

# Designing complex molecular qubits by using QC simulator and relativistic quantum chemistry

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kuchemQCL

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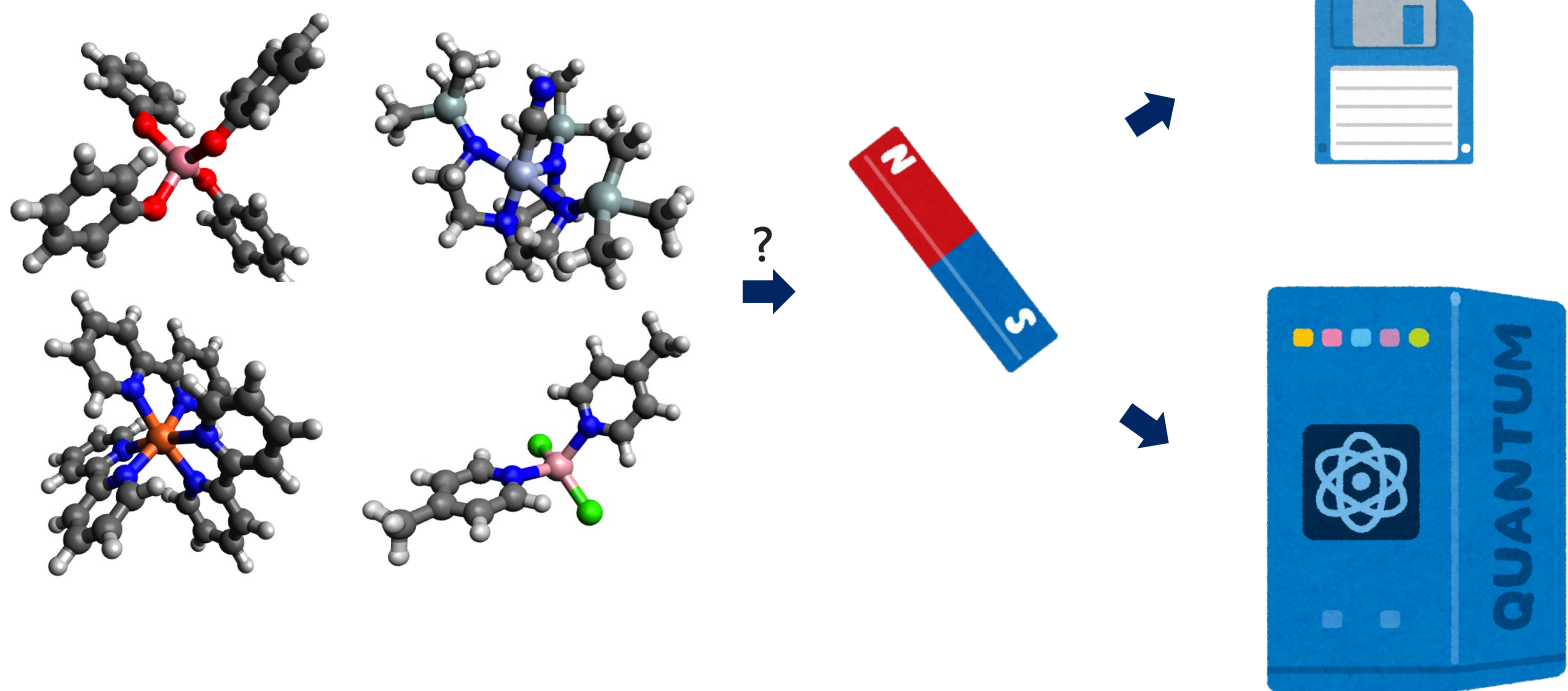
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# Introduction – Single-Molecule Magnets

## | Metal complex as molecular qubit candidate

Single-molecule magnets (SMMs) consist of metal-complex molecules that exhibit magnetic hysteresis below a blocking temperature ( $\sim 80$  K).

