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

kuchemQCL

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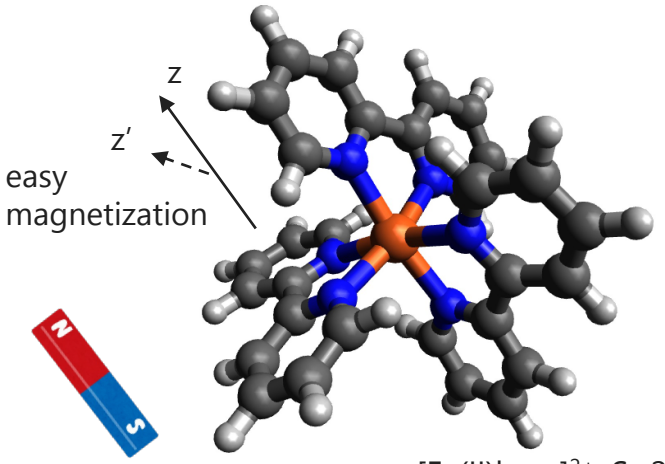
Introduction

| Metal complex as molecular qubit candidate

Single molecule magnets (SMMs) are candidates for molecular qubits

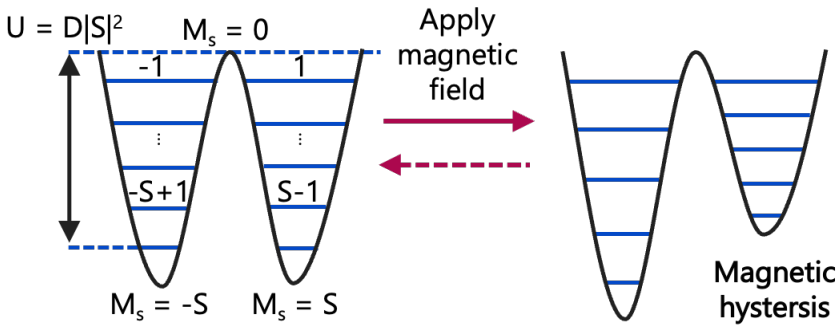
Metal complex molecules that have total spin of S>1 shows zero-field splitting (ZFS), which leads to magnetic hysteresis

ZFS parameter, D, is a key to design SMMs, which can be efficiently calculated by wavefunction theories



