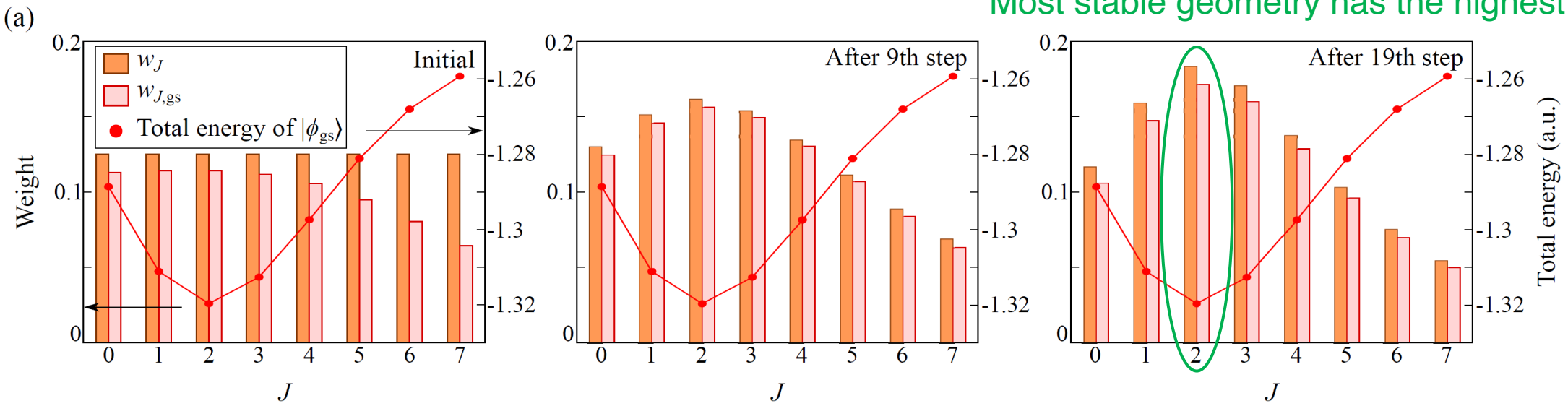
Numerical diagonalization



Geometry optimization

By using n_{qn} = 3 qubits, we tried 2^{nqn} = 8 candidate bond lengths for optimization: $d_J = 0.55 + 0.5J$ (J = 0, …, 7)

Most stable geometry has the highest prob.



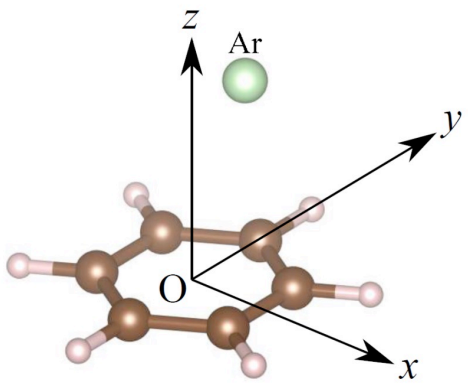
(Example 2) Classical nuclei-only system as a special case

Ar atom above a benzene molecule

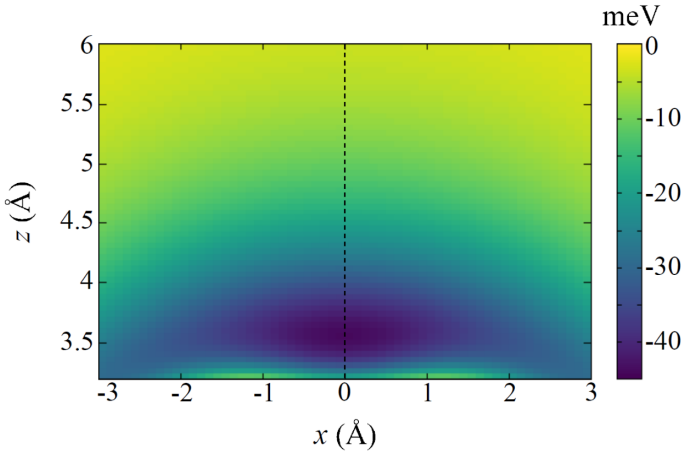
Treat only nuclei

Improved Lennard-Jones potential

Pirani et al, Chem. Phys. Lett. **394**, 37 (2004)



