Research Activity in Nakai Group

Target	Algorithm	Theory
Nuclear Wavefunction	**NOMO**	NOMO-HF NOMO-MBPT NOMO-CC
Ground State	**DC**	DC-HF DC-DFT DC-DFTB
Electron Correlation	**DC**	DC-MP2 DC-CCSD DC-CCSD(T)
Excited State	**DC**	DC-TDDFT DC-CCLR DC-TDDFTB
Ground-State Dynamics	MD	DC-DFTB-MD DC-DFTB-MetaD
Non-adiabatic Dynamics	FSSH	DC-TDDFTB-FSSH DC-SF-TDDFTB-FSSH
Relativity	**LUT**	LUT-IOTC LUT-IOTC/LUT-IOTC
Machine Learning	ML	ML-EC ML-KEDF

Program

GAMESS

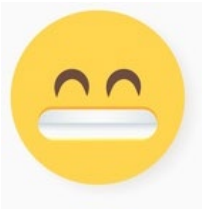
DCDFTBMD

RAQET
RELATIVISTIC AND QUANTUM ELECTRONIC THEORY

??

Programing in Nakai Group

- … Mark seems to like **LUT** more than the other relativistic methods.



GAMESS Documentation

```
$CONTRL group
…
RELWFN    Selects all-electron scalar relativity treatment.
          See the $RELWFN input group for more information,
          including nuclear derivative availability.
        = NONE use the basic Schrodinger equation (default)
        = LUT-IOTC local unitary transformation modification
                   of IOTC, due to H.Nakai, J.Seino, Y.Nakajima.
                   This is the fastest and most numerically
                   reliable scalar relativity method, so it is
                   preferred over RESC, DK, or IOTC.
        = IOTC infinite-order two-component method of …
        = DK   Douglas-Kroll transformation, available at …
        = RESC relativistic elimination of small component,…
        = NESC normalised elimination of small component,…
```

Function of DCDFTBMD Program

Function	
Energy, Gradient, Hessian	Closed-shell system: DFTB1/2/3, Orbital resolved SCC Open-shell system: Spin-polarized DFTB
Linear-scaling method	Divide and conquer (DC)
Charge-charge interaction	Ewald, FMM, Spline interpolation
SCC corrections	Chemical potential equalization, DFTB+U, Weighted Mulliken scheme, On-site corrected DFTB, Long-range correction (LC-DFTB2), Finite-temperature calculation, Point charge for external field effect, Static electric field for external field effect Implicit solvation model (GBSA/ALPB)
SCC convergence	Broyden, Simple mixing, Anderson, DIIS
Excited-state calculation	Time-dependent DFTB, Spin-flip time-dependent DFTB
Dispersion correction	Slater-Kirkwood, Lennard-Jones, DFT-D2/D3/D4, DFT-ulg, dDMC, D3H4, D3H5, D3X, DFT-TS, MBD
Property evaluation	Mulliken charge, CM3/CM5 charge, Mayer bond order, Dipole moment, Static polarizability, Atom resolved energy

