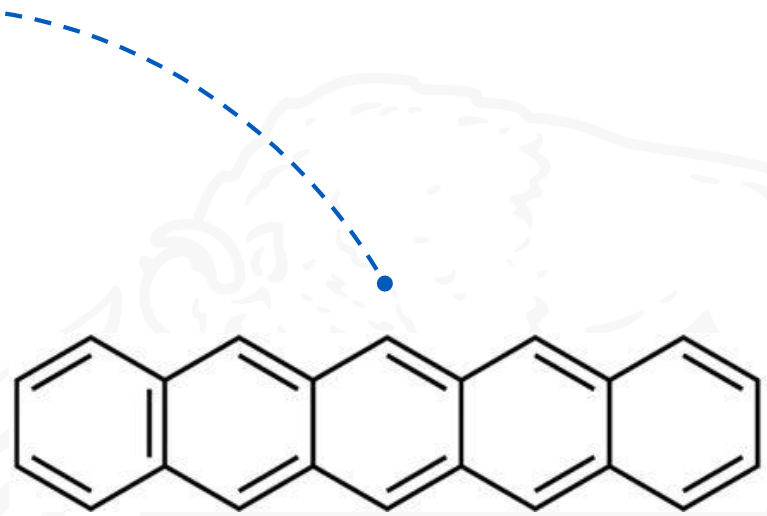
Nonadiabatic Molecular Dynamics with Subsystem Density Functional Theory:

Application to Crystalline Pentacene

Speaker: Qingxin Zhang

University at Buffalo The State University of New York

Organic semiconductor---Pentacene($C_{22}H_{14}$)

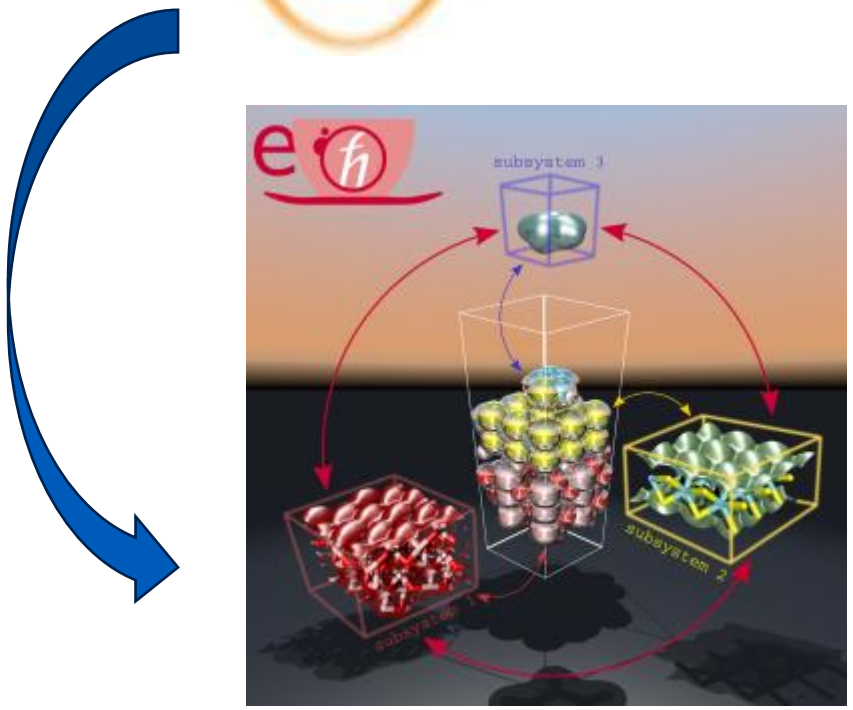


- Low cost due to the flexibility
- Has the potential to participate in multiple excitation and generation and singlet fission
- Widely studied in experiments and theoretical calculations, its potential exceeds the Shockley-Quesnel limit for solar energy conversion efficiency

Science

HOME › SCIENCE › VOL. 340, NO. 6130 › EXTERNAL QUANTUM EFFICIENCY ABOVE 100% IN A SINGLET-EXCITON-FISSION–BASED ORGANIC PHOTOVOLTAIC CELL

External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission–Based Organic Photovoltaic Cell