candidates for information storage, spintronics, and **molecular qubits**



# Introduction – Zero-field splitting

## | SMMs result from relativistic effects

In open-shell systems with **total spin of  $S \geq 1$** ,

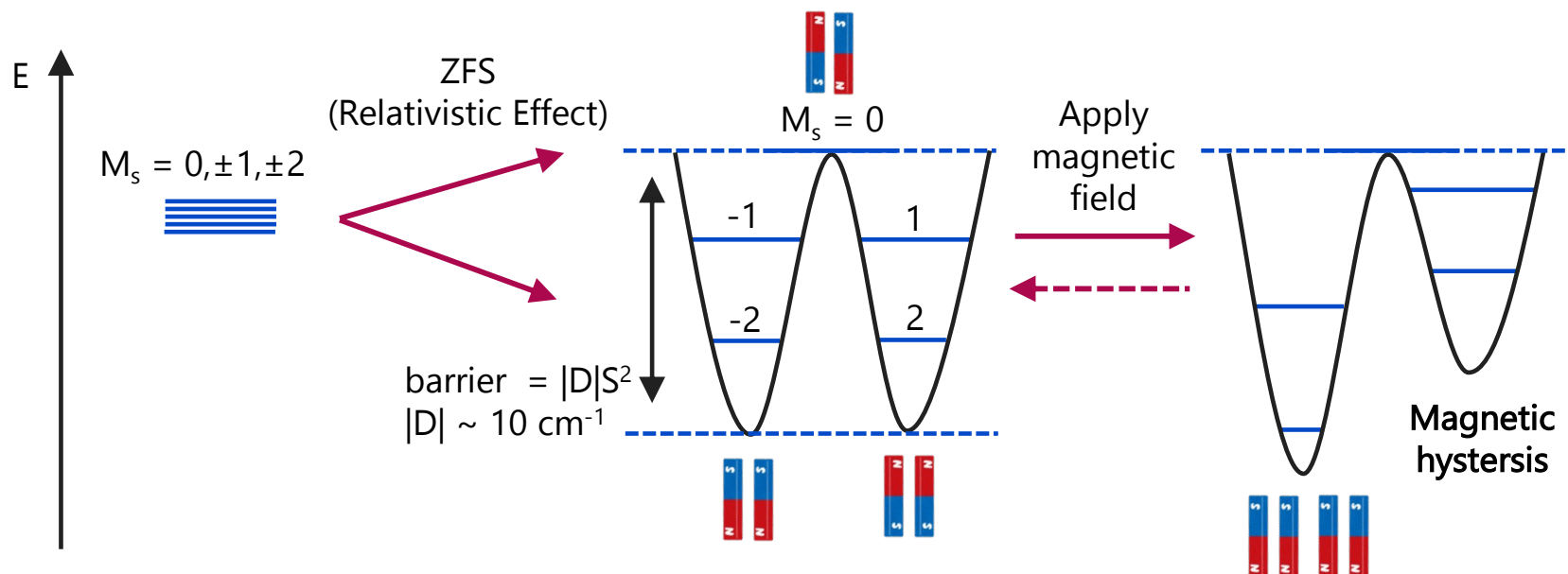
Degeneracy of ground spin multiplet is broken by **zero-field splitting (ZFS)**,

which results from **spin-orbit / spin-spin coupling (relativistic effect)**

**ZFS parameter,  $D$** , determines the energy barrier for reversal of spin (high barrier is better)

**A key to design SMMs**, efficiently calculated with relativistic quantum chemistry methods

e.g. a system with  $S=2$



# Our demonstration and its target molecule

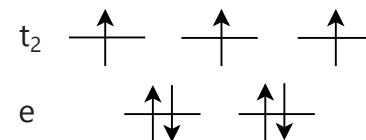
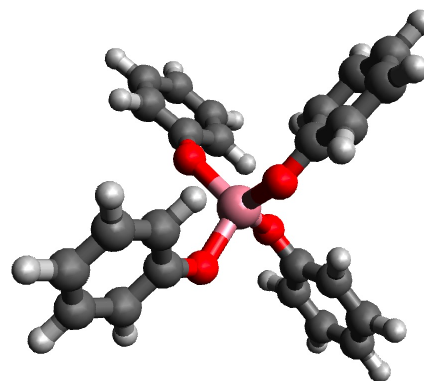
## | Target [Co(II)(OPh)<sub>4</sub>]<sup>2-</sup> complex