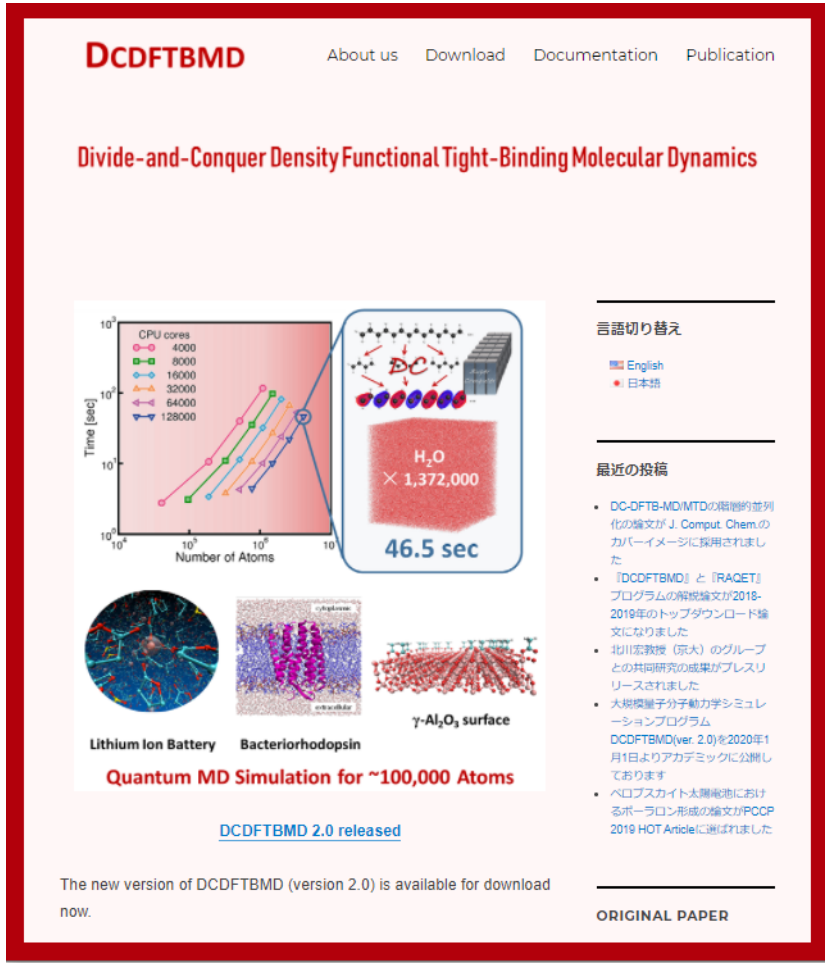
Function of DCDFTBMD Program *(cnt'd)*

Function	
Local geometry optimization	BFGS, Steepest descent, Conjugate gradient, Quick-min, FIRE
Global optimization	Monte Carlo minimization (Basin hopping)
Reaction path finding	Nudged elastic band (NEB)
Transition state search	Dimer method
Vibrational analysis	Harmonic frequency, IR intensity, Raman activity, Thermochemical quantities
MD ensemble	NVE, NVT, NPT
MD thermostat	Velocity scaling, Nose-Hoover chain, Berendsen, Andersen
MD option	RATTLE, Soft potential, Lagrange interpolation initial guess charge, Least square fitting initial guess charge
MD sampling	Metadynamics (MetaD), Well-tempered metaD, Multiple-walkers metaD, Replica exchange MD, Parallel-tempering metaD
Non-adiabatic MD	Fewest switches trajectory surface hopping (FSSH)
Quantum dynamics	Path Integral MD (PIMD), Ring Polymer MD (RPMD)

Release of DCDFTBMD Program

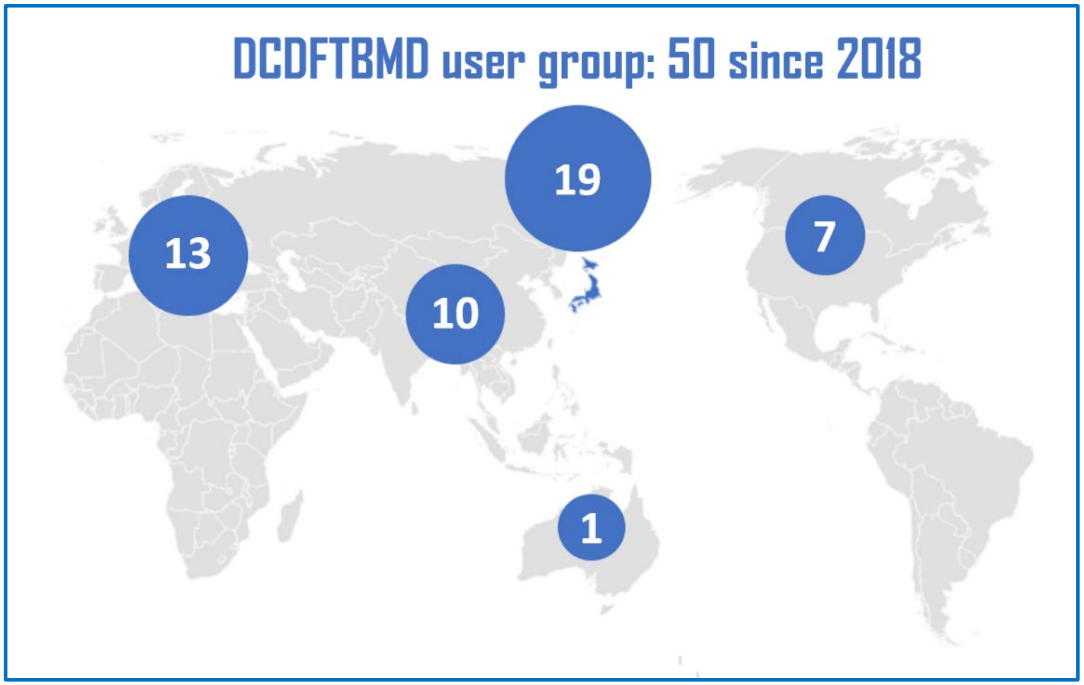
Release as academic-free software

- http://www.chem.waseda.ac.jp/dcdftbmd
- November 1st, 2018



Worldwide users

(2020.10.10)



Y. Nishimura, H. Nakai, *J. Comput. Chem.*, **40**, 1538 (2019).
Y. Nishimura, T. Yoshikawa, H. Nakai, *J. Comput. Chem. Jpn.*, **17**, A21 (2018).