Interaction energy

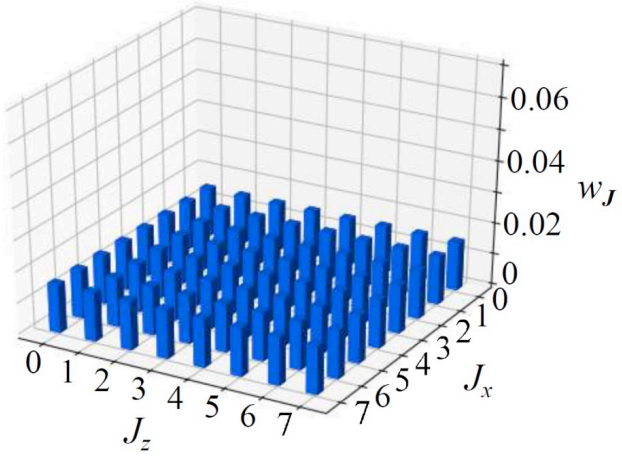


Geometry optimization using PITE

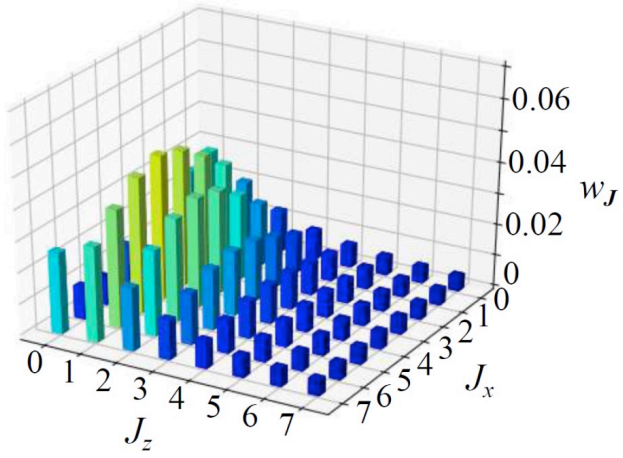
n_{qn} = 3 for each of *x* and *z* directions

Most stable geometry has the highest probability

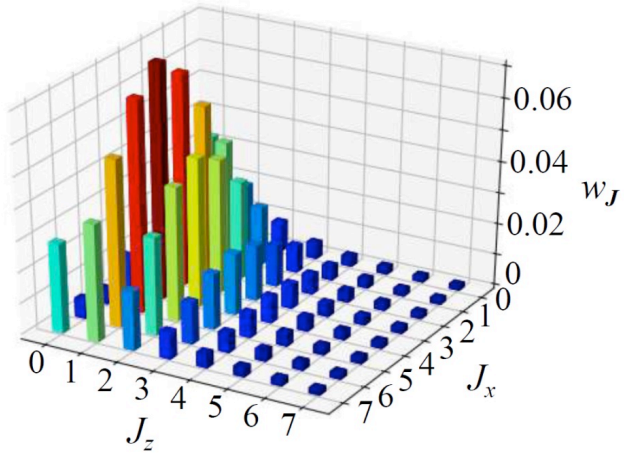
Initial



After 11th step



After 19th step



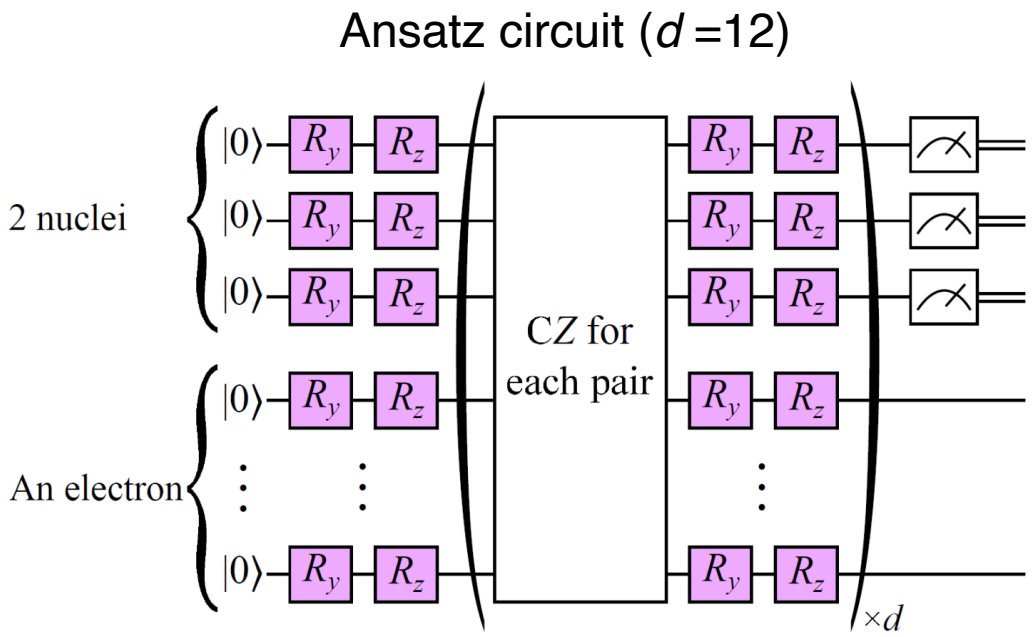
Reduce the number of qubits by using force-field