Formula : C<sub>24</sub>H<sub>20</sub>CoO<sub>4</sub> , **225** electrons

total spin is  $S=3/2$  (quartet)

experimental D value :  $-11.1 \text{ cm}^{-1} = 0.16 \text{ kcal/mol}$

ref. <https://linkinghub.elsevier.com/retrieve/pii/S0277538713002842>



## | Our demonstration plan

### Dirac-CASCI for [Co(II)(OPh)<sub>4</sub>]<sup>2-</sup> on VQE / SSVQE

$$\hat{H}_{\text{rel}} = \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} v_{pq,rs} \hat{E}_{pq,rs}$$

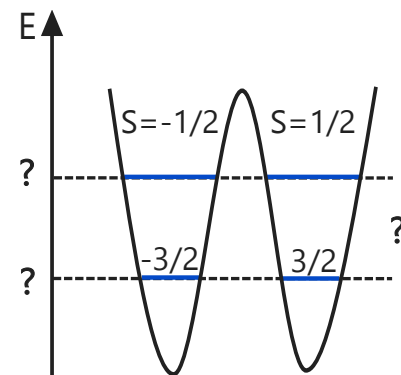
$$\hat{h}(1) = c^2(\beta - I_4) + c(\boldsymbol{\alpha}_1 \cdot \hat{\mathbf{p}}_1) - \sum_A^{\text{atoms}} \frac{Z_A}{r_{1A}} \text{erf}(\sqrt{\zeta_A} r_{1A})$$

$$\hat{v}(1,2) = \frac{1}{r_{12}} - \left( \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{r_{12}} + \frac{(\boldsymbol{\alpha}_1 \cdot \nabla_1)(\boldsymbol{\alpha}_2 \cdot \nabla_2)r_{12}}{2} \right)$$

Relativistic electronic Hamiltonian  
Complex-valued !

$$\langle \Psi_{\text{CAS}} | \hat{H}_{\text{rel}} | \Psi_{\text{CAS}} \rangle$$

Diagonalize  
Dirac-CASCI Hamiltonian



Obtain energies and D value

# Method 1. Classical-bit calculation

## | Relativistic quantum chemistry calculations

We performed Dirac-HF and subsequently Dirac-CASSCF calculation to **obtain exact energies** and **coefficients of the second-quantized H**

$$\hat{H}_{\text{rel}} = \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} v_{pq,rs} \hat{E}_{pq,rs}$$

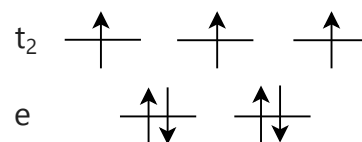
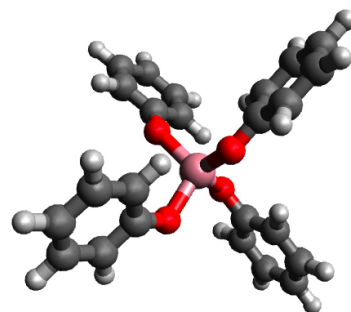
$$\hat{h}(1) = c^2(\beta - I_4) + c(\boldsymbol{\alpha}_1 \cdot \hat{\mathbf{p}}_1) - \sum_A^{\text{atoms}} \frac{Z_A}{r_{1A}} \text{erf}(\sqrt{\zeta_A} r_{1A})$$

$$\hat{v}(1,2) = \frac{1}{r_{12}} - \underbrace{\left( \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{r_{12}} + \frac{(\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla}_2)r_{12}}{2} \right)}_{\text{Omitted in our calculations}}$$

Omitted in our calculations

## | CAS wavefunction and FCIDUMP

1e- and 2e-integrals of active orbitals are obtained as FCIDUMP format  
→ Hamiltonian coefficient files for next steps



CAS consists of 7 electrons in 5 3d-orbitals

## | Packages and reference

We used **BAGEL** (developed by Shiozaki group @ Northwestern Univ., <https://nubakery.org>) to perform Dirac-HF and Dirac-CASSCF

ref. <https://doi.org/10.1016/j.poly.2013.04.008>

# Method 2. Quantum algorithm

## | Quantum algorithm

We utilized Dirac-CAS Hamiltonian obtained with BAGEL for VQE / SSVQE algorithms followed Quantum Native Dojo article 6.2 and 6.3

ref. [https://dojo.qulacs.org/ja/latest/notebooks/6\\_quantum\\_chemistry\\_calculation.html](https://dojo.qulacs.org/ja/latest/notebooks/6_quantum_chemistry_calculation.html)