Large-Scale Reaction Simulation

- Bond formation/cleavage
- Electron transfer

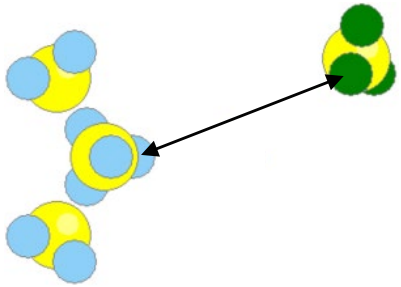
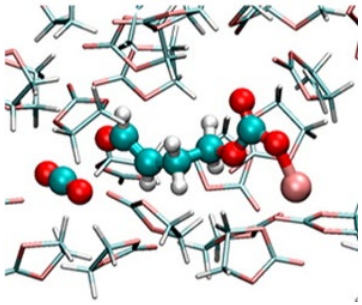
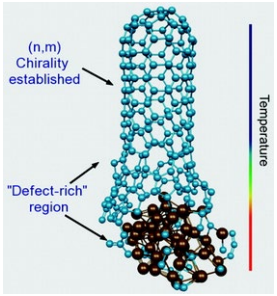
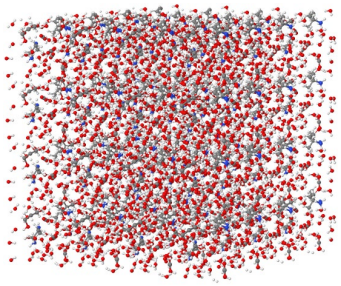
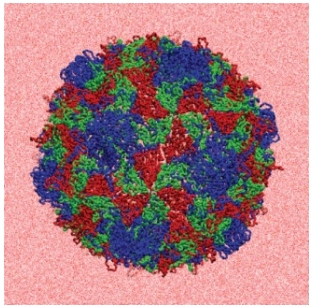
→ Quantum Mechanics (QM)

- Dynamical behavior

→ Molecular Dynamics (MD)