e.g. $[Fe(II)bpy_3]^{2+}$, S=2

When S>1, ZFS appears

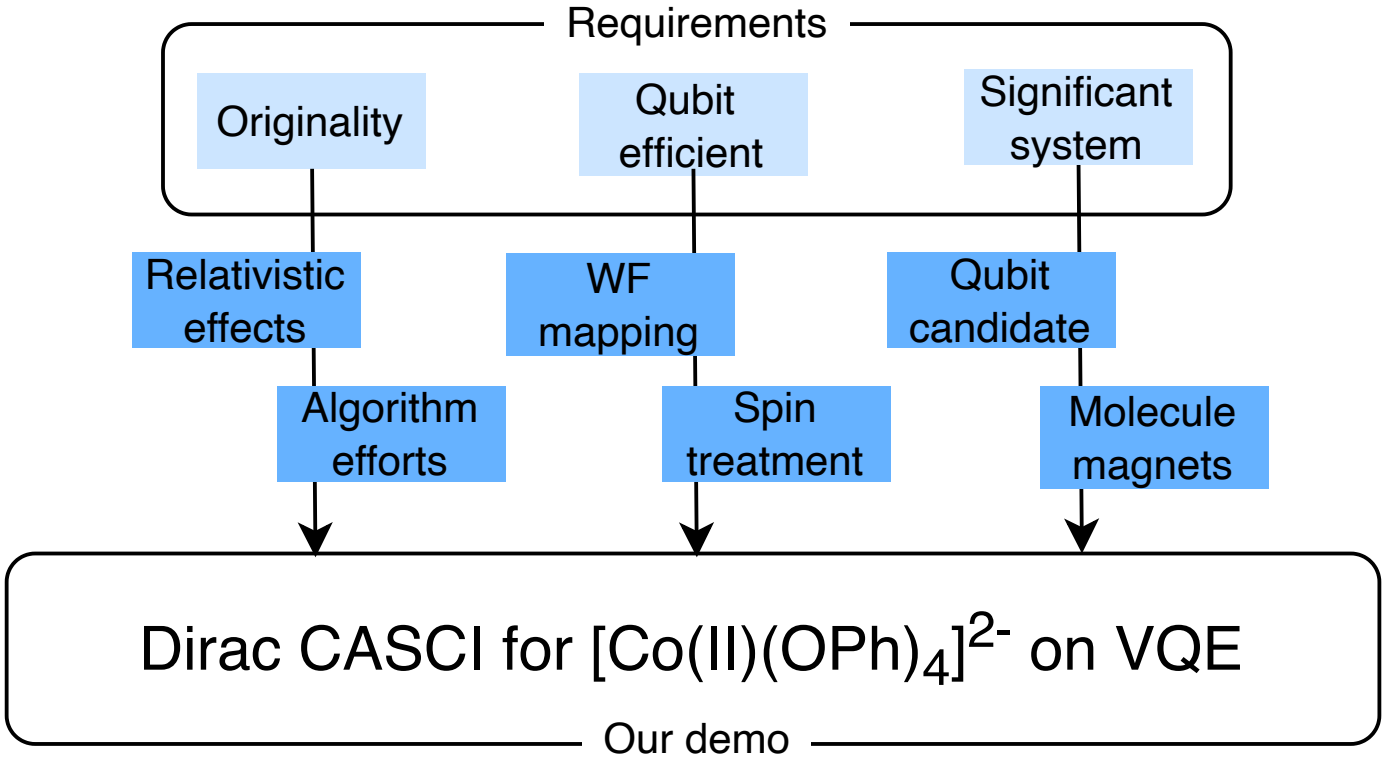


| Relativistic calculation is needed

Spin-orbit coupling should be considered in these systems

→ **relativistic quantum chemistry methods**

Our demonstration

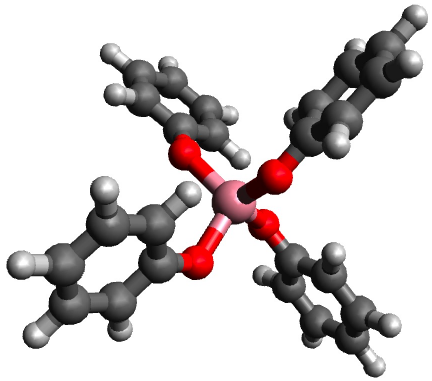


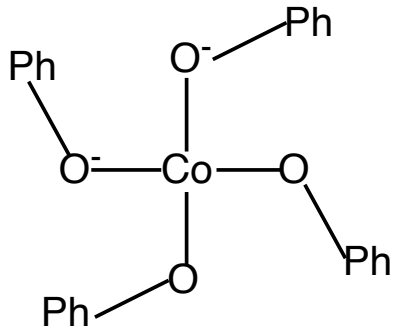
| $[Co(II)(OPh)_4]^{2-}$ complex

Formula : $C_{24}H_{20}CoO_4$, 225 electrons

Total spin is S=3/2 (quartet)

ref. https://doi.org/10.1021/ja2100142





Method 1. Classical calculation

| Relativistic quantum chemistry calculations

We used Dirac-Coulomb Hamiltonian

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

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

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

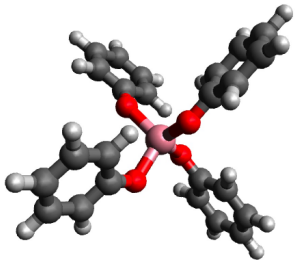
Omitted in our calculations

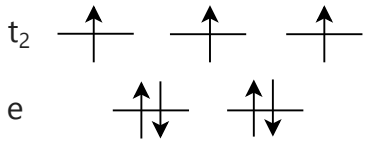
We performed Dirac-Hartree-Fock (Dirac-HF) and subsequently Dirac-complete active space self-consistent field (Dirac-CASSCF) method to obtain exact values

| CAS wavefunction and FCIDUMP

1e- and 2e-integrals of active orbitals are obtained as FCIDUMP format

Sum of nuclear and core orbital energy is treated as constant





CAS consists of
7 electrons in 5 3d-orbitals

| Packages and reference

We used **BAGEL** (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 / SS-VQE algorithms

ref. https://dojo.qulacs.org/ja/latest/notebooks/6_quantum_chemistry_calculation.html

Anzats : hardware-efficient

Noise free

Depth is equal to the number of qubits

| Cost function for SS-VQE

It is reported that VQE / SS-VQE 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

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

Integrals in FCIDUMP that can be restored from symmetry **are not written in the files!**

→ We implemented scripts that fills integral matrices (fill_fcidump.py)

