GPU-accelerated large-scale excited-state simulation based on divide-and-conquer time-dependent density-functional tight-binding

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Introduction

WASEDA University

- Waseda University
  PhD, Department of Chemistry and Biochemistry, Nakai group (March, 2015)
- April 2015- March 2016
  Research Associate, Waseda University
- April 2016- March 2018
  Assistant Professor, Waseda University
- April 2018- Present
  Lecturer, Waseda University

Linear-scaling open-shell and excited-state theory

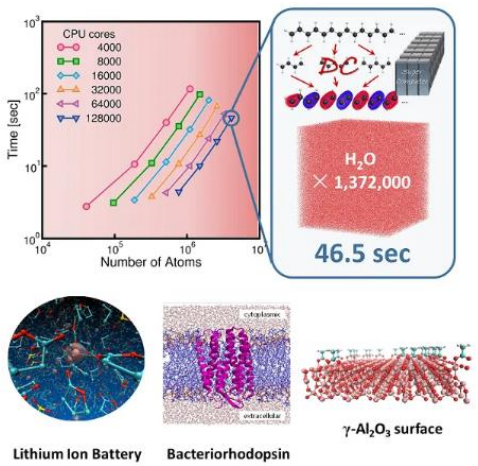
Contents

- DC-DFTB-MD
  - Divide-and-conquer density-functional tight-binding molecular dynamics
  - Ground state, massively parallel
- DC-TDDFTB-MD
  - Divide-and-conquer time-dependent density-functional tight-binding molecular dynamics
  - Excited state
- Acceleration of DC-TDDFTB-MD with GPU

Development of DC-DFTB-MD program: DC-DFTB-MD

- MD and geometry optimization for large systems
- Written in Fortran 90/95
- K computer, Fujitsu FX10, PC cluster (Linux), ...

Academic free



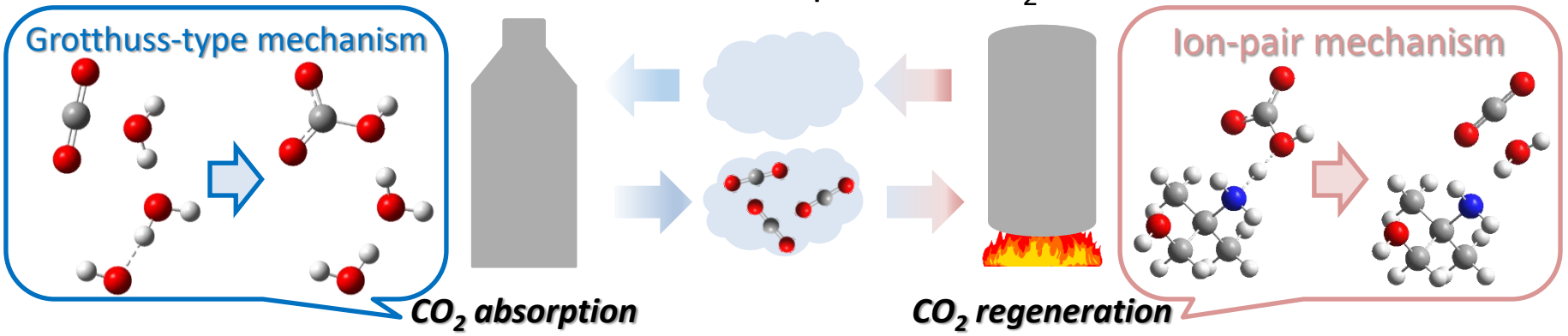
Main features	
Energy and Gradient (Cluster and PBC models)	DFTB1/2/3, Spin-polarized DFTB
Linear-scaling method	Divide-and-conquer (DC)
Dispersion correction	Slater-Kirkwood, Lennard-Jones, DFT-D2, DFT-D3
SCC convergence	Broyden, Simple mixing, Anderson, DIIS
MD ensemble	*NVE*, *NVT*, *NPH*, *NPT*
Thermostat and [Barostat]	Velocity scaling, Nosé-Hoover chain, Berendsen, Andersen, Langevin, [Berendsen]
MD option	RATTLE constraint, Soft potential, Simulated annealing, Lagrange interpolation of initial guess charges
Geometry optimization	BFGS, Steepest descent, Conjugate gradient

http://www.chem.waseda.ac.jp/dcdftbmd/

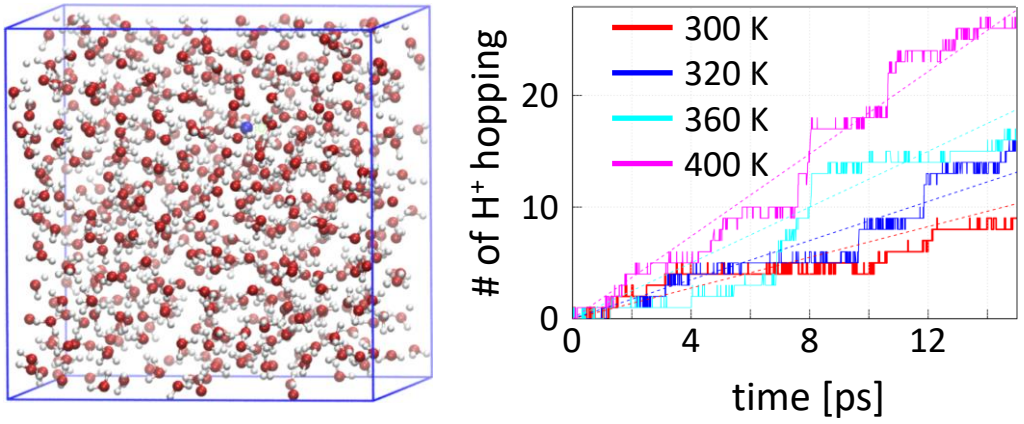
Target: Chemical reaction dynamics of large Systems

Our recent illustrative applications

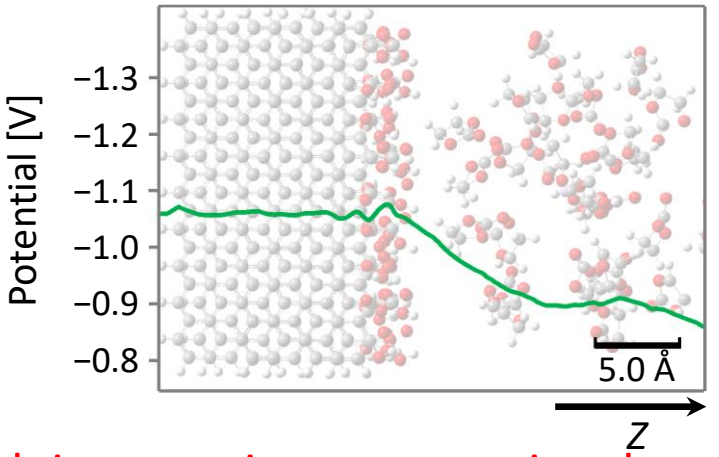
Chemical absorption of CO_2



Proton diffusion in bulk water



Lithium ion devices

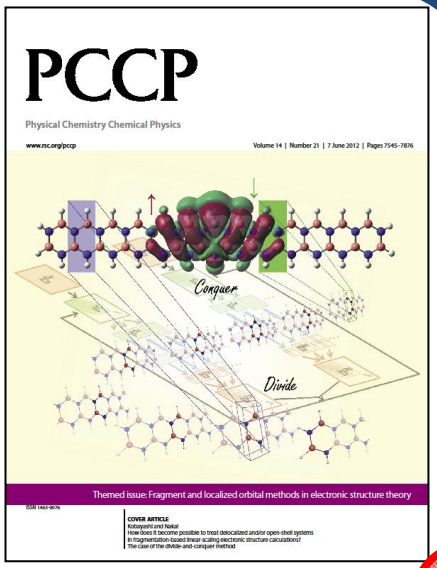


Quantum mechanical treatment of whole system with inexpensive computational cost

Our three pillars for chemical reaction dynamics

DC

Divide-
and-
Conquer
***O*(*N*)**



DFTB

Density-
Functional
Tight-
Binding
SEQM-MD

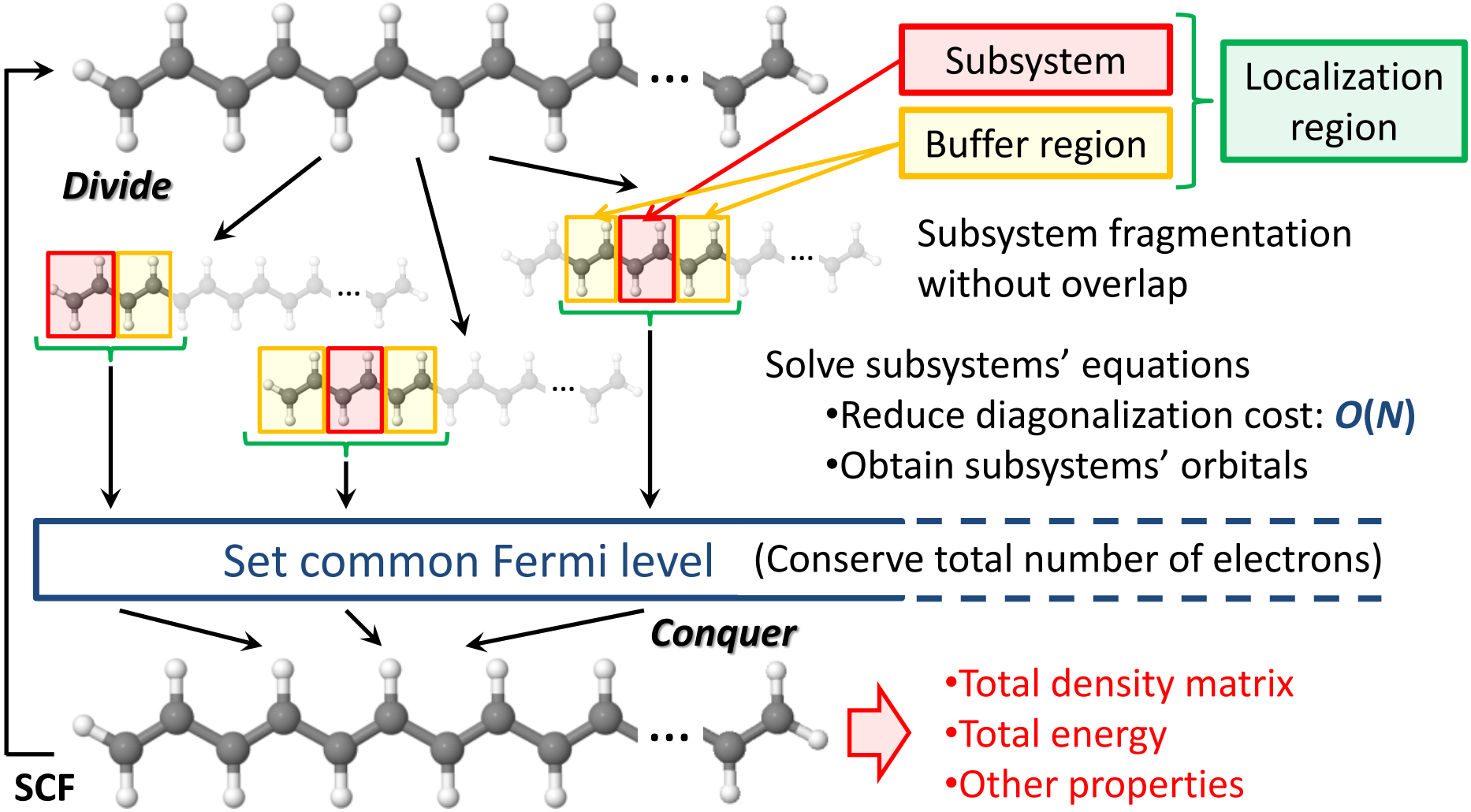
K computer

Massively parallel DC-DFTB-MD computations

- *O*(*N*): Linear-scaling
- SEQM-MD: **S**emi-**E**mpirical **Q**uantum **M**echanics-**M**olecular **D**ynamics