The embedded Quantum ESPRESSO package

Subsystem DFT (sDFT)

$$\rho(r) = \sum_I \rho_I(r), \ I \text{ for subsystem} \quad (1)$$

$$\frac{\delta E}{\delta \rho_I(r)} = 0, \forall I \quad (2)$$

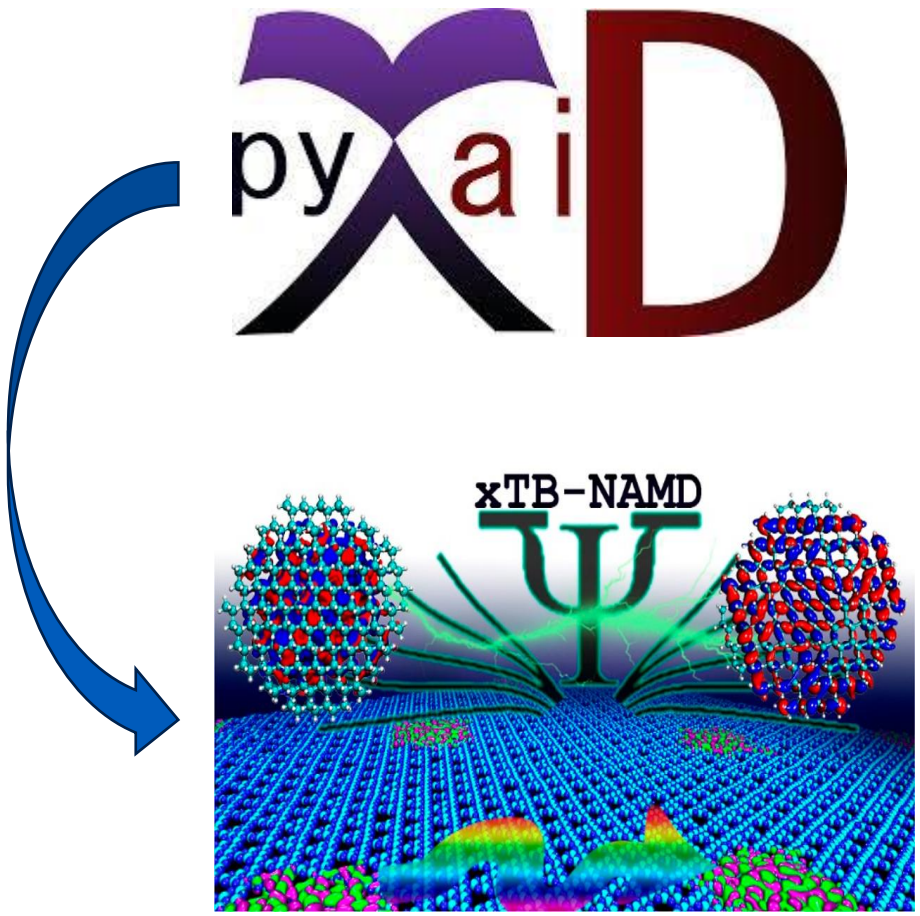
$$\left[-\frac{1}{2}\nabla^2 + v_s[\rho_I](r) + v_{emb}^I[\{\rho_I\}](r)\right]\phi_i^I(r) = \varepsilon_i^I \phi_i^I(r) \quad (3)$$

$$v_{emb}^I[\{\rho_I\}](r) = \frac{\delta E^{nad}[\{\rho_I\}]}{\delta \rho_I(r)} \quad (4)$$

$$E^{nad}[\{\rho_I\}] = E[\rho] - \sum_I E[\rho_I] \quad (5)$$

- compared with KS-DFT
- the number of subsystems
- the limitation of eQE

Nonadiabatic Molecular Dynamics



Libra: An open-Source “methodology discovery” library for quantum and classical dynamics simulations

$$\Psi(\boldsymbol{r}: t) = \sum_{I=0}^{N-1} c_I(t)\, \Phi_I\big(\boldsymbol{r}; \boldsymbol{R}(t)\big) \tag{6}$$

$$\hat{H}_{el}\big(\boldsymbol{r}; \boldsymbol{R}(t)\big)\, \Phi_I\big(\boldsymbol{r}; \boldsymbol{R}(t)\big) = E_i(R(t))\, \Phi_I\big(\boldsymbol{r}; \boldsymbol{R}(t)\big) \tag{7}$$