Orbital swap

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

Electron swap

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

Kramers permutation

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

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

| Adaptation of complex-valued Hamiltonian

In Qamuy and Qulacs, complex-valued FCIDUMP and Anti-Hermite Pauli operators are not supported

→ We defined cost function as

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

Workflow of our demo

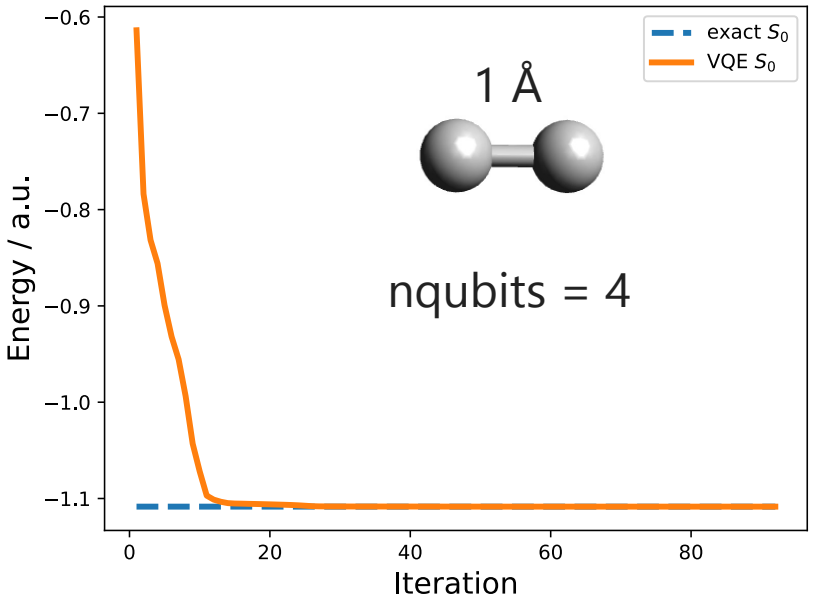
Libraries	Processes	Returns
BAGEL	Dirac Hartree-Fock and Dirac CASSCF	Complex-valued FCIDUMP E_{core} , part of matrices $(p\|q)$ and $(pq\|rs)$ Exact values for comparison
our script	Fill integral matrices by using symmetry rules	Complete matrices $(p\|q)$ and $(pq\|rs)$
OpenFermion	Get second quantized $\hat{H}$ JW transformation	JW Hamiltonian (Sum of Pauli operator products)
Qulacs	Set quantum circuit VQE / SS-VQE	Cost function (No sampling)
SciPy	Minimize cost function (BFGS method)	CASCI Energy, CI coefficients

Result 1. H_2 and O_2

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

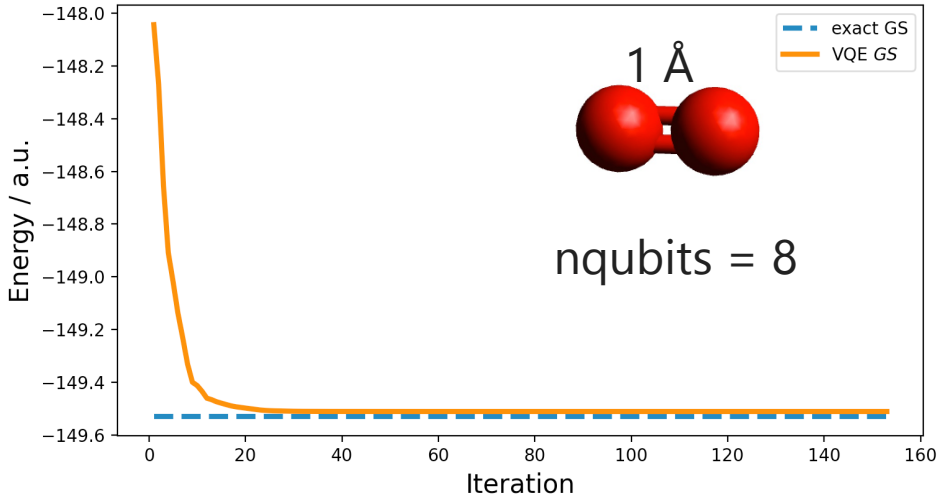
Exact values are obtained with BAGEL

| H_2 in singlet states, CAS(2e, 2o)



Exact -1.10844849 a.u.
Error is less than 1e-9 a.u.
Well converged!