Divide-and-Conquer (DC) method

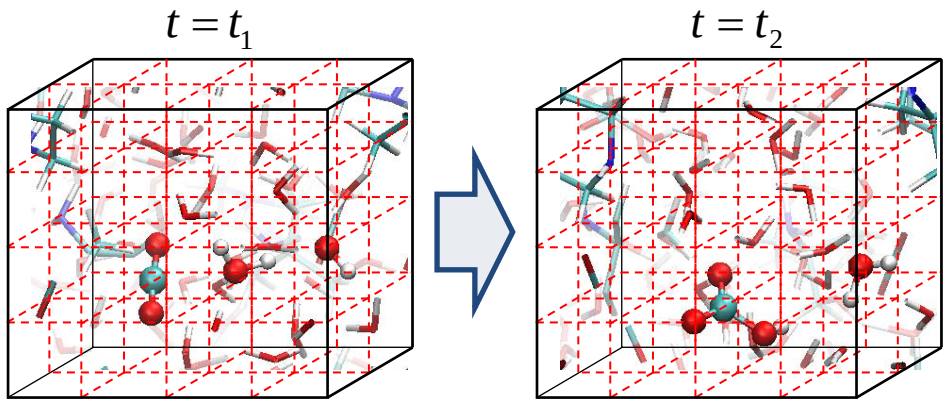
One of fragmentation techniques to achieve linear-scaling[1,2]



[1] M. Kobayashi, H. Nakai, in *Linear-Scaling Techniques in Computational Chemistry and Physics*, (2011), pp. 97–127.
[2] W. Yang, T.-S. Lee, *J. Chem. Phys.* **103**, 5674 (1995).

Advantages of DC method in QM-MD simulations

- Automatized fragmentation of subsystems at each time step



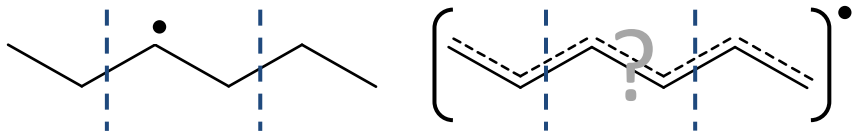
- Fragmentation due to locality of density matrix
- Accuracy and cost control by changing buffer size
- No need of chemical intuition

Applicable to dynamical bond formation and cleavage

- Unnecessary to predefine electron & spin numbers of subsystems (Determine at each SCF step)

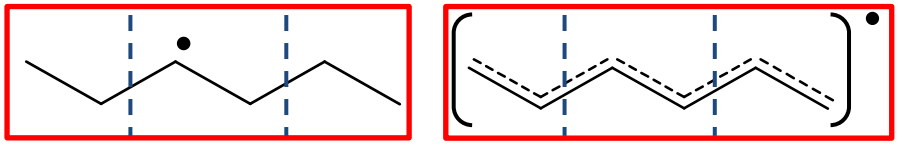
Conventional fragmentation method

$S_1 = 0$ $S_2 = 1/2$ $S_3 = 0$ $S_1 = ?$ $S_2 = ?$ $S_3 = ?$



DC method

$S = 1/2$ $S = 1/2$



Applicable to electron and spin delocalized systems

Density-Functional Tight-Binding (DFTB) method

SEQM derived from density functional theory (DFT)[1,2]

DFTB1 DFTB2 DFTB3

$$E_{\mathrm{DFTB}} = \sum_{\mu\nu}^{\mathrm{AO}} D_{\mu\nu} H^0_{\mu\nu} + \sum_{A>B}^{\mathrm{atom}} E^{\mathrm{rep}}_{AB} + \frac{1}{2}\sum_{AB}^{\mathrm{atom}} \gamma_{AB}\Delta q_A \Delta q_B + \frac{1}{3}\sum_{AB}^{\mathrm{atom}} \Gamma_{AB}\Delta q_A^2 \Delta q_B$$

① ② ③ ④

- $D_{\mu\nu}$: Density matrix
- Δq_A: Induced Mulliken charge on atom A

Evaluate using parameters determined by DFT calculations

①: Charge independent term

- Precomputed Hamiltonian and overlap matrices
- Two-center approximation

⇨ No integral evaluation at runtime

②: Short-ranged two-body repulsive term

- Core-core repulsion
- DFT double-counting contribution

⇨ Key ingredient for reasonable accuracy and transferability

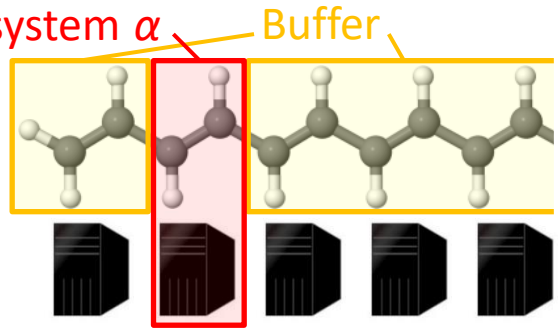
③, ④: Charge dependent term

- Δq_A is determined self-consistently (SCC)
- Monopole approximation

⇨ Proper description of chemical bonds in MD with small cost

[1] M. Elstner, G. Seifert, *Phil. Trans. R. Soc. A* **372**, 20120483 (2014).
[2] M. Gaus, Q. Cui, M. Elstner, *WIREs Comput. Mol. Sci.* **4**, 49 (2014).

Parallel procedure of DC-DFTB energy calculation



Evaluate $H^{0,\alpha}$, S^{α}, γ^{α}, Γ^{α}, E^{rep}

Update Hamiltonian H^{α}

Diagonalize to get c^{α} & ε^{α}

MPI comm.

Set common Fermi level ε_{F}

MPI comm.

Construct density D^{α}

Evaluate Mulliken charge q^{α}

MPI comm.

Evaluate Mulliken charge q

SCC

- Hybrid of MPI/OpenMP
  - MPI: Assign subsystems to processes
  - OpenMP: Operations for localization regions

DFTB1 DFTB2 DFTB3

$$H_{\mu\nu} = H^{0}_{\mu\nu} + S_{\mu\nu}\sum_{C}^{\mathrm{atom}}\frac{1}{2}\left(\gamma_{AC}+\gamma_{BC}\right)\Delta q_C + S_{\mu\nu}\sum_{C}^{\mathrm{atom}}\left(\frac{1}{3}\left(\Delta q_A\Gamma_{AC}+\Delta q_B\Gamma_{BC}\right)+\frac{\Delta q_C}{6}\left(\Gamma_{CA}+\Gamma_{CA}\right)\right)\Delta q_C$$

Solve equations: $\sum_{\nu} c^{\alpha}_{\nu i}\left(H^{\alpha}_{\mu\nu}-\varepsilon^{\alpha}_{i}S^{\alpha}_{\mu\nu}\right)=0$

Constraint of total number of electrons n_{e}:

$$n_{\mathrm{e}} = 2\sum_{\alpha}^{\mathrm{subsystem}}\sum_{i}^{\mathrm{MO}(\alpha)} f_{\beta}\left(\varepsilon_{\mathrm{F}}-\varepsilon^{\alpha}_{i}\right)\sum_{\mu\nu} p^{\alpha}_{\mu\nu}c^{\alpha}_{\mu i}c^{\alpha *}_{\nu i}S^{\alpha}_{\nu\mu}$$

$$D^{\alpha}_{\mu\nu} = 2\sum_{i}^{\mathrm{MO}(\alpha)} f_{\beta}\left(\varepsilon_{\mathrm{F}}-\varepsilon^{\alpha}_{i}\right)c^{\alpha}_{\mu i}c^{\alpha *}_{\nu i}$$

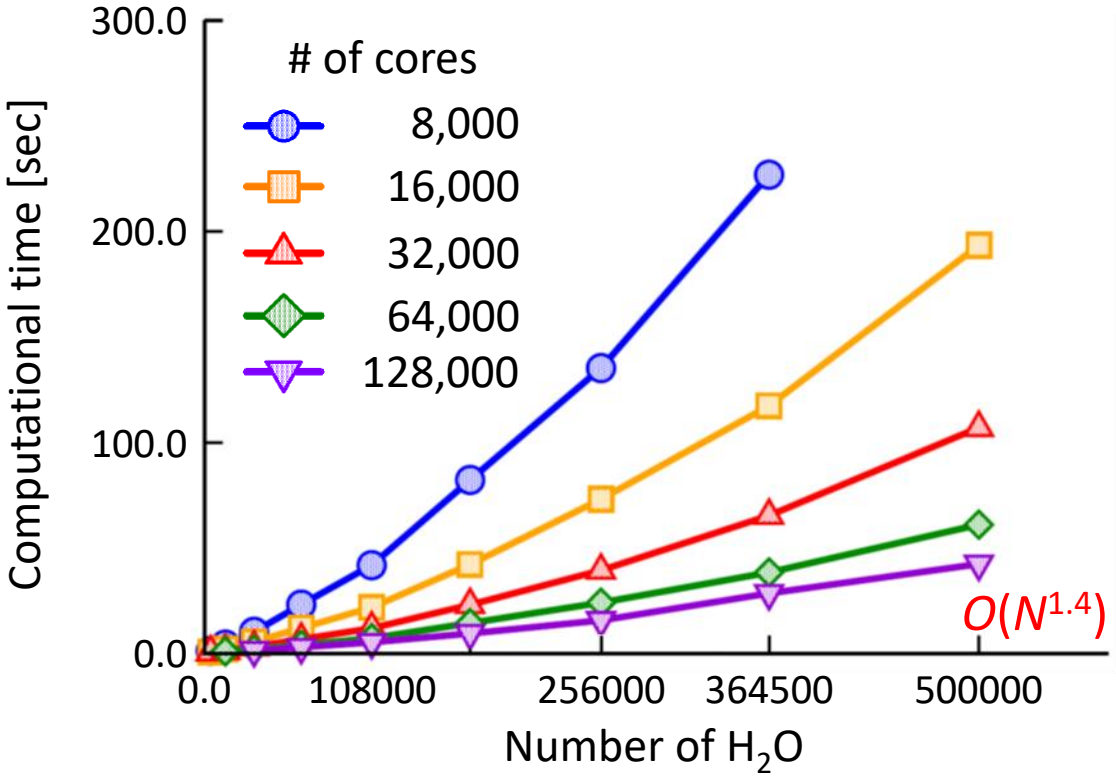
$$q^{\alpha}_{A} = \sum_{\mu\in A}\sum_{\nu\in L(\alpha)} D^{\alpha}_{\mu\nu}S^{\alpha}_{\nu\mu}$$

- $f_{\beta}(x)$: Fermi function $f_{\beta}(x)=\frac{1}{1+\exp(-\beta x)}$
- p^{α}: partition matrix