Ansatz : hardware-efficient like

Noise free

Depth is equal to the number of qubits, that is, 2 x the number of active orbitals

## | Cost function for SSVQE

It is reported that **VQE / SSVQE are not efficient for degenerate systems**

ref. <http://arxiv.org/abs/2111.02448>

→We tried to avoid this problem by **tuning weights in the cost function**

## | Packages

We used OpenFermion, Qulacs, SciPy, and some self-made python scripts

# Implementation efforts 1

## | Symmetry for 2e-integrals of Dirac-HF/CASSCF

Integrals terms in FCIDUMP that can be restored from symmetry are omitted in the files

→ We implemented scripts that fills missing terms ( fill\_fcidump.py )

Orbital swap

$$(pq|rs) = (qp|sr)^*$$

Electron swap

$$(pq|rs) = (rs|pq)$$

Kramers permutation

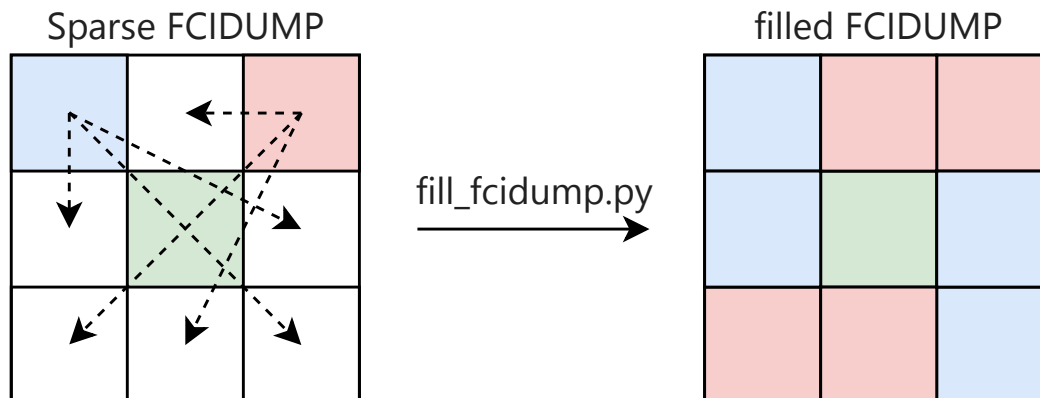
$$(pq|rs) = (pq|\bar{s}\bar{r}) = (\bar{q}\bar{p}|rs) = (\bar{q}\bar{p}|\bar{s}\bar{r})$$

$$(\bar{p}q|rs) = (\bar{p}q|\bar{s}\bar{r}) = -(\bar{q}p|rs) = -(\bar{q}p|\bar{s}\bar{r})$$

$$(\bar{p}q|\bar{r}s) = -(\bar{p}q|\bar{s}r) = (\bar{q}p|\bar{r}s) = (\bar{q}p|\bar{s}r)$$

$$(\bar{p}q|r\bar{s}) = -(\bar{p}q|s\bar{r}) = -(\bar{q}p|r\bar{s}) = (\bar{q}p|s\bar{r})$$

(We implemented, but not necessary for BAGEL)



ref. <https://doi.org/10.1063/1.3592148>

# Implementation efforts 2

## | Adaptation of complex-valued Hamiltonian

Coefficients of relativistic Hamiltonian are **complex-valued**

However,

**Qamuy** (experimentally) supported **only real-valued FCIDUMP**

and **|Q>** Qulacs only accepts **Pauli products with real-valued coefficients**

→ We defined cost function as

$$\langle \Psi(\theta) | \text{Re}(H_{\text{rel}}^{\text{Pauli}}) | \Psi(\theta) \rangle - \underbrace{\langle \Psi(\theta) | \frac{1}{i} \text{Im}(H_{\text{rel}}^{\text{Pauli}}) | \Psi(\theta) \rangle}_{\text{Hermite!}}$$

Anti-Hermite

to adjust for Qulacs



# Workflow of our demo

## Libraries



## Processes

Dirac Hartree-Fock and  
Dirac CASSCF  
Classical-bit calculation



Complex-valued FCIDUMP  
 $E_{\text{core}}$ , part of terms  $(p|q)$  and  $(pq|rs)$   
Exact values for comparison



our script

Fill missing integral terms  
by using symmetry rules



Complete  $(p|q)$  and  $(pq|rs)$   
Get second quantized  $\hat{H}$



OpenFermion

JW transformation



JW Hamiltonian  
(Sum of Pauli operator products)