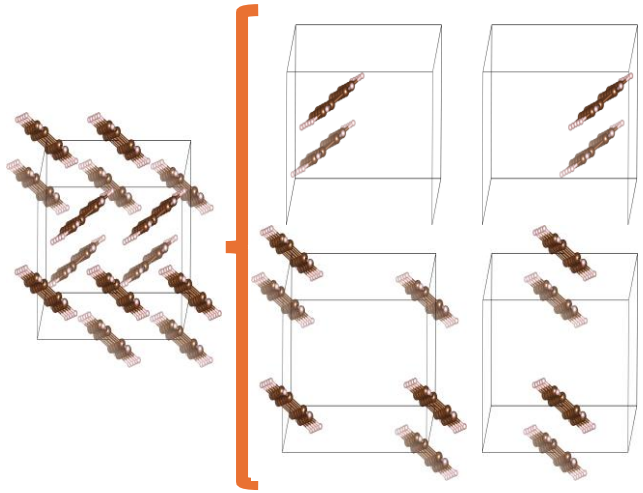
$$i\hbar \frac{\partial c_i(t)}{\partial t} = \sum_j \big[E_j(t)\delta_{i,j} - \mathrm{i}\hbar D_{i,j}(t)\big] c_j(t)$$
$$= \sum_j H_{i,j}^{vib}(t) c_j(t) \tag{8}$$

1. Fewest switches surface hopping(FSSH)
2. Global flux surface hopping(GFSH)
3. Instantaneous decoherence at attempted hops (ID-A)
4. Modified simplified decay of mixing (mSDM)
5. Decoherence-induced surface hopping (DISH) *
6. Instantaneous decoherence at frustrated hops (ID-F)*

(*stands for new methods)

Use Python code *cell_split* to cut the system into multiple fragments (each fragment contains 36 atoms)

- 2x1x1 system (144 atoms) → (4 fragments)
- 2x2x1 system (288 atoms) → (8 fragments)
- 3x3x1 system (648 atoms) → (18 fragments)



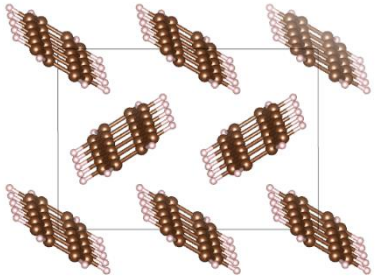
"fde_cell_split" is a parameter setting in the eQE input file

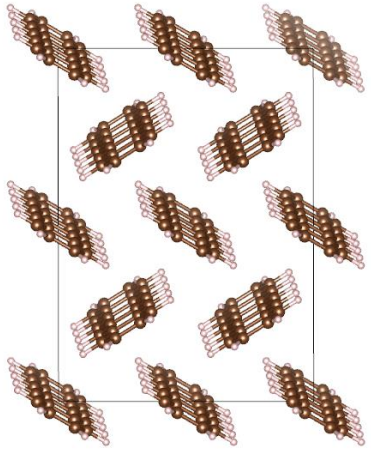
- fde_cell_split(1) = 0.8
- fde_cell_split(2) = 1
- fde_cell_split(3) = 1

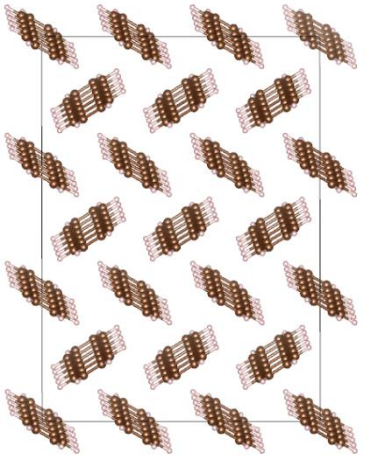
Job submission instruction:
The **4** of **6** settings are arranged in fragment_procs.in