SCC Convergence check: $\max\left|q-q_{\mathrm{old}}\right|<\delta$

Parallel performance of DC-DFTB energy calculation

Size dependence of computational time

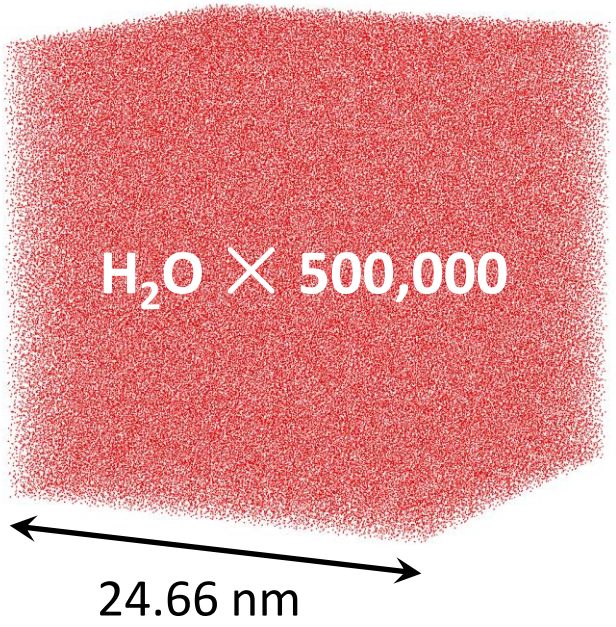


Computational time of $(H_2O)_{500000}$

# of cores	16,000	32,000	64,000	128,000
Time [sec]	193.4	107.0	61.1	46.5
Speed-up	16000.0	28908.7	50673.9	72935.4

$(H_2O)_n$

n = 4,000–500,000



- Density: 1.0 g/cm^3
- DC-DFTB2
- Subsystem: 1 H_2O
- Buffer radius : 6 Å
- K computer

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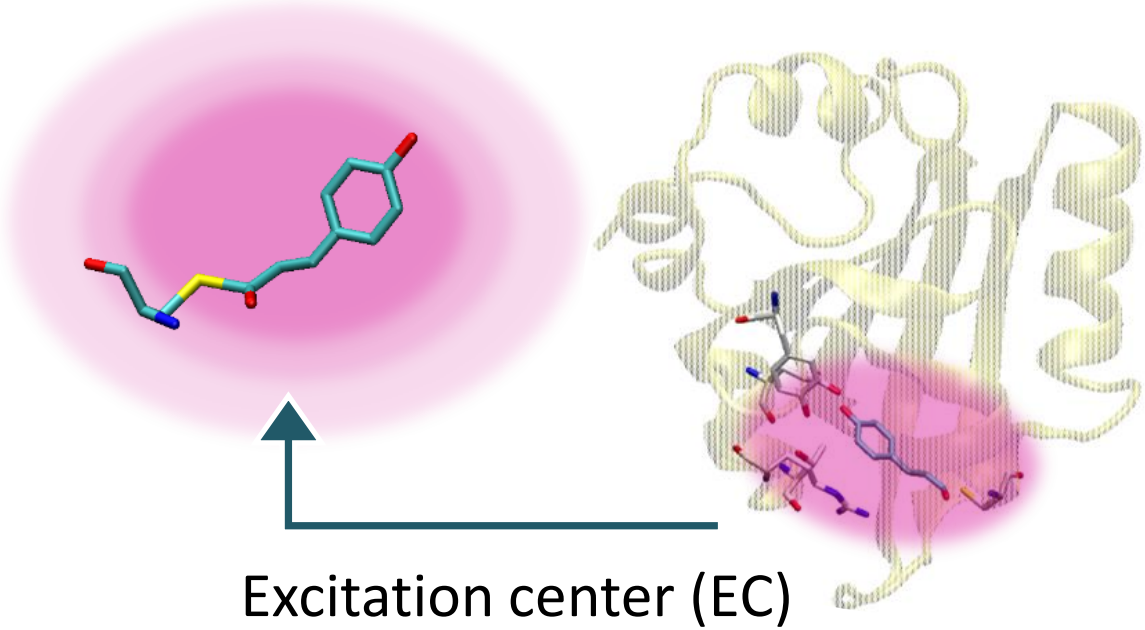
DC-based excited-state theory

DC-based time-dependent density-functional tight-binding theory

Ground-state (DC-DFTB)

Select EC region

Excited state for EC region (DC-TDDFTB)



Excitation center (EC) in effect outside EC

Casida's formalism

$$\begin{pmatrix} \mathbf{A}^s & \mathbf{B}^s \\ \mathbf{B}^{s*} & \mathbf{A}^{s*} \end{pmatrix} \begin{pmatrix} \mathbf{X}^s \\ \mathbf{Y}^s \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}^s \\ \mathbf{Y}^s \end{pmatrix}$$

[1] T. Yoshikawa, M. Kobayashi, A. Fujii, and H. Nakai, *J. Phys. Chem. B*, **117**, 5565 (2013).

[2] N. Komoto, T. Yoshikawa, J. Ono, Y. Nishimura, and H. Nakai, *J. Chem. Theor. Comput.*, **15**, 1719 (2019).

Time-dependent DFT(B) energy/energy gradient

- Excitation energy: linear-response theory
  - Hermit eigenvalue problem: Davidson algorithm

$$\left(\mathbf{A}-\mathbf{B}\right)^{1/2}\left(\mathbf{A}+\mathbf{B}\right)\left(\mathbf{A}-\mathbf{B}\right)^{1/2}\mathbf{c}_I=\omega_I^2\mathbf{c}_I$$

$$A_{ia,jb}=\delta_{ij}\delta_{ab}\left(\varepsilon_a-\varepsilon_i\right)+K_{ia,jb}\qquad B_{ia,jb}=K_{ia,bj}$$

ε : orbital energy i,j: occupied orbital a,b: unoccupied orbital

- Excitation energy gradient

$$\frac{\partial\omega}{\partial R_{\alpha x}}=\sum_{\mu\nu}\frac{\partial H^0_{\mu\nu}}{\partial R_{\alpha x}}\Delta D_{\mu\nu}+\frac{1}{2}\sum_{\mu\nu\lambda\sigma}\frac{\partial K_{\mu\nu\lambda\sigma}}{\partial R_{\alpha x}}\Delta\Gamma_{\mu\nu\lambda\sigma}-\sum_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial R_{\alpha x}}\Delta W_{\mu\nu}$$

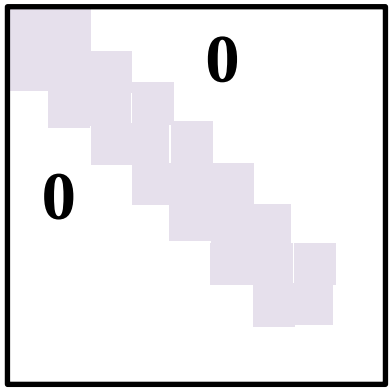
  - Z-vector method
    - Evaluate one-body, energy-weighted, and two-body density matrices
    - Avoid the explicit evaluation of MO coefficient derivative for $3\times N_{\text{atom}}$

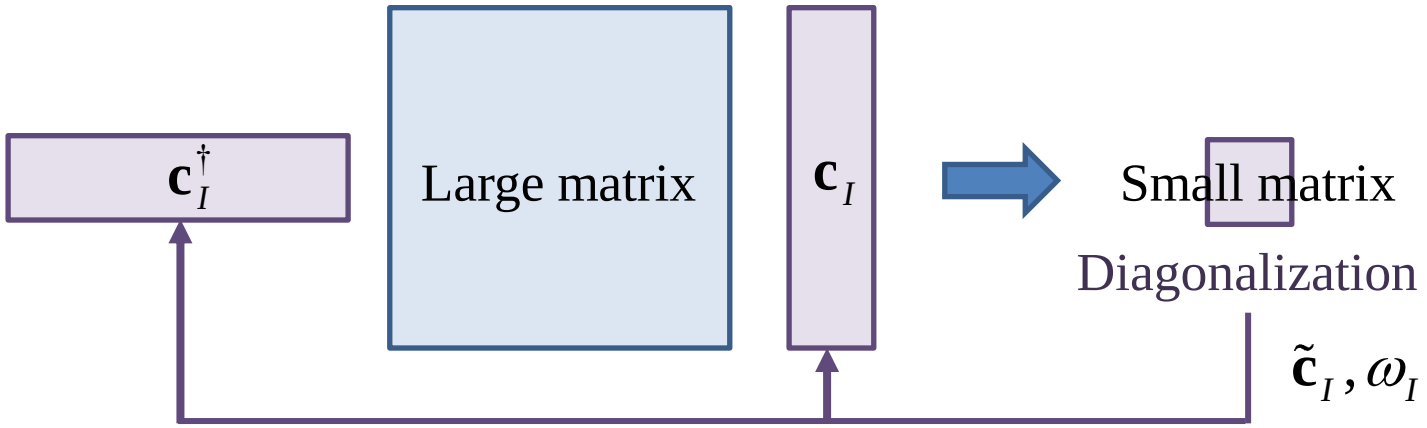
TDDFTB energy: Davidson algorithm

- Diagonalization for sparse matrix
  - Hermit eigenvalue problem

$$\boldsymbol{\Omega}\mathbf{c}_I = \omega_I^2 \mathbf{c}_I$$

$$\boldsymbol{\Omega} = (\mathbf{A}-\mathbf{B})^{1/2}(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B})^{1/2}$$





TDDFTB energy: Davidson algorithm

- Coupling matrix K (for example DFTB2)

$$K_{ia,jb} = \sum_{\alpha,\beta}^{Atom} q_{\alpha}^{ia} \gamma_{\alpha\beta} q_{\beta}^{jb}$$

μ,ν: AO
α,β: Atom

- Mulliken atomic transition charges

$$q_{\alpha}^{ia} = \frac{1}{2} \sum_{\mu\in\alpha} \sum_{\nu} \left(C_{\mu i} S_{\mu\nu} C_{\nu\alpha} + C_{\nu i} S_{\nu\mu} C_{\mu\alpha} \right)$$

C: MO coefficent
S: overlap matrix

- Construction of $\mathbf{\Omega} = \left(\mathbf{A}-\mathbf{B}\right)^{1/2} \left(\mathbf{A}+\mathbf{B}\right) \left(\mathbf{A}-\mathbf{B}\right)^{1/2}$
  - Standard: AO-MO transformation for each Davidson iteration

$$\Omega_{ia,I} = \omega_{ia}^2 F_{ia} + 4 \sum_{jb} \sum_{\mu\nu\lambda\sigma} \sqrt{\omega_{ia}} C_{\mu i} C_{\nu\alpha} K_{\mu\nu,\lambda\sigma} \sqrt{\omega_{jb}} C_{\lambda j} C_{\sigma b} c_{jb,I}$$

  - In-core: store q_{α}^{ia} in memory

$$\Omega_{ia,I} = \omega_{ia}^2 F_{ia} + 4 \sum_{A} q_{A}^{ia} \sqrt{\omega_{ia}} \left(\sum_{B} \gamma_{AB} \left(\sum_{jb} \sqrt{\omega_{jb}} q_{A}^{jb} F_{jb} \right) \right)$$

Algorithm of (DC-)TDDFTB

Step 1: Set initial trial vector

Sort in ascending order for difference of orbital energies

$\omega_{ia} = \varepsilon_a - \varepsilon_i$ ε : orbital energy *i,j*: occupied orbital *a,b*: unoccupied orbital

Step 2: Construct hermit matrix $\mathbf{\Omega}$

Standard	In-core
Step 2-1: MO-AO transformation for trail vector	Step 2-1: Construct Mulliken atomic transition charges
Step 2-2: Construct AO based $\mathbf{\Omega}$	Step 2-1: Construct $\mathbf{\Omega}$ directly from trial vector
Step 2-3: AO-MO transformation $\mathbf{\Omega}$	

Step 3: Diagonalize hermit matrix $\mathbf{\Omega}$

Step 4: Update trial vector

SCF

SCF

TDDFTB energy gradient: Z-vector method

- Lagrangian of excitation energy in TDDFTB

$$\mathcal{L} = \langle X+Y | (A+B) | X+Y \rangle + \langle X-Y | (A-B) | X-Y \rangle$$
$$-\omega \{ \langle X+Y | X-Y \rangle - 1 \} + \sum_{ia} Z_{ia} H_{ia} - \sum_{pq, p \le q} \Delta W_{pq}^{TD} (S_{pq} - \delta_{pq})$$