Qulacs

Set quantum circuit  
VQE / SSVQE



Cost function (No sampling)



SciPy

Minimize cost function  
(BFGS method)



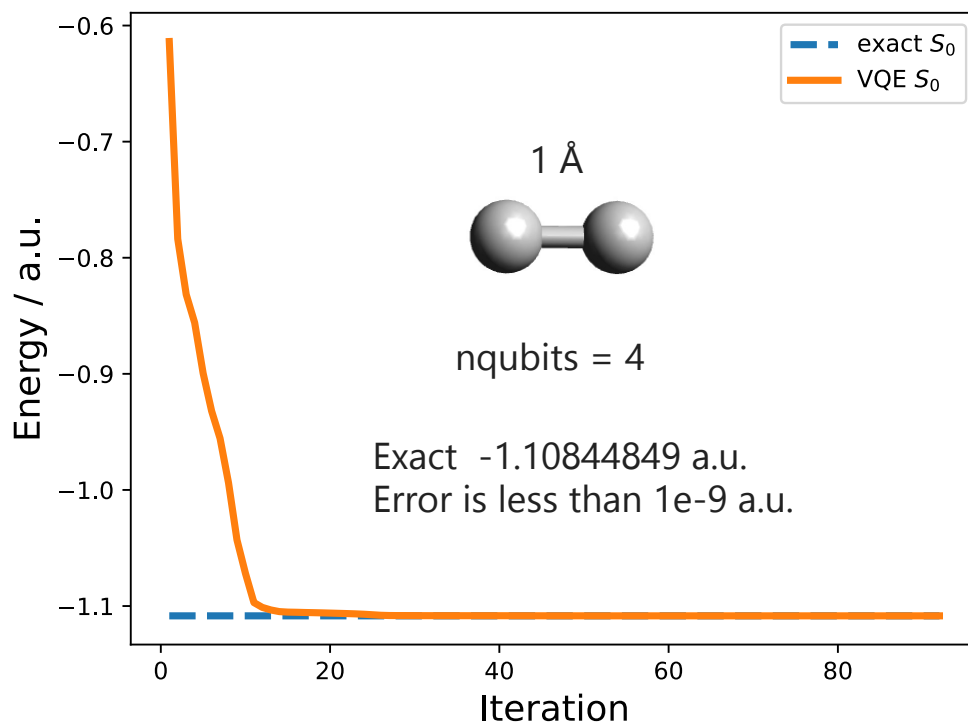
CASCI Energy, CI coefficients

# Result 1. H<sub>2</sub> (benchmark)

Demonstrations for small molecules, relativistic VQE-CASCI

Exact values are obtained with BAGEL

| Ground state of H<sub>2</sub>, CAS(2e, 2o)