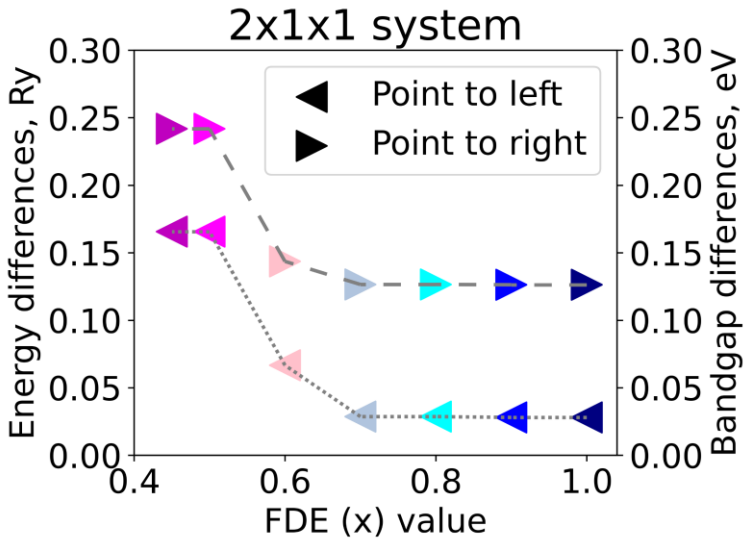
mpirun -np **24** fdepw.x -ni **4** -in pentacene-211

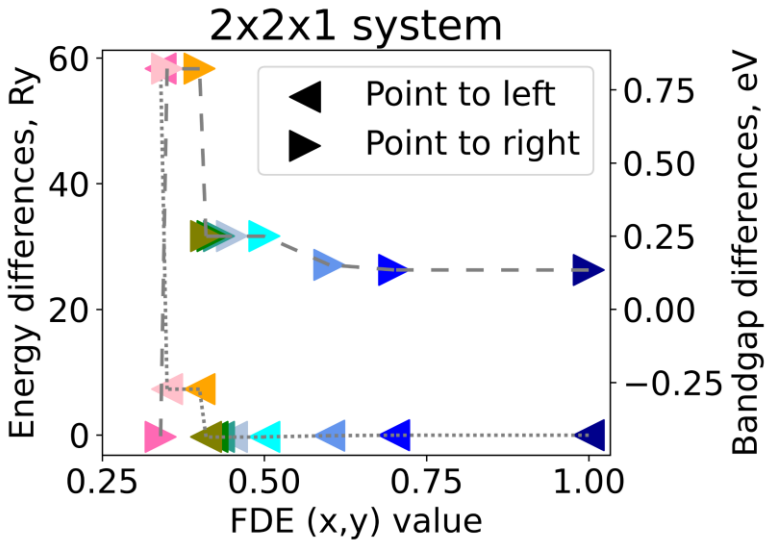
https://github.com/AkimovLab/Project_Libra-eQE

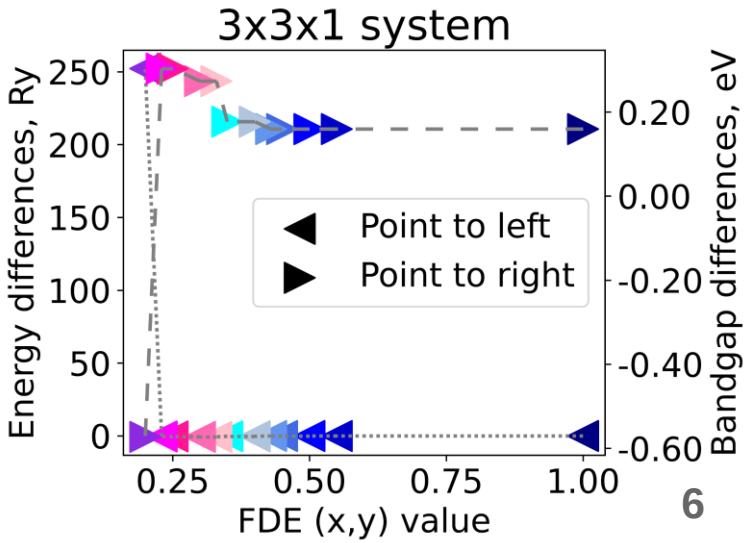


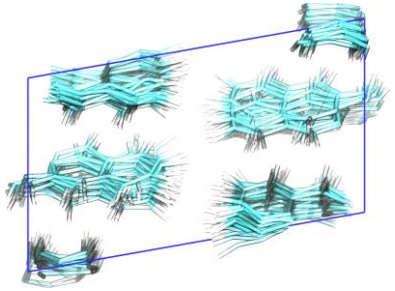