- Z-Vector equation

$$\frac{\partial \mathcal{L}}{\partial C_{\mu p}} = 0 \longrightarrow \sum_{jb} (A+B)_{ia,jb} Z_{jb} = -R_{ia}$$

Stationary condition — Linear equations

$$R_{ia} = \sum_b \{ (X+Y)_{ib} H^+_{ab}[(\mathbf{X}+\mathbf{Y})] \} + H^+_{ia}[\mathbf{T}] - \sum_j \{ (X+Y)_{ja} H^+_{ji}[(\mathbf{X}+\mathbf{Y})] \}.$$

$$H^+_{pq}[\mathbf{V}] = \sum_{ru} K_{pq,ru} V_{ru}$$

- One-body, two-body, and energy weighted DM by Z-vector

$$\frac{\partial \omega}{\partial R_{\alpha x}} = \sum_{\mu\nu} \frac{\partial H^0_{\mu\nu}}{\partial R_{\alpha x}} \Delta D_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \frac{\partial K_{\mu\nu\lambda\sigma}}{\partial R_{\alpha x}} \Delta \Gamma_{\mu\nu\lambda\sigma} - \sum_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial R_{\alpha x}} \Delta W_{\mu\nu}$$

TDDFTB energy gradient: Z-vector method

- Preconditioned conjugate gradient (PCG) method
  - Solve iteratively symmetric and positive linear equations

Step 1: Construct Z-vector

Step 1-1: Set initial Z vector (Jaccobi preconditioner) $Z_{ia}^{0} = \varepsilon_a - \varepsilon_i$

Step 1-2: Construct residual vector

$$r_{ia}^{k+1} = r_{ia}^{k} - \alpha^{k} \sum_{jb} \left(A+B\right)_{ia,jb} d_{ia}^{k}$$

SCF

Step 1-3: Update Z vector

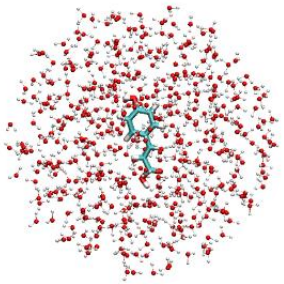
$$Z_{ia}^{k+1} = Z_{ia}^{k} + \alpha^{k} d_{ia}^{k}$$

Step 2: Construct density matrix

Step 3: Evaluate gradient

Performance of (DC-)TDDFTB method

- Wall-clock time [second]
  - Molecular: *p*-cumaric acid + 228H_2O
  - Method: TDDFTB2/3ob



Energy

	TDDFTB	DC-TDDFTB
Step 1	0.367	0.137
Step 2	1.943	0.293
Step 3	0.000	0.000
Step 4	0.127	0.037

Energy gradient

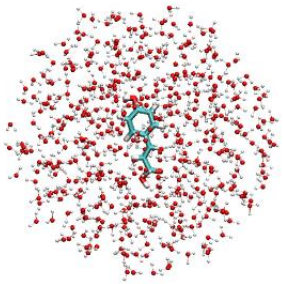
	TDDFTB	DC-TDDFTB
Step 1	19.565	4.222
Step 2	0.200	0.066
Step 3	0.240	0.091

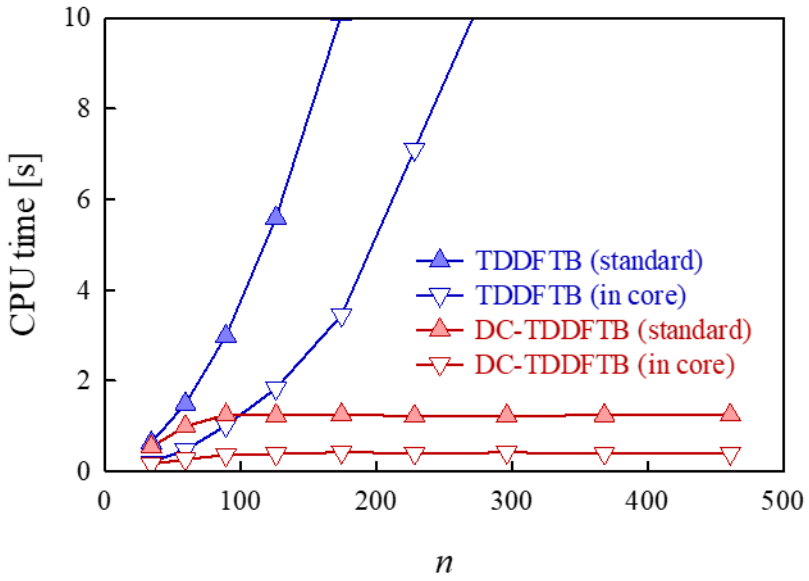
✓DC calculations reduce the computational cost,
especially for largest computational step in each algorithm.

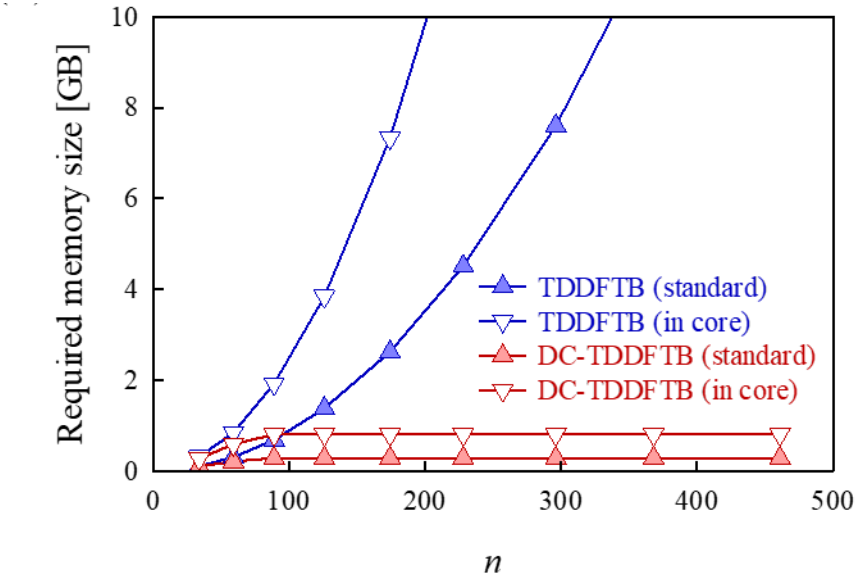
CPU: Intel Xeon Gold 6136 (3.00 GHz) 12 cores

System-size dependency: total TDDFT calculation

- CPU time and required memory
  - Molecular: *p*-cumaric acid + $n$$H_2O$
  - Method: TDDFTB2/3ob







✓In core algorithm reduce the wall times by large memory region

✓DC calculations reduce the CPU time and required memory

CPU: Intel Xeon Gold 6136 (3.00 GHz) 12 cores

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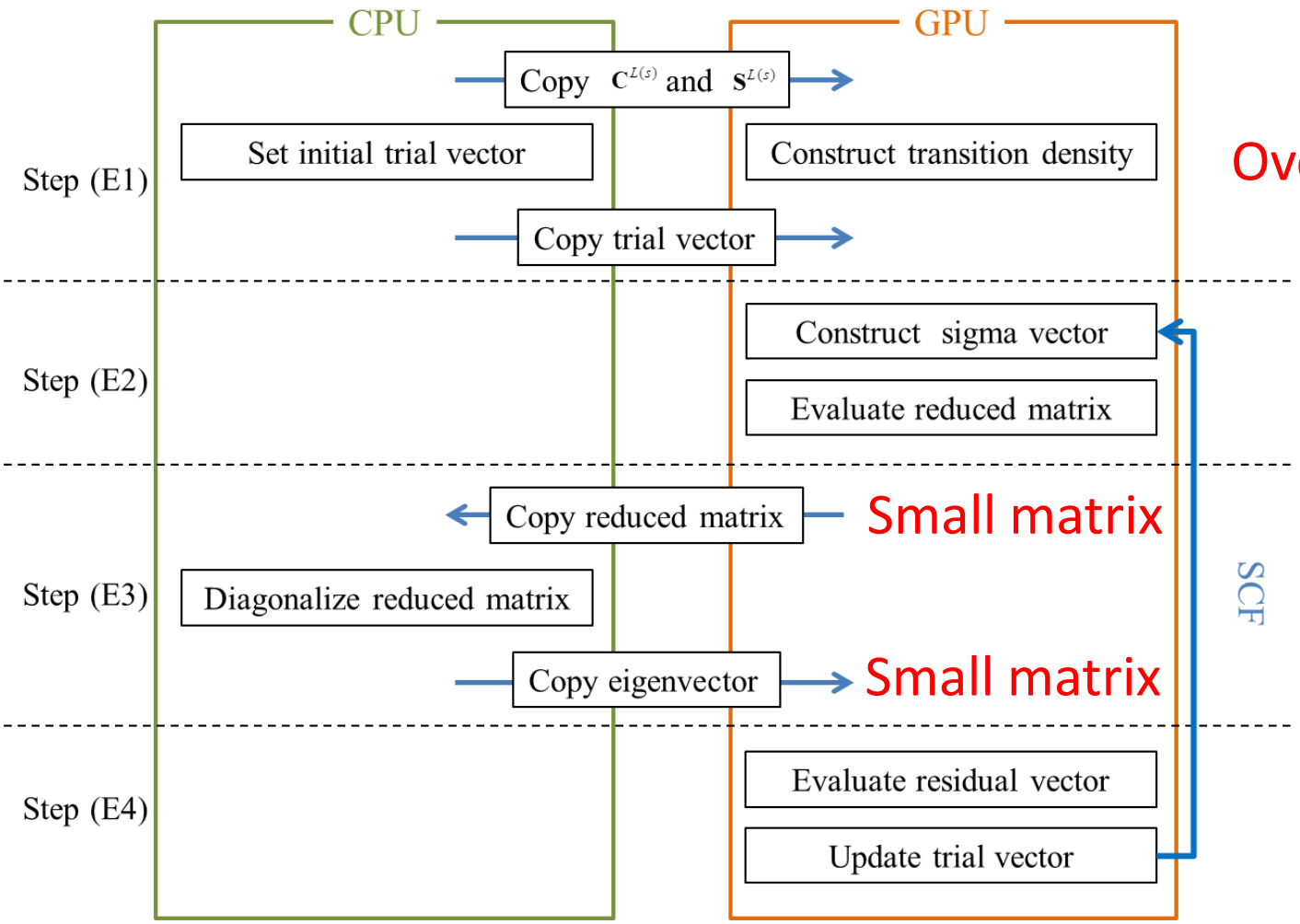
Implementation with GPU: TDDFT energy