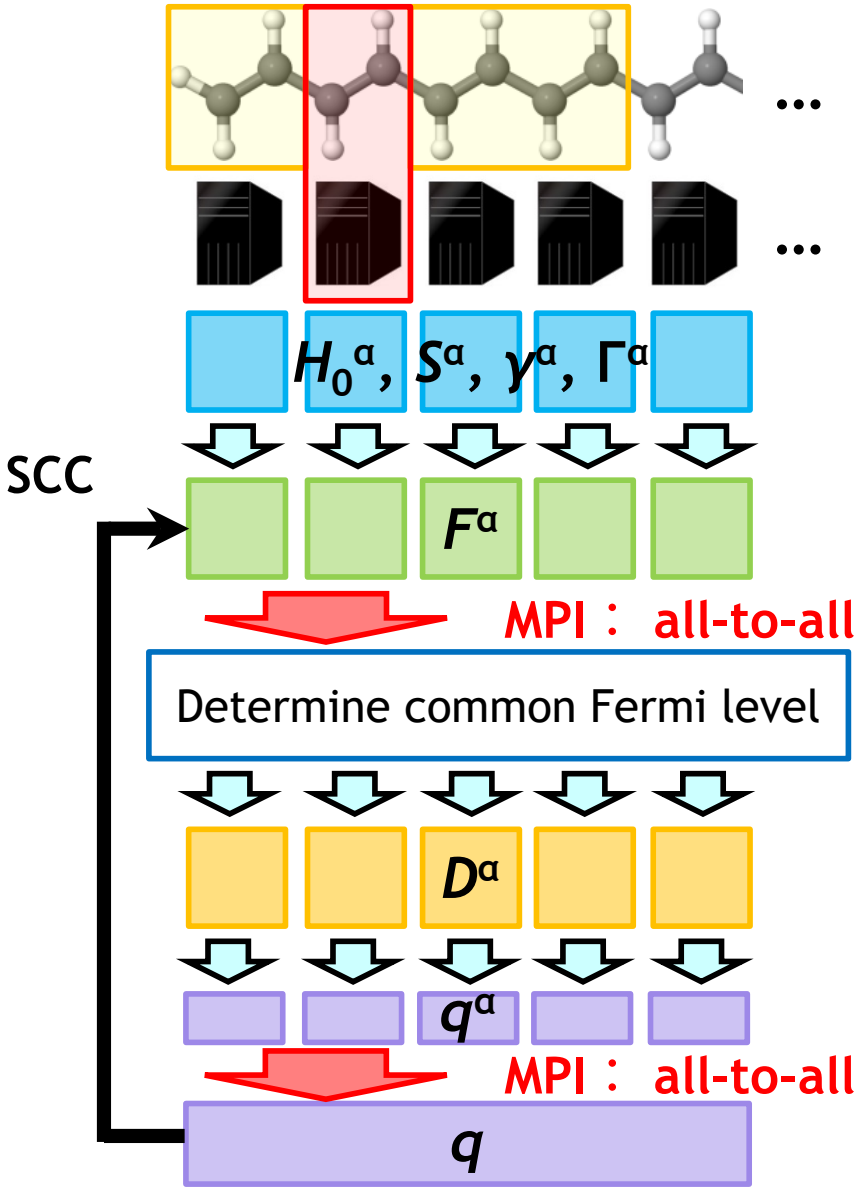
- Tens of thousands of atoms

→ Linear-Scaling Method

QM-MD				Classical MD
WFT	DFT	DFTB	DC-DFTB	MM
Cluster collision	Electrolyte decomposition	Growth of nanotube	CO_2 chemisorption	Virus
				
< 100	< 1,000	< 1,000	~1,000,000	~10,000,000

Big gap!!

Massive-Parallel DC-DFTB Code



1) Assign each fragment to each node

2) Determine localization region and save its information

3) Calculate E^{rep}

4) Calculate H_0^a & S^a

5) Calculate γ^a & Γ^a

6) Calculate E_{DFTB}

7) Construct Fock matrix, F^a

8) Diagonalize F^a

9) Construct subsystem's density matrix, D^a

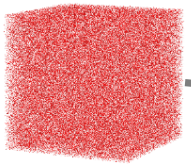
10) Calculate subsystem's charge, q^a

11) Calculate total charge, q

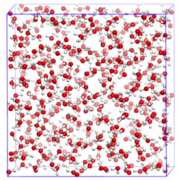
H. Nishizawa, Y. Nishimura, K. Kobayashi, S. Irle, H. Nakai, *J. Comput. Chem.*, **37**, 1983 (2016).

Applications of DCDFTBMD Program

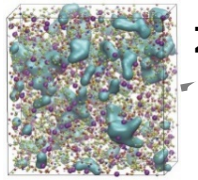
Water box
(~23×10^6 atoms)



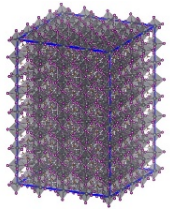
OH- containing
aqueous solution
(*JPCB*, 2017)

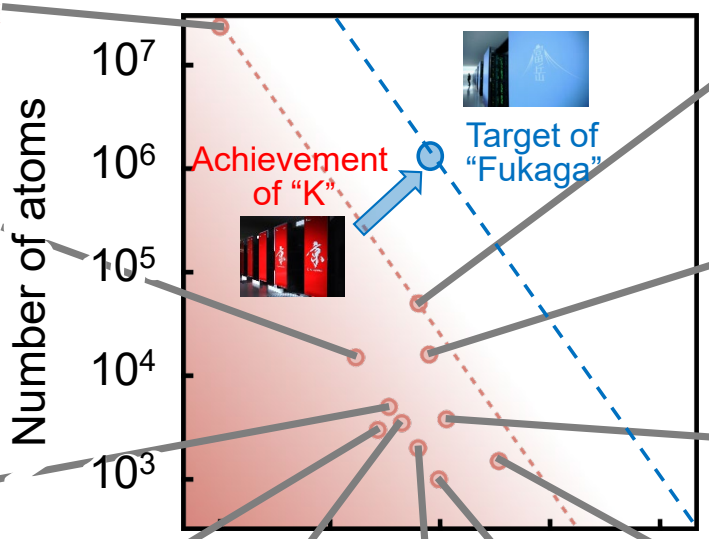


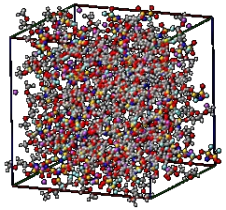
Na$^+$/K$^+$-
hydrate-melt
(*ACIE*, 2019)



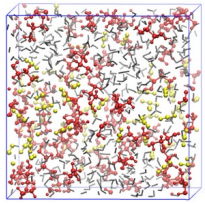
Lead iodide
perovskite
material
(*PCCP*, 2020)



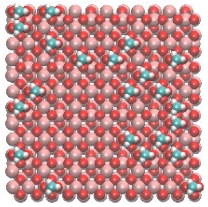




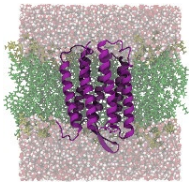
Superconcentrated
electrolyte solution
(*JPCB*, 2018)



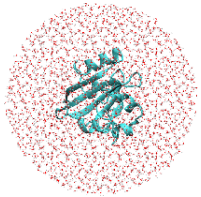
CO_2 capture
in amine solution
(*BCSJ*, 2017)