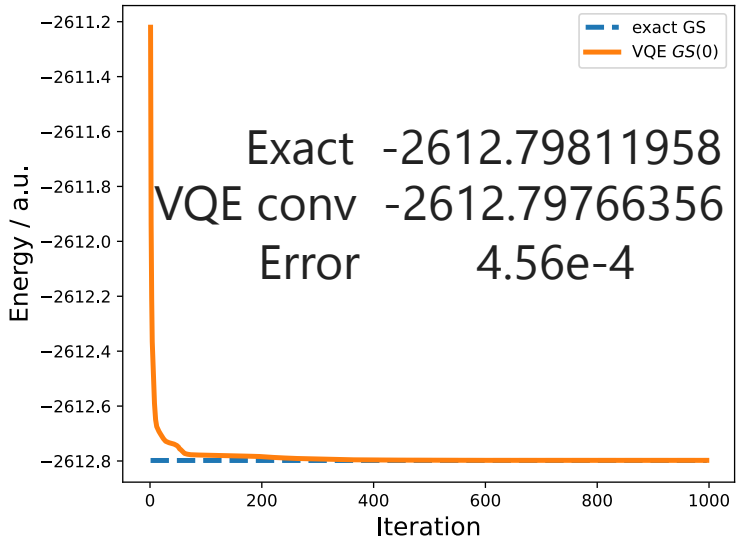
| O_2 in triplet states, CAS(4e, 4o)

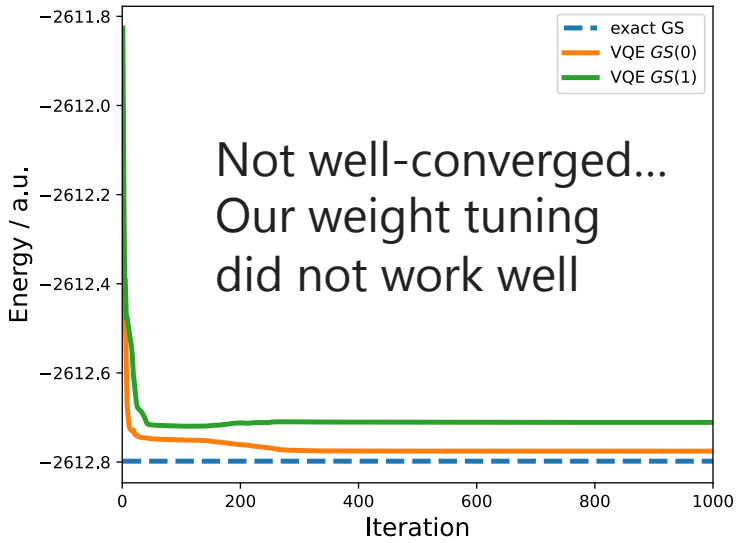


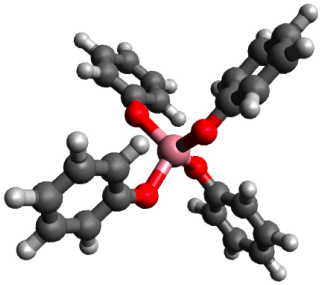
Exact -149.52905903 a.u.
VQE conv -149.51136880 a.u.
Error 1.77e-2 a.u.

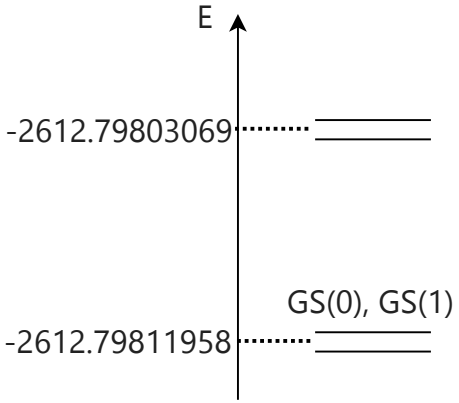
Result 2. $[Co(OPh)_4]^{2-}$

| $[Co(OPh)_4]^{2-}$ complex, CAS(7e, 5o)









GS is 4-tet (s = 3/2)
Degenerate as above

Cost function is tuned as

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

→weights should be tuned further?
largely dependent on θ_{init}
difficult to conv at global min.

Conclusions, Members, and Acknowledgements

| Conclusions

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

Our efforts : cost function and weight tuning **see README.md for more detail!!!**

Energy convergence is not good, due to weights of SS-VQE cost function, degeneracy, or anzats…?

Future prospects : fix convergence problem, **obtain D value from SS-VQE**, orbital optimization…?

| 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

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