Overlap

Small matrix

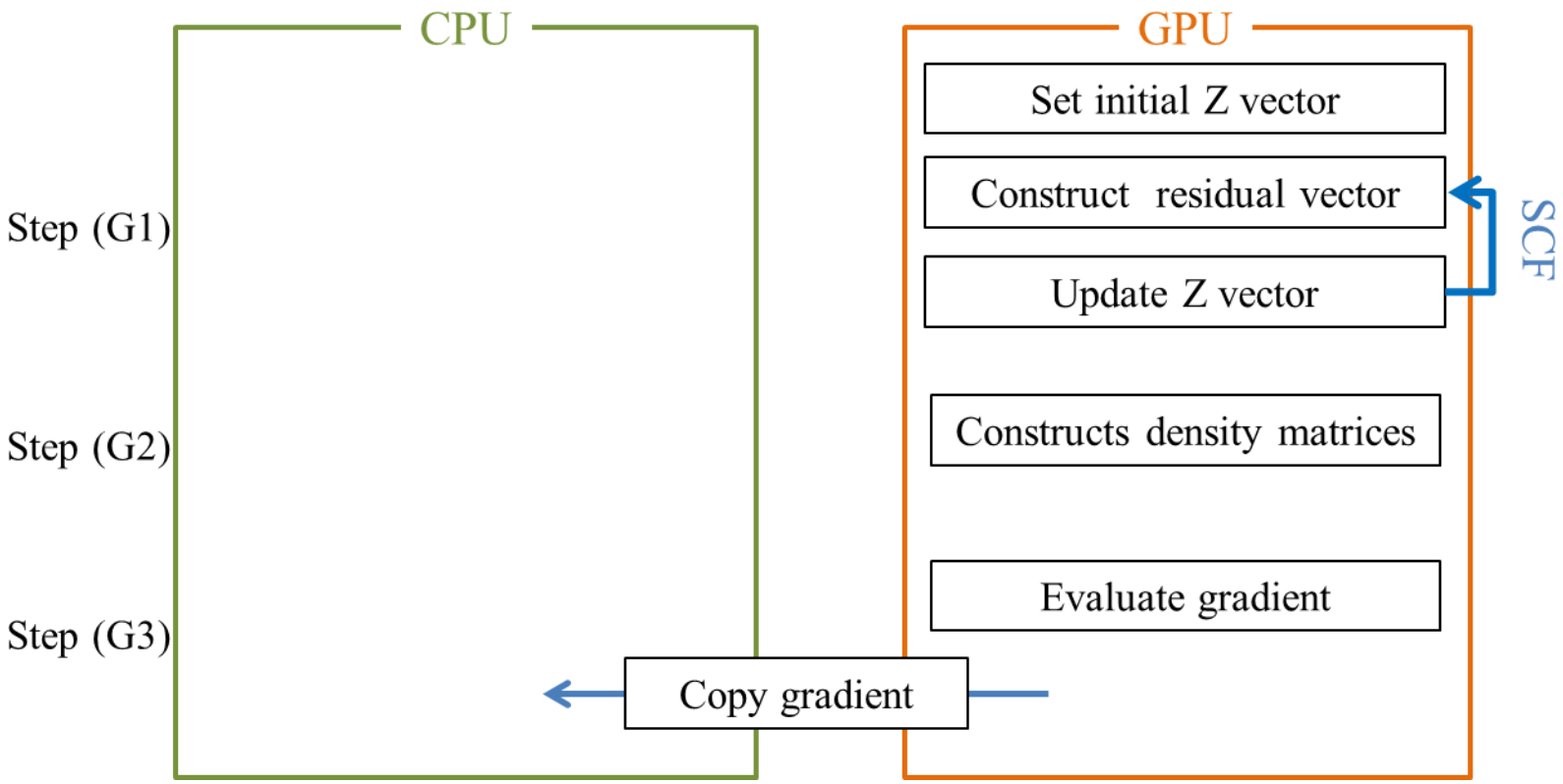
Small matrix

Low efficiency on GPU

✓ In-core algorithm because of implementation with dgemm

$$\Omega_{ia,I} = \omega_{ia}^2 F_{ia} + 4\sum_A q_A^{ia}\sqrt{\omega_{ia}}\left(\sum_B \gamma_{AB}\left(\sum_{jb}\sqrt{\omega_{jb}}\,q_A^{jb}F_{jb}\right)\right)$$

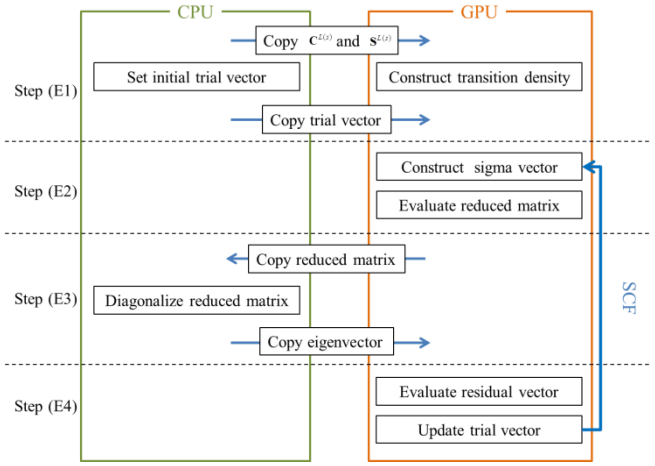
Implementation with GPU: TDDFT energy gradient



- ✓ Acceleration of most procedure with cublas library CublasDGEMM, CublasDAXPY, Cublasddot
- ✓ DC method: small require memory and communications with CPU and GPU

Performance of (DC-)TDDFTB method

- Wall-clock time [second]:
  TDDFTB energy
  - Molecular: *p*-cumaric acid + 228H_2O
  - Method: TDDFTB2/3ob



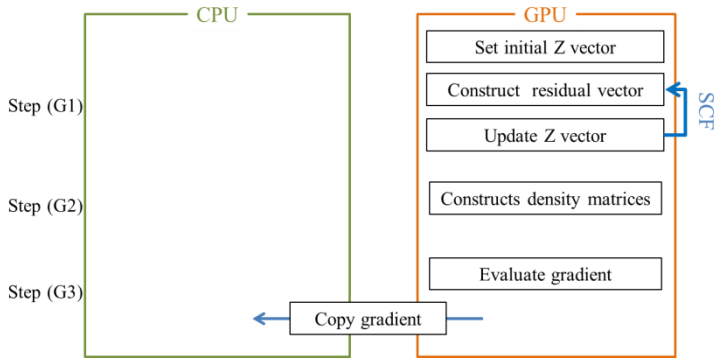
	TDDFTB CPU	TDDFTB GPU	DC-TDDFTB CPU	DC-TDDFTB GPU
Step 1	0.367	0.013	0.137	0.005
Step 2	1.943	0.075	0.293	0.010
Step 3	0.000	0.002	0.000	0.002
Step 4	0.127	0.003	0.037	0.002

✓Step 1, 2, and 4: computational cost ↓
Step 3: computational cost ↑

CPU: Intel Xeon Gold 6136 (3.00 GHz) 12 cores, GPU: V100

Performance of (DC-)TDDFTB method

- Wall-clock time [second]:
  TDDFTB energy gradient
  - Molecular: *p*-cumaric acid + 228H_2O
  - Method: TDDFTB2/3ob



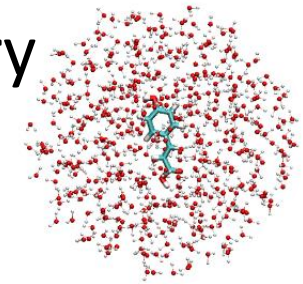
	TDDFTB CPU	TDDFTB GPU	DC-TDDFTB CPU	DC-TDDFTB GPU
Step 1	19.565	0.630	4.222	0.066
Step 2	0.200	0.023	0.066	0.009
Step 3	0.240	0.014	0.091	0.005

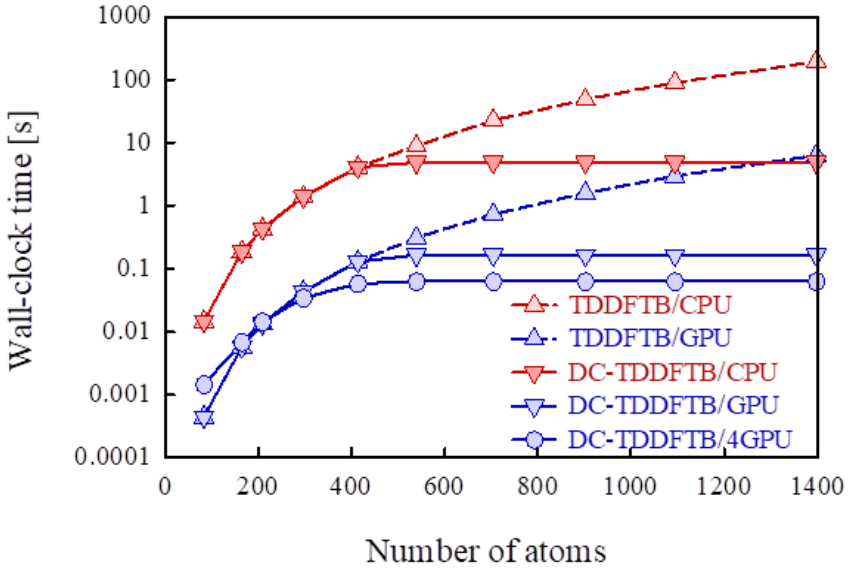
✓All steps: computational cost ↓
Step 4: Required communication cost↑ but small especially DC

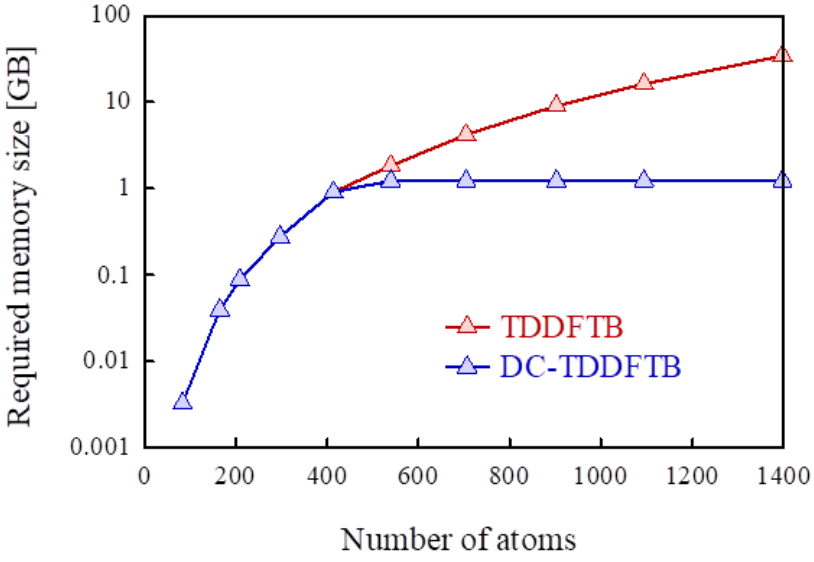
CPU: Intel Xeon Gold 6136 (3.00 GHz) 12 cores, GPU: V100

System-size dependency: total TDDFT calculation

- Wall-clock time and required memory
  - Molecular: *p*-cumaric acid + $n$$H_2O$
  - Method: TDDFTB2/3ob







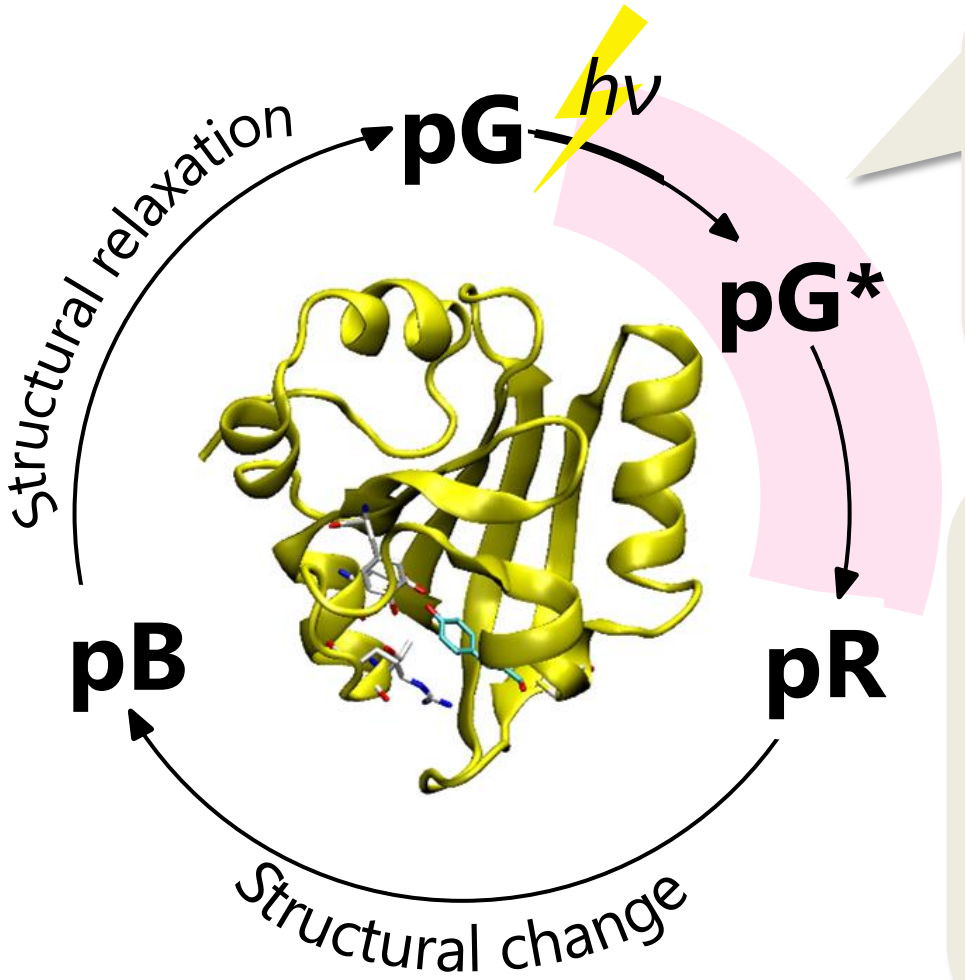
✓DC method: required memory small GPU good!!