Carbonaceous species diffusion
on γ-Al_2O_3 surface
(*ACS Omega*, 2020)

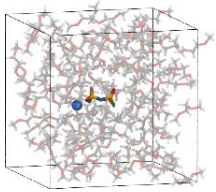


Bacteriorhodopsin
embedded in lipid
membrane with
water



Photoactive
yellow protein
(*JCCJ*, 2018)

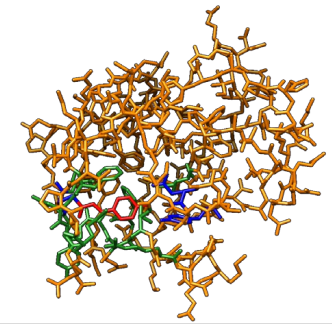
Bacteriorhodopsin
in gas phase
(*JPCB*, 2020)



Na$^+$ containing
electrolyte
solution
(*ACIE*, 2019)

Excited-State Calculation of PYP

- DC-type Excited-State Calculations
  - Methods: DC-TDDFTB, DC-TDDFT, DC-SACCI
  - Model: Whole PYP

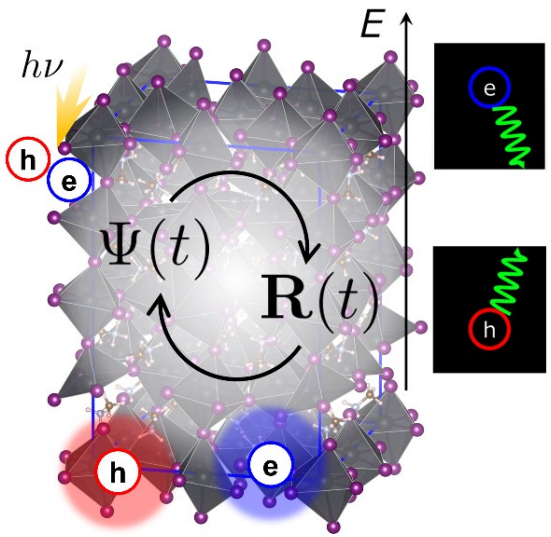


Method	Excitation Energy [eV]	(diff.)	Wall Time [sec]
DC-TDDFTB	2.17	(-0.61)	1.25
DC-TDLCDFTB	2.80	(0.02)	2.04
DC-TDBLYP	2.33	(-0.45)	663.82
DC-TDB3LYP	3.12	(0.35)	776.40
DC-TDLCBLYP	2.85	(0.07)	1017.04
DC-SACCI	2.89	(0.11)	2484.00
Exptl.	2.78	—	—

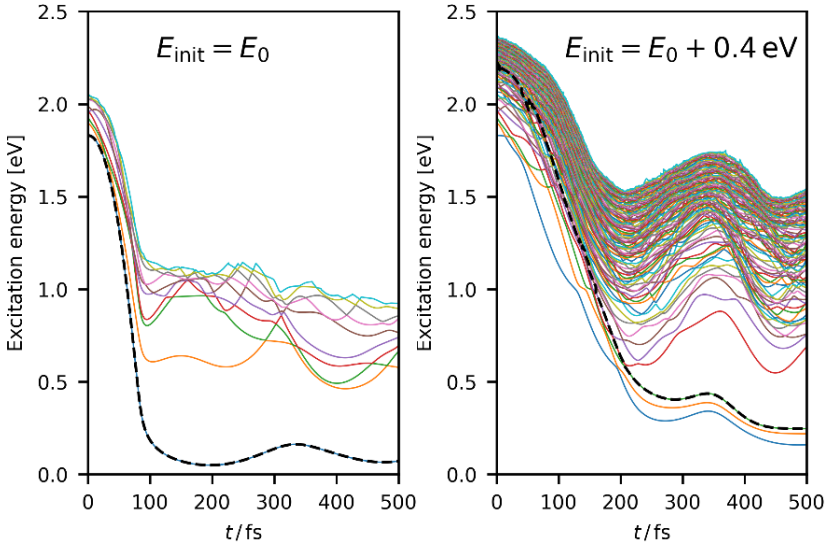
T. Yoshikawa, N. Komoto, j. Ono, Y. Nishimura, H. Nakai, *J. Chem. Theory Comput.*, **15**, 1719 (2019).