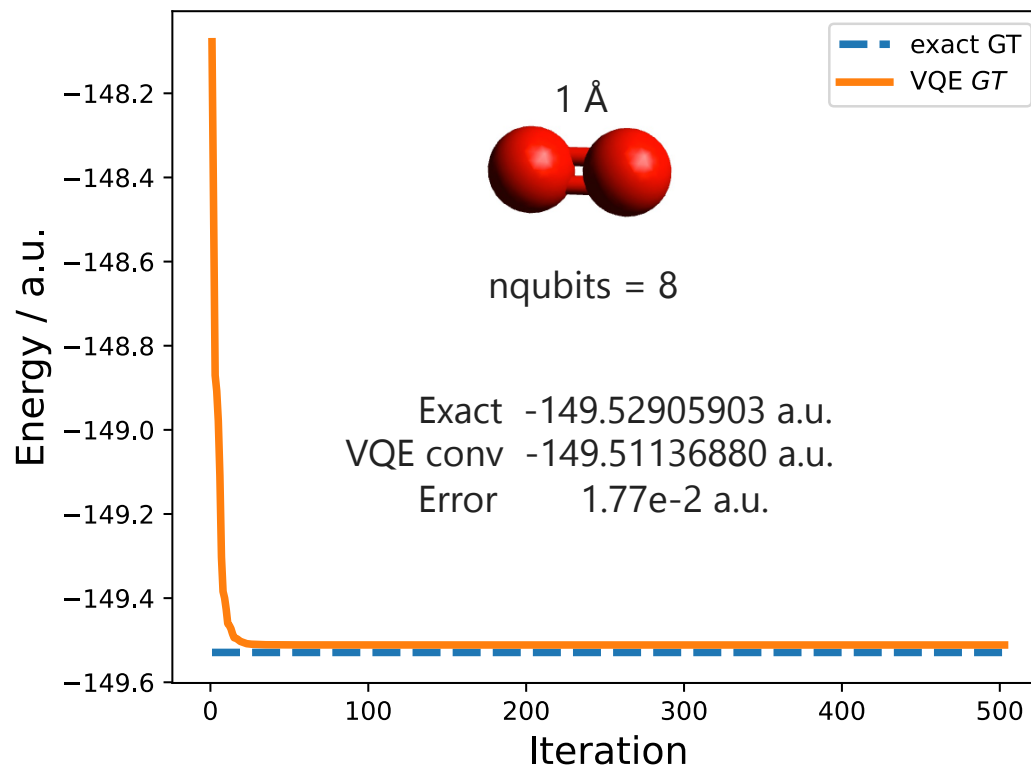
Well converged! Implementation validated

## Result 2. O<sub>2</sub> (benchmark)

Demonstrations for small molecules, **relativistic VQE-CASCI**

Exact values are obtained with BAGEL

| Ground triplet of O<sub>2</sub> , CAS(4e, 4o)



Degenerate triplets  
(Exact)

0 : -149.52905903

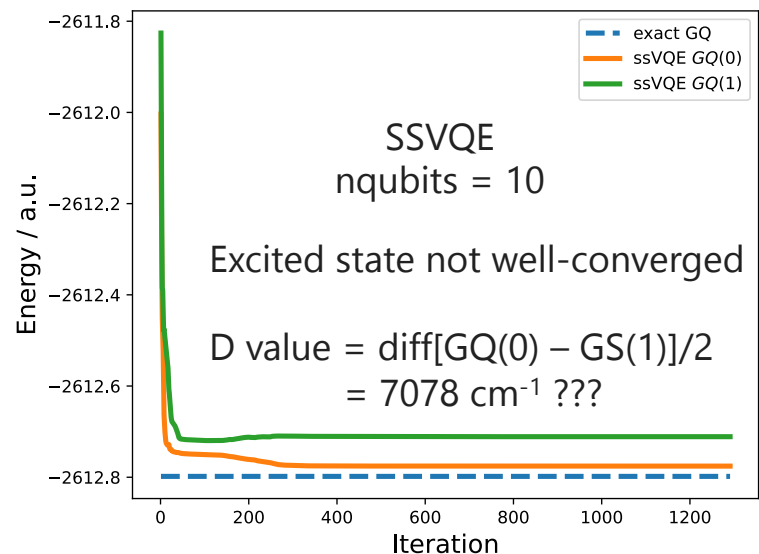
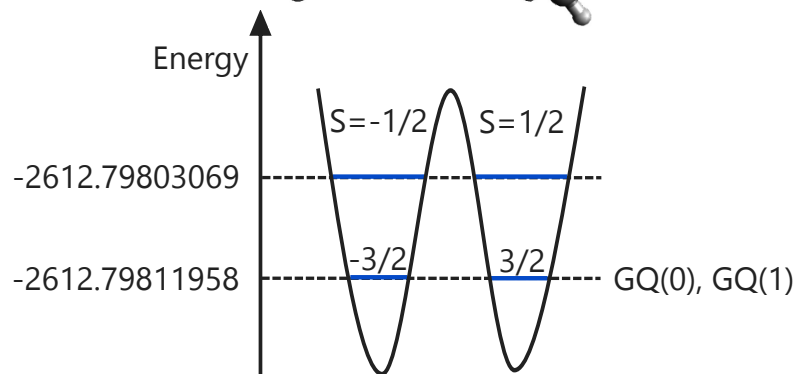
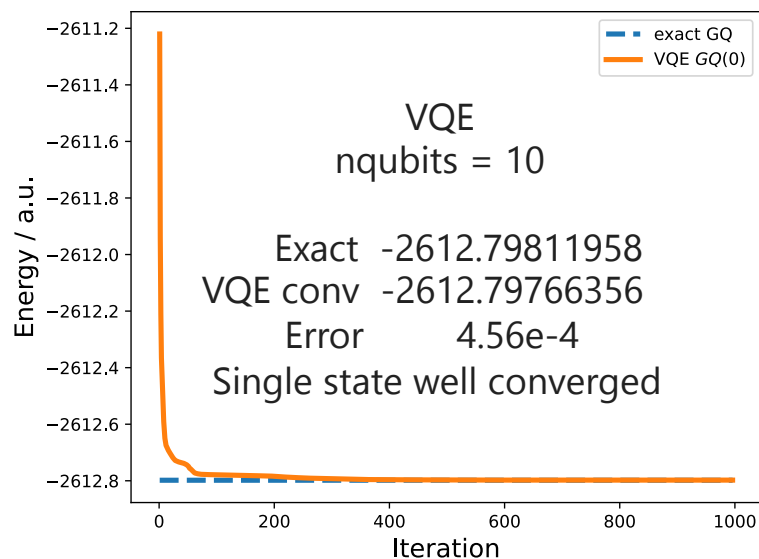
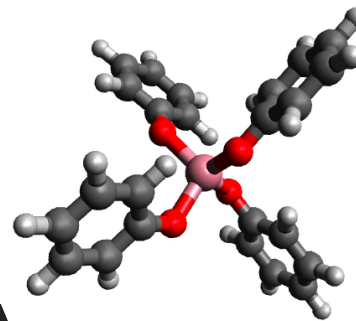
1 : -149.52353159