✓Multi-GPU: about 3.12 times with 4 GPUs on same bord

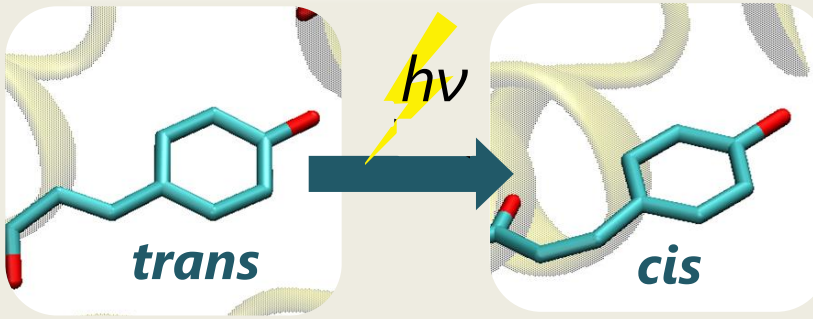
CPU: Intel Xeon Gold 6136 (3.00 GHz) 12 cores, GPU: V100

Application: photoactive yellow protein

- Photoreaction cycle



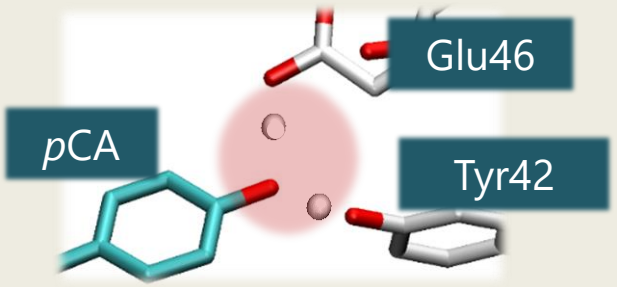
Photoisomarization
p-cumaric acid(*p*CA)



Hydrogen bond
for around amino acid

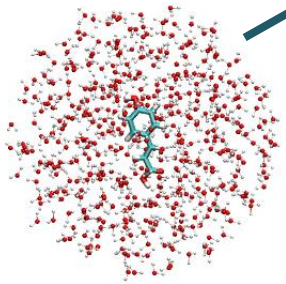
In water		In PYP
284 nm	→	446 nm

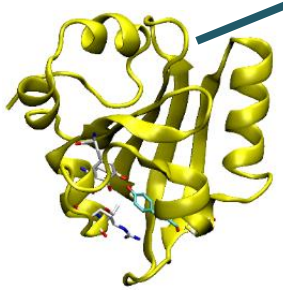
redshift



Application: photoactive yellow protein

Method	Excitation energy [eV]				CPU time
	*p*CA+461H_2O	(diff.)	PYP	(diff.)	
DC-CIS	4.64	(0.64)	4.22	(1.44)	~30 min.
DC-TDBLYP	3.76	(-0.24)	2.33	(-0.45)	~3 hours
DC-TDLCBLYP	4.10	(-0.27)	2.85	(0.07)	~3 hours
DC-TDDFTB	3.68	(-0.32)	2.17	(-0.61	
DC-TDLCDFTB	4.07	(-0.30)	2.80	(0.02	
Exptl.	4.00	—	2.78	–	





TDBLYP: 6-31G**,

TDDFTB/3ob, Excited center: *p*

1 amino acid, *p*CA, Buffer size:

Å (for PYP),

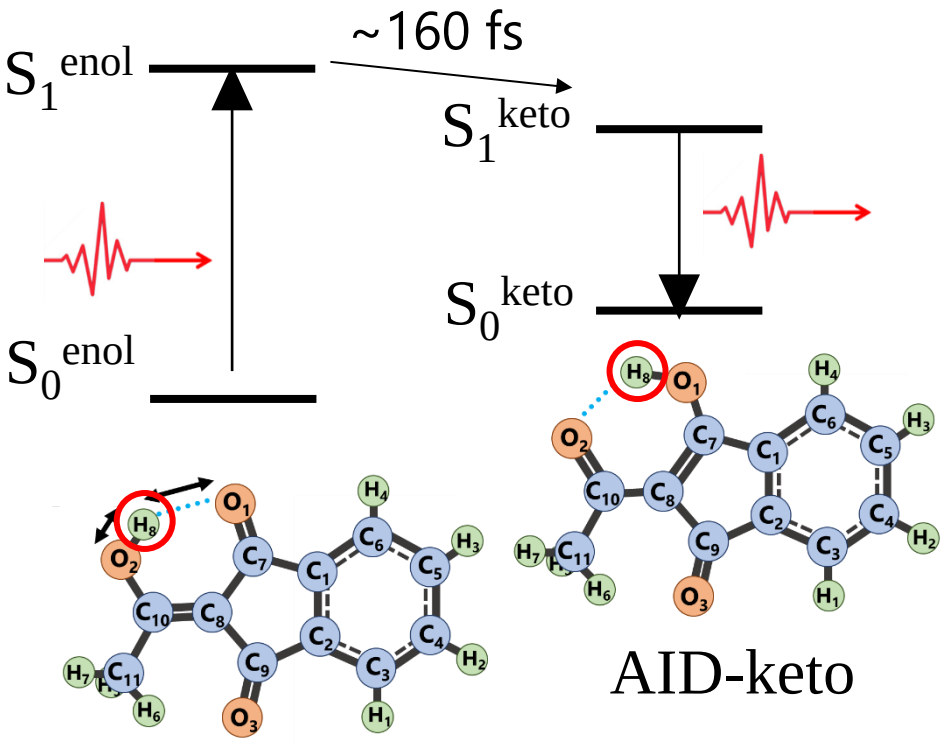
16 cores of an Intel Xeon Gold

JCTC, 15, 2019
(front cover)

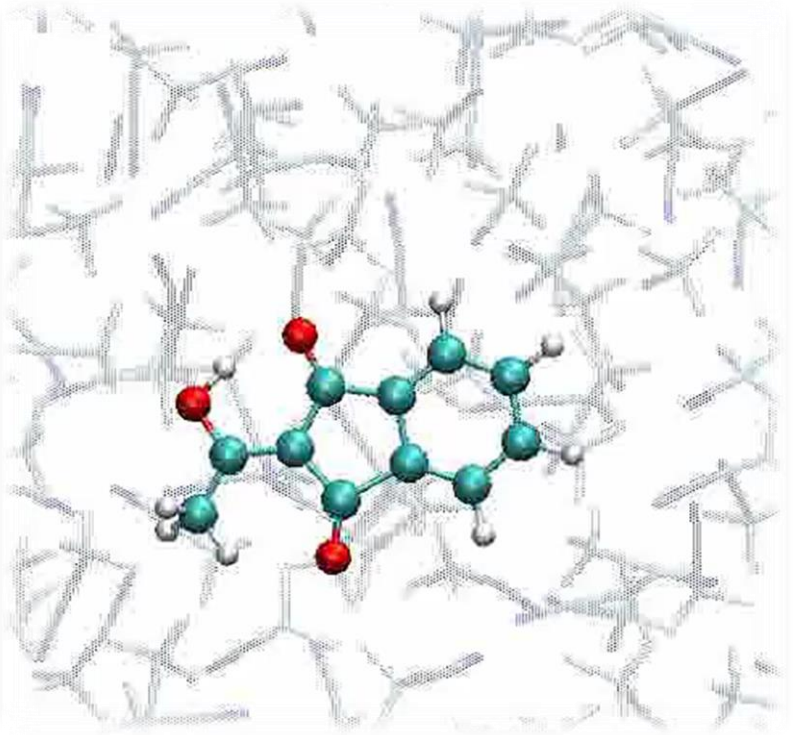
✓TDDFTB method could reproduce the excitation e
TDDFT calculations within seconds in single point

Application: excited-state single proton transfer

Excited state proton transfer
of 2-acetylindan-1,3-dione (AID)



Ground state



- 1 ps DC-DFTB-MD simulation in ground state
- Solvent: acetonitrile
- *NVE* ensembles
- 3ob parameter set
- Buffer size: 5.0 Å