Perovskite Solar Cell Materials

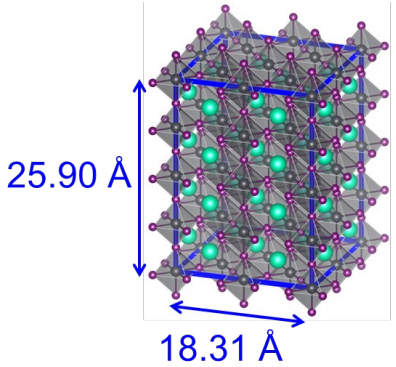
- Photoexcited-State Dynamics
  - Surface hopping simulations probed charge separation processes



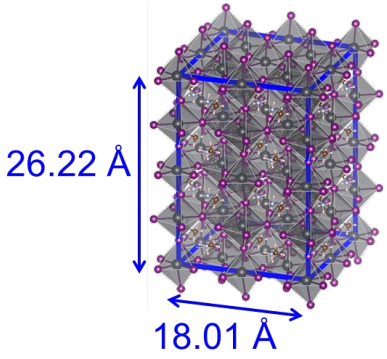
- Potential energy surfaces



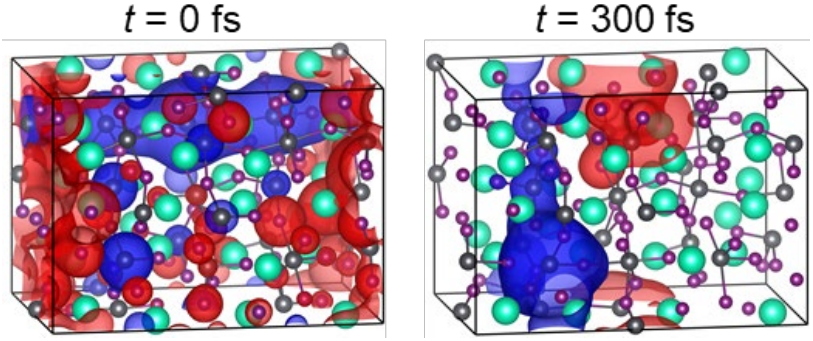
$CsPbI_3$



$MAPbI_3$



- Separation of hole (+, red) and electron (-, blue)