2 : -149.52353157

Not well converged due to degeneracy ? Ansatz error ?

# Result 3. $[\text{Co(OPh)}_4]^{2-}$

## | Ground Quartets of $[\text{Co(OPh)}_4]^{2-}$ , CAS(7e, 5o)



Cost function for SSVQE is tuned as

$$L(\theta) = 2\langle \text{GQ}(0) | \hat{H} | \text{GQ}(0) \rangle + 1\langle \text{GQ}(1) | \hat{H} | \text{GQ}(1) \rangle$$

→ weights should be tuned further?

largely dependent on  $\theta_{\text{init}}$ ,

ansatz error ?

# Conclusions

We present Dirac-CASCI simulation of  $[\text{Co(II)(OPh)}_4]^{2-}$  on VQE / SSVQE

Our efforts : implementation of Dirac-CASCI on VQE / SSVQE

cost function for relativistic Hamiltonian

excited state calculation

weight tuning for cost function of SSVQE

→ see README.md for more detail !!!

Energy is well-converged for  $\text{H}_2$  molecule → our implementation is validated

Single state VQE for  $[\text{Co(II)(OPh)}_4]^{2-}$  converged well

Energies are not well-converged for degenerate systems ( $\text{O}_2$  and  $[\text{Co(II)(OPh)}_4]^{2-}$ ) due to weights of SSVQE cost function, degeneracy, or ansatz...?

# Improvement plans

## | Ansatz

In this challenge, we used hardware-efficient like ansatz in Dojo 6.2 and 6.3

→ UCCD / UCCSD ansatz or fermionic-adaptive ansatz should be better?

If ansatz that includes Kramers symmetry is developed, it should be very efficient