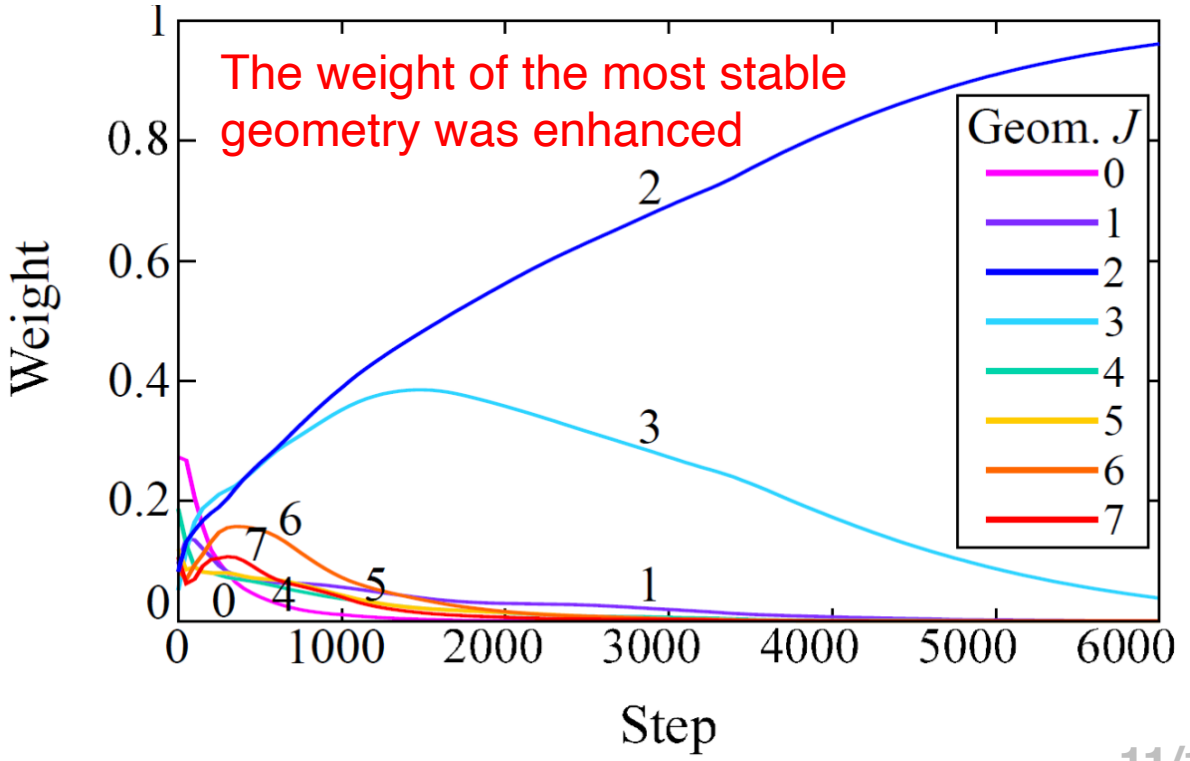
(Example 3) Geometry optimization based on variational calculation

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

Geometry optimization of H_2^+ model system

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



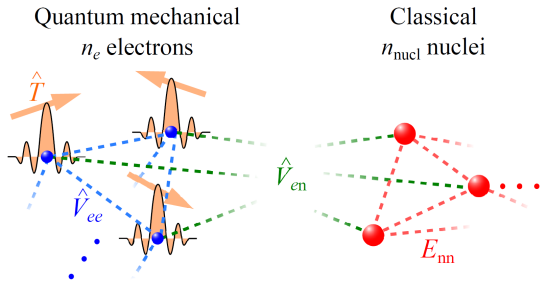


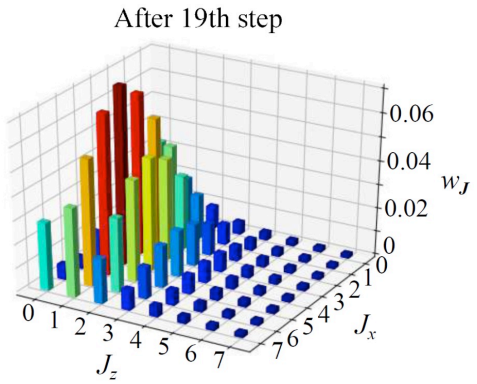
McLachlan, Mol. Phys. **8**, 39 (1964)
Jones et al., Phys. Rev. A **99**, 062304 (2019)

Conclusions

Summary

- ✓ Proposed a quantum algorithm for geometry optimization.
- ✓ The most stable geometry is calculated from a superposition of all candidate geometries.





This talk

Kosugi, Nishi, and Matsushita, arXiv:2210.09883

Related studies

Detail of PITE

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

Under a magnetic field

Kosugi, Nishi, and Matsushita, arXiv:2212.13800

With amplitude amplification

Nishi, Kosugi, Nishiya and Matsushita, arXiv:2212.13816