H. Uratani, H. Nakai, *J. Phys. Chem. Lett.* **11**, 4448 (2020).

RAQET Program

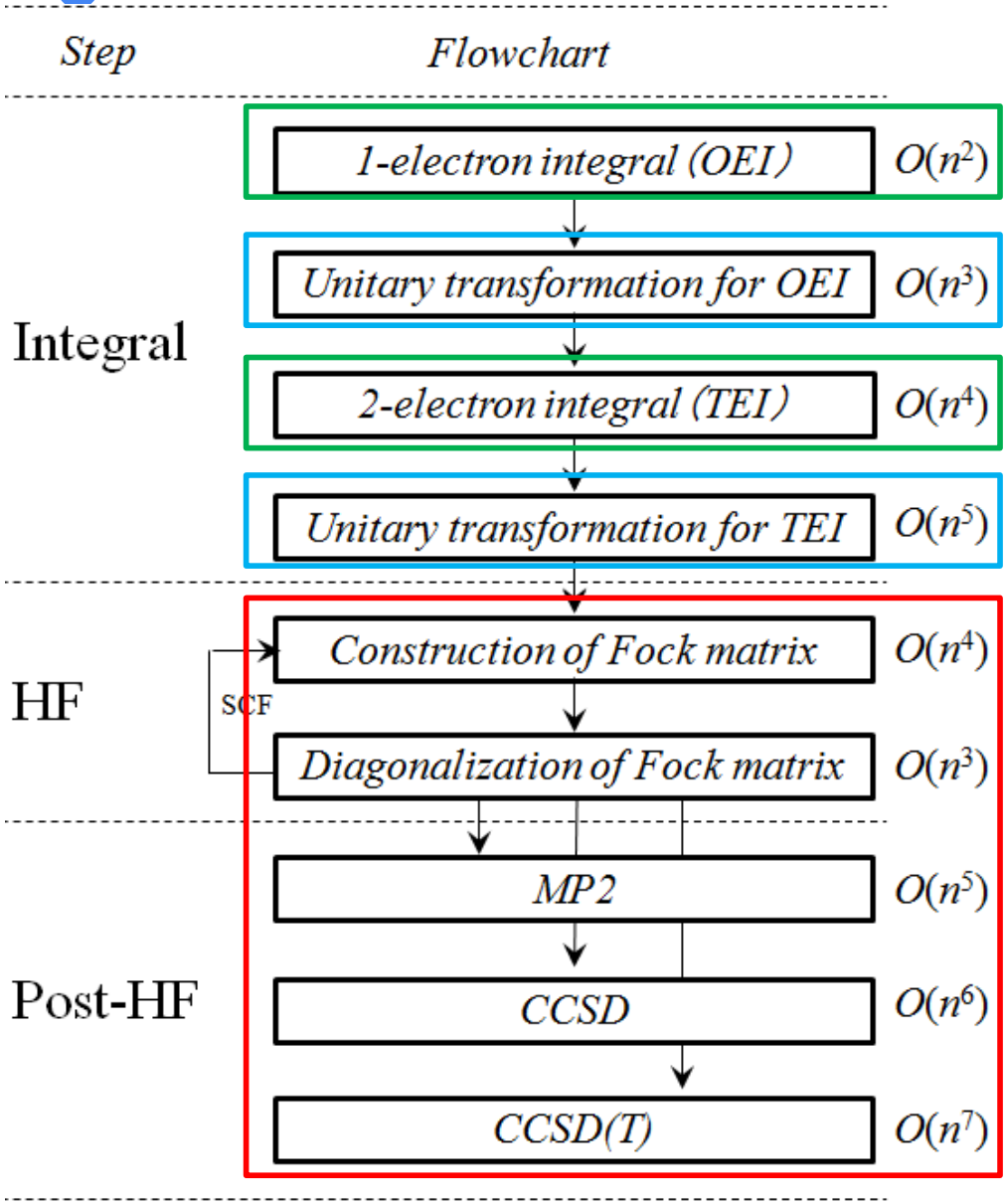
- Efficient 1c & 2c Rel QC Program

RAQET
RELATIVISTIC AND QUANTUM ELECTRONIC THEORY

Functions	Details
HF	R, U, RO, KR, KU, KRO, G (disk, direct)
MP2	R, U, RO, KR, KU, KRO, G (disk, direct)
DFT	R, U, RO, KR, KU, KRO, G (collinear, non-collinear, PCC)
Correlation	MPn, CI, CC
Excited State	EOM-CC, TDDFT(R, U, G)
Hamiltonian	NR, DKHn/NR, IODKH/NR(SF/SD, LUT), IODKH/IODKH (SF/SD, LUT)
Initial Guess	Hcore, Extended Hückel, Atomic density, Small basis, MO read, DM readGradient
Hamil. Gradient	NR, IODKH/NR(SF/SD, LUT), IODKH/IODKH (SF/SD, LUT)
HF Gradient	R, U, RO, KR, KU, KRO, G
MP2 Gradient	R, U, RO, KR, KU, KRO, G
Basis Function	Cartesian, Spherical harmonics
1E Integral	Overlap, Kinetic, V, pVp (derivative)
2E Integral	ERI, pVp, ppVpp (derivative), FMM
Integral Algorithm	ACE-RR, ACE-TRR (GC/SC), Gauss-Rys, PH+MD (SMASH)
Core Potential	MCP, AIMP, FCP, FCP-MP
SCF Conv.	C1-DIIS, C2-DIIS, E-DIIS, SO-SCF, Level shifting, Fock extrapolation, Damping, FON
Linear Scaling	DC-SCF, DC-correlation
Optimization	BFGS, RFO, Cartesian coordinate, Redundant coordinate, G-DIIS, Hessian
Others	Expectation values, Electric/Magnetic properties, Solvent effect

M. Hayami, J. Seino, Y. Nakajima, M. Nakano, Y. Ikabata, T. Yoshikawa, T. Oyama, K. Hiraga, S. Hirata, H. Nakai, *J. Comput. Chem.*, 39, 2333 (2018).

Feature of RAQET Program



- Overall Linear-Scaling Rel QC Method

Accompanying Coordinate Expansion & Transferred Recurrence Relation (ACE-TRR)
for efficient evaluation of OEI & TEI

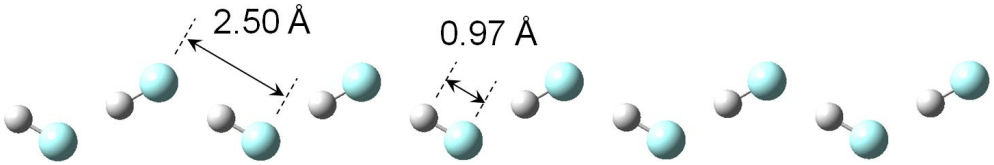
Local Unitary Transformation (LUT)
for efficient construction of 2c Rel Hamiltonian