Application: excited-state single proton transfer

Excited state proton transfer
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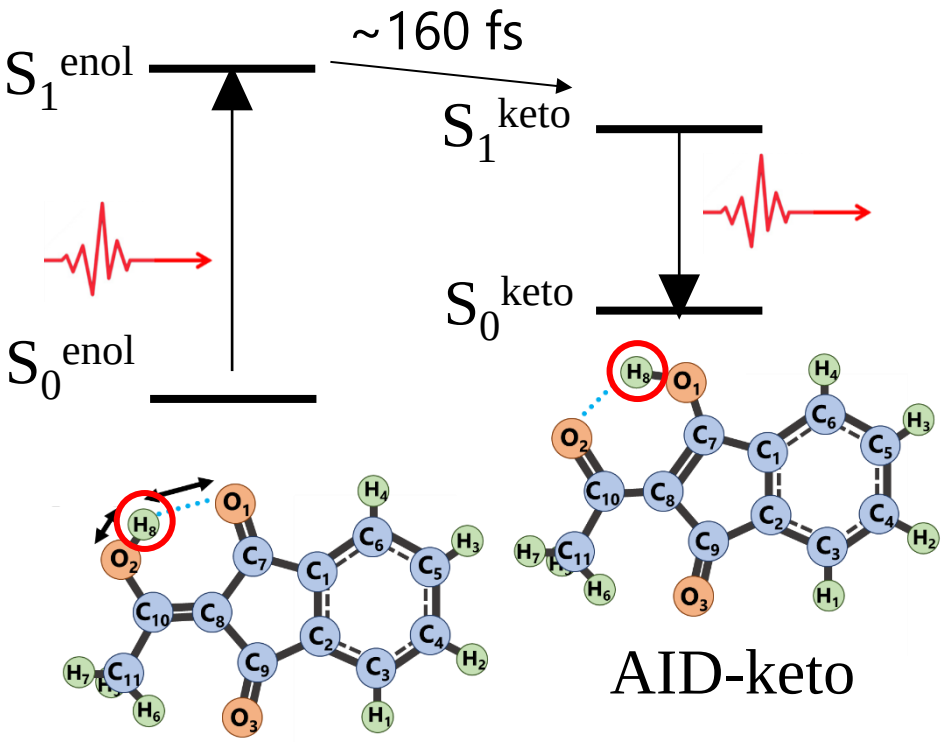
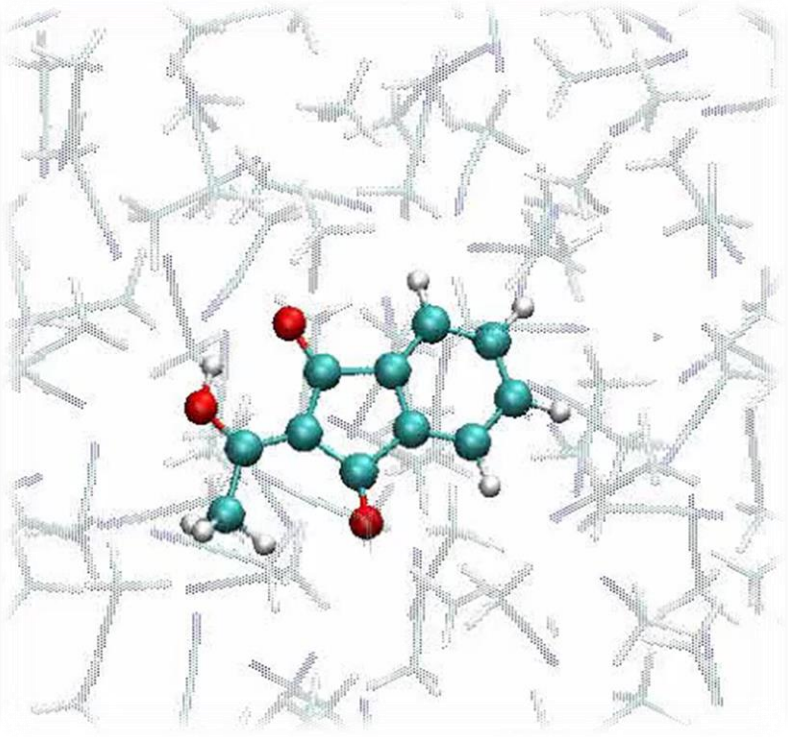


1 ps simulations

CPU: ~11 hours GPU:~20 mins

Excited state



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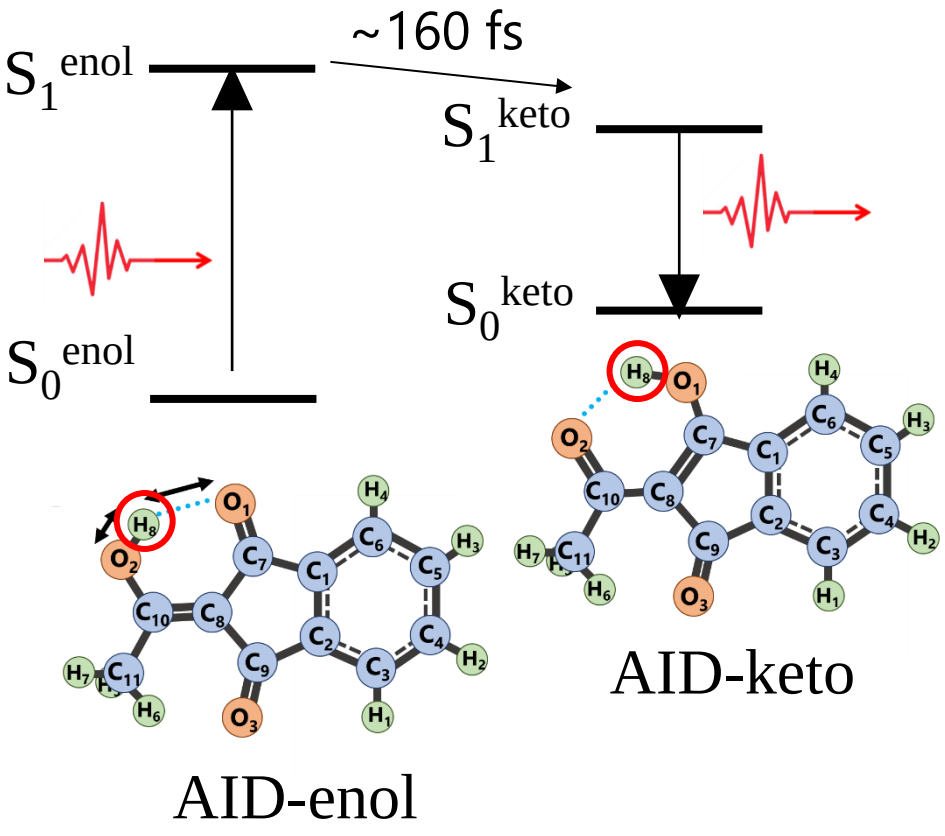
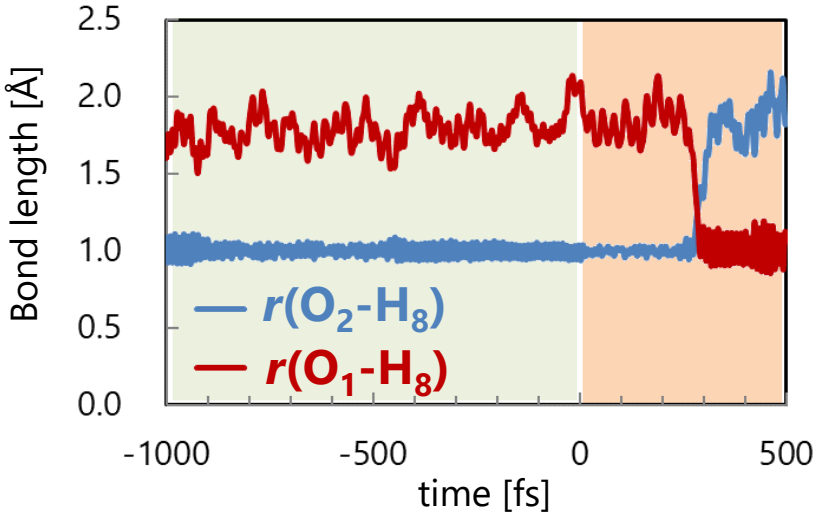
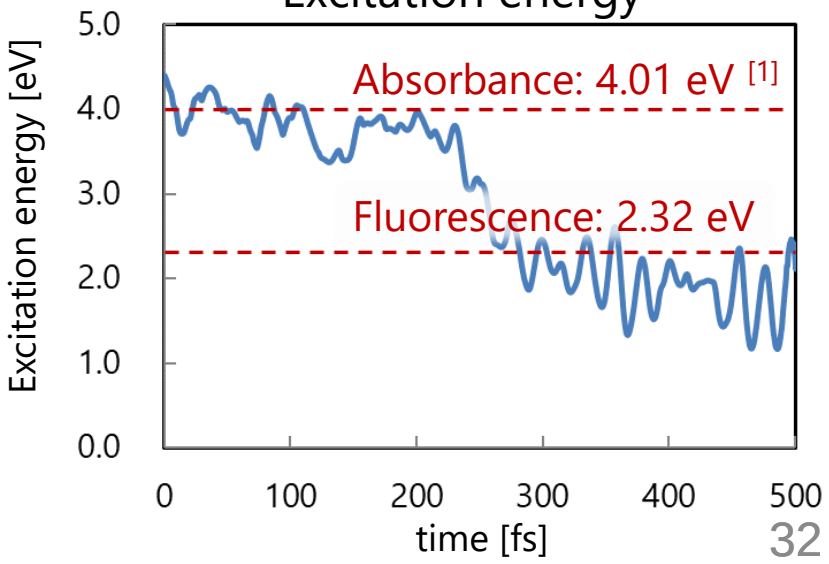


Bond length between O-H atoms



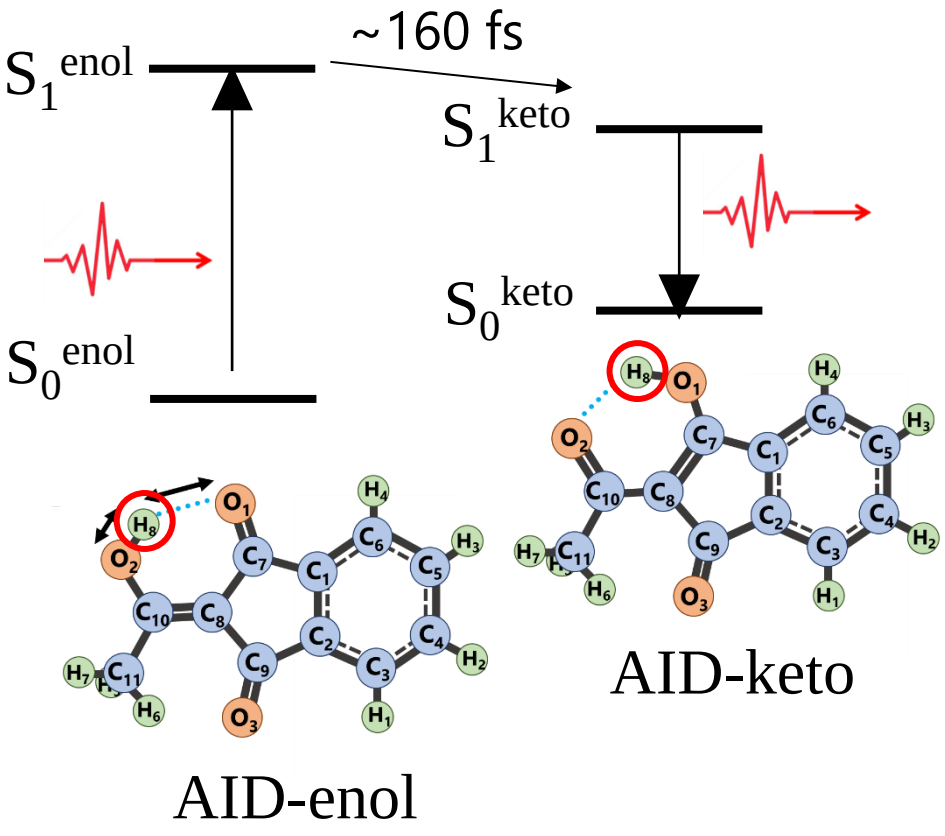
Excitation energy



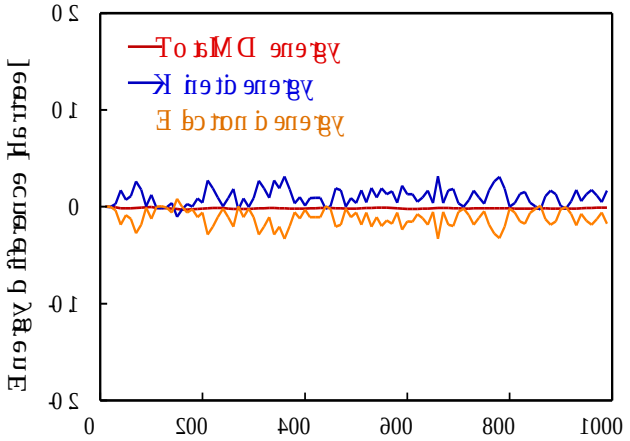
[1] P. K. Verma, A. Steinbacher, A. Schmiedel, P. Nuernberger, T. Brixner, *Struct. Dyn.*, **3**, 023606 (2015).