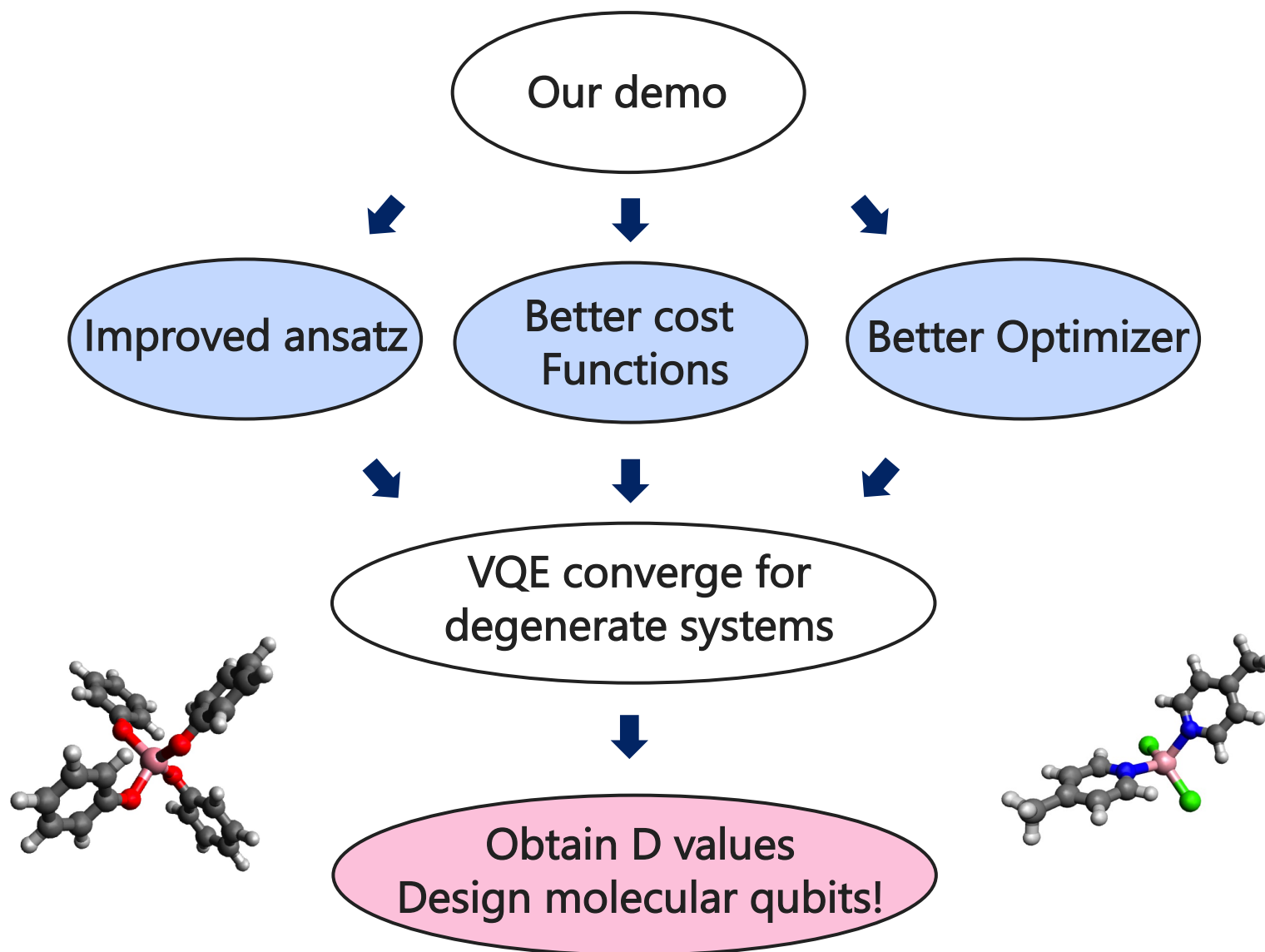
## | Cost function for SSVQE

Adding a penalty term for reversal of two degenerate states?

$$\begin{aligned} L(\theta) = & c_0 \langle \text{GS}(0) | \hat{H} | \text{GS}(0) \rangle \\ & + c_1 \langle \text{GS}(1) | \hat{H} | \text{GS}(1) \rangle \\ & + \text{penalty}(\text{GS}(0) \leftrightarrow \text{GS}(1)) \end{aligned}$$

→ We could not develop this term in this challenge

# Prospects



# Members and Acknowledgements

## | Members of team kuchemQCL

NISHIO, Soichiro – team management, research, classical calculation, coding, and presentation

HINO, Kentaro – coding, research, team management, and presentation

UEDA, Koki - coding

MIYOKAWA, Katsuki – classical calculations

TSUMURA, Masaya - coding

YOSHIDA, Takumi – classical calculations

We are graduate students at theoretical chemistry lab. of Graduate School of Science, Kyoto University

## | Acknowledgements

We thank theoretical chemistry lab. of Graduate School of Science, Kyoto University,  
and GOTO Gaku (alumnus) for calculation data of  $[\text{Co(II)(OPh)}_4]^{2-}$  in his master thesis (2022)



# Thank you for listening!