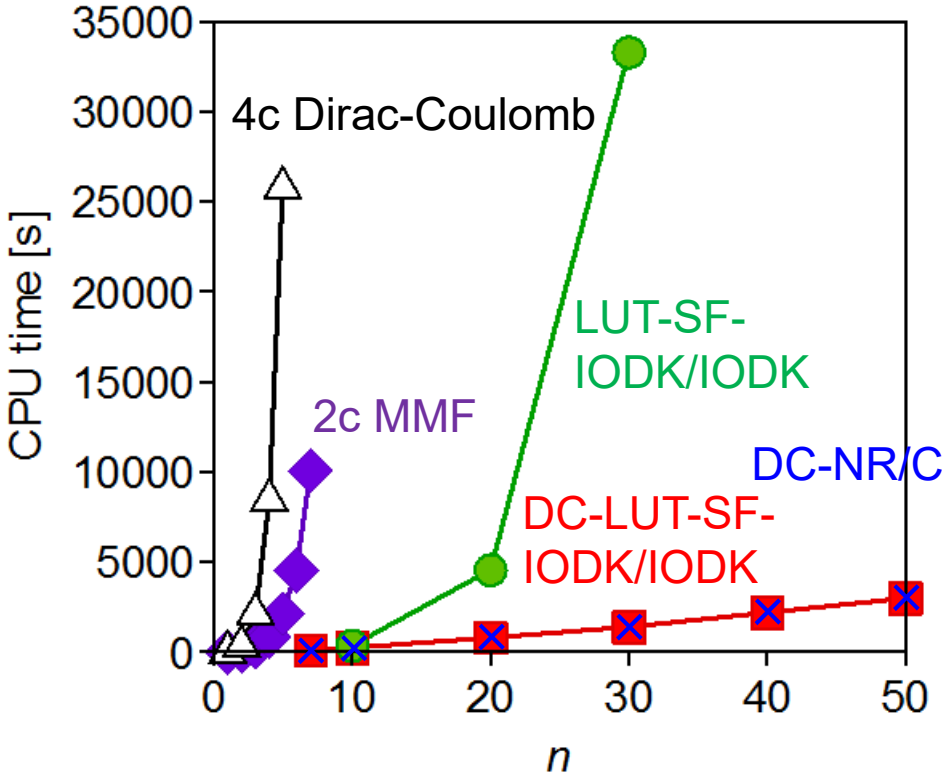
Divide-and-Conquer (DC)
for efficient calculation of HF & Post-HF schemes

M. Hayami, J. Seino, H. Nakai, *J. Comput. Chem.*, 35, 1517 (2014).
J. Seino, H. Nakai, *J. Chem. Phys.*, 136, 244102 (2012).

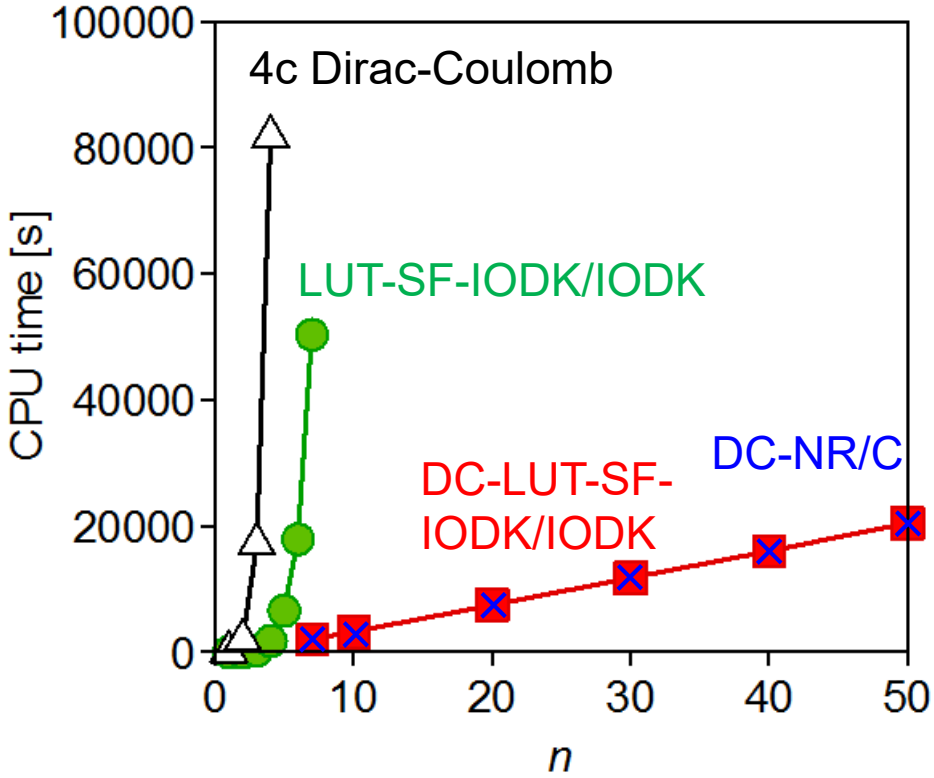
Performance of RAQET Program

- CPU Time of $(HCl)_n$ Molecule[5]
  - BS: Primitive 6-311G**
  - DC-HF Buffer: 5 units
  - DC-Corr. Buffer: 2 units





CPU time for MP2 calculations.



CPU time for CCSD calculations.

J. Seino, H. Nakai, *J. Chem. Phys.*, **139**, 034109 (2013).

Download of RAQET Program

- Download at www.chem.waseda.ac.jp/raqet/
  - Registration (1 License for 1 Group)