Application: excited-state single proton transfer

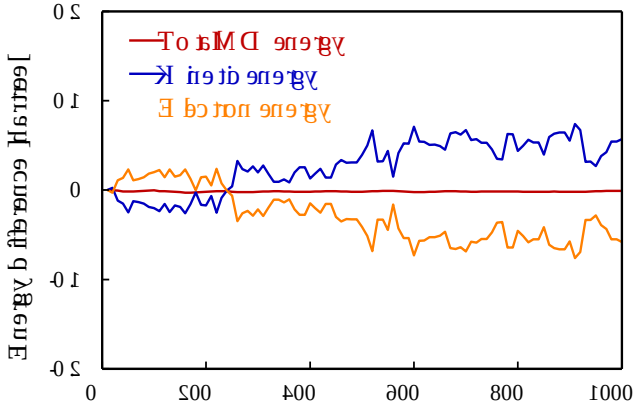
Excited state proton transfer
of 2-acetylindan-1,3-dione (AID)



Ground state



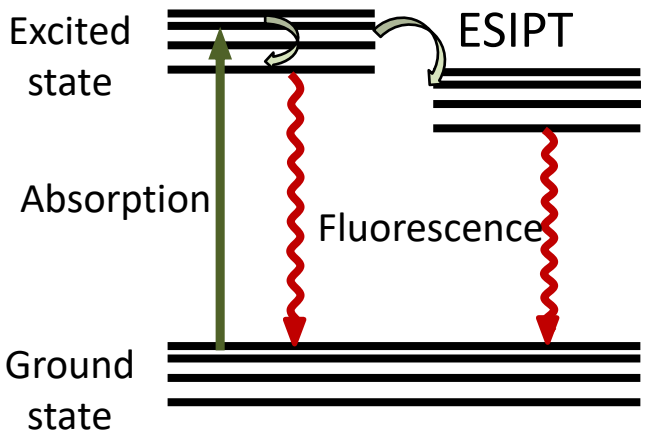
Excited state



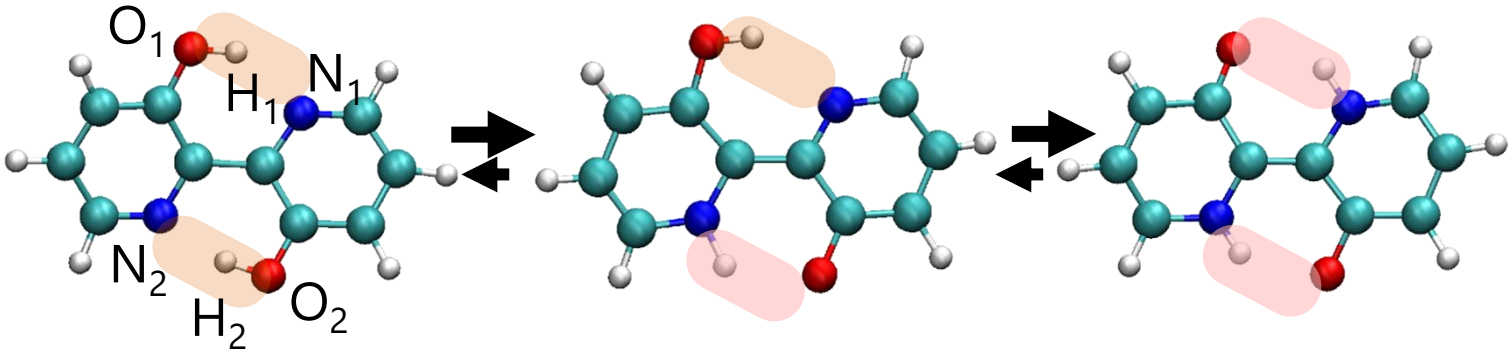
[1] P. K. Verma, A. Steinbacher, A. Schmiedel, P. Nuernberger, T. Brixner, *Struct. Dyn.*, **3**, 023606 (2015).

Excited-state intramolecular proton transfer (ESIPT)

- Application for organic electro-luminescence and biosensor
- Large red-shift fluorescence spectrum



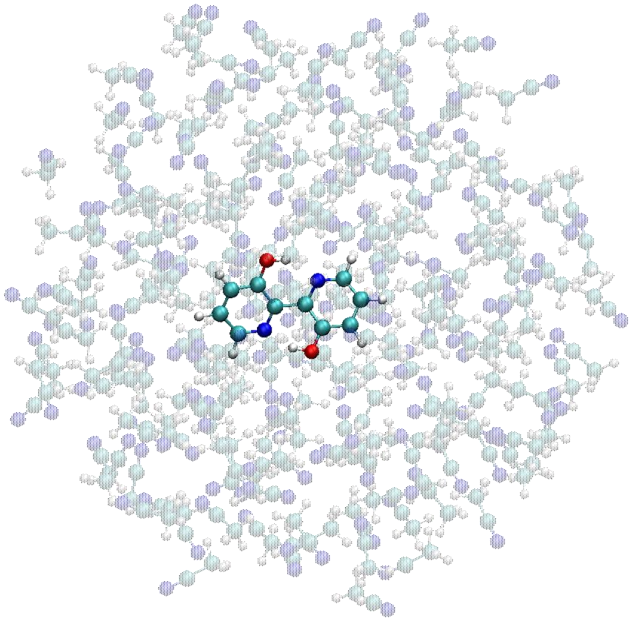
- 2,2'-Bipyridine-3,3'-diol ($BP(OH)_2$)
  - Excited-sate intramolecular double proton transfer in polar solvent



dienol monoketo diketo

Excited-state intramolecular proton transfer (ESIPT)

- Computational details



Model

$BP(OH)_2$+ 185 acetonitrile molecules (droplet) after equilibration

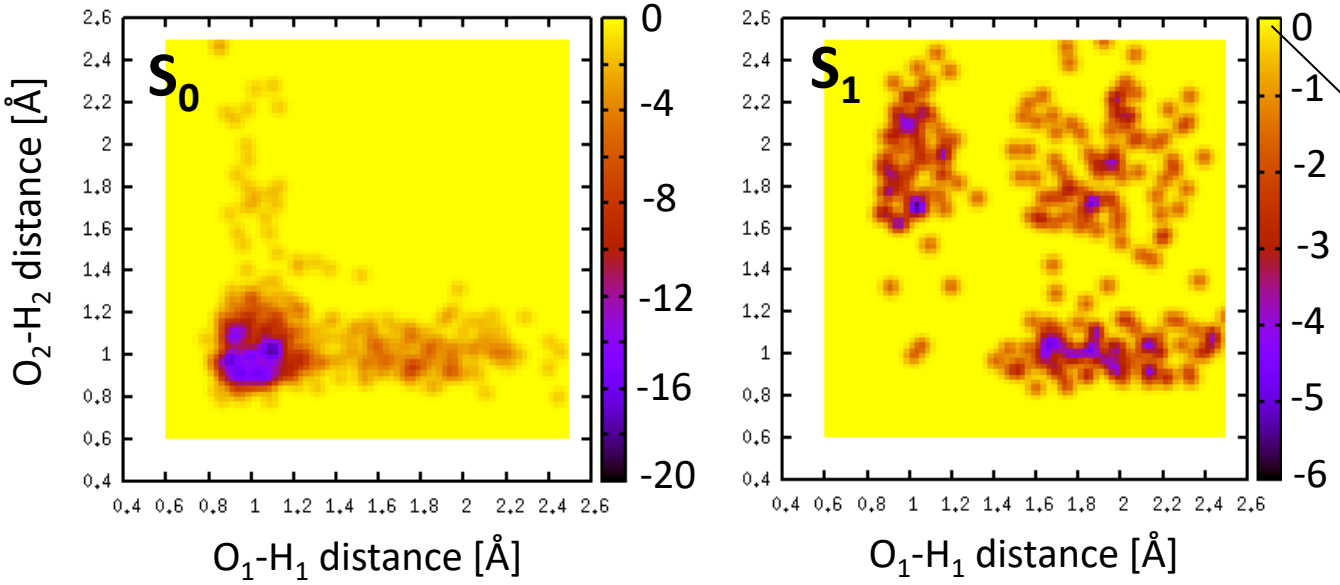
DC-(TD)LCDFTB metaDynamics

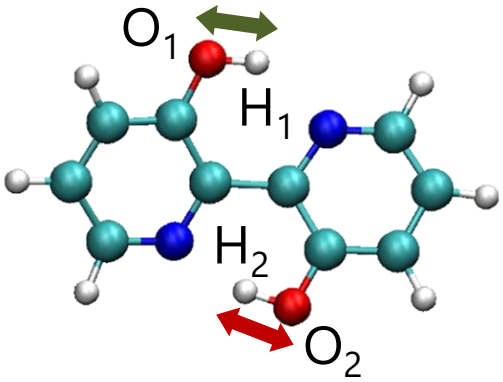
- ✓ *NVT* run for 9 ps at 300 K in ground state (DC-LCDFB)
- ✓ *NVE* run for 5 ps in excited state (DC-TDLCDFTB)
- ✓ Δt = 0.5 fs
- ✓ Parameter: OB2[1]
- ✓ Subsystem: $BP(OH)_2$, acetonitrile
- ✓ Excitation canter: $BP(OH)_2$
- ✓ Buffer size: 5.0 Å
- ✓ Soft potential: r = 17.0 Å
- ✓ Dispersion correction: Grimme's DFT-D3
- ✓ Corrective variable: O-H distance
- ✓ Gaussian potential height: 1.88 kcal·mol^{-1}
- ✓ Gaussian potential width: 0.025 Å
- ✓ Frequency of gaussian potential addition : 20 fs
- ✓ Bias temperature: 9000 K

[1] V. Q. Vuong, J. A. Kuriappan, M. Kubillus, J. J. Kranz, T. Mast, T. A. Niehaus, S. Irle, and M. Elstner, *J. Chem. Theory Comput.*, **14**, 115 (2018).

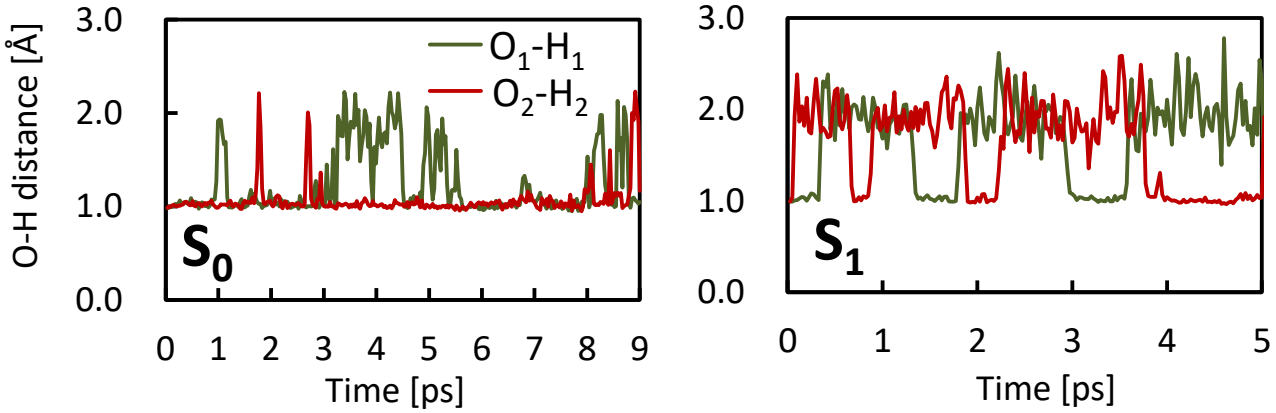
Excited-state intramolecular proton transfer (ESIPT)

- Free energy surface for O-H distances





Time series of O-H distances



✓Proton transfer occurred easily in S_1 state.

Summary

- Development of Divide-and-conquer-based time-dependent density-functional tight-binding theory for large excited-state systems: DC-TDDFTB-MD
- Compatibility of DC and GPU
- Further work: Ground state for GPU more large and long-time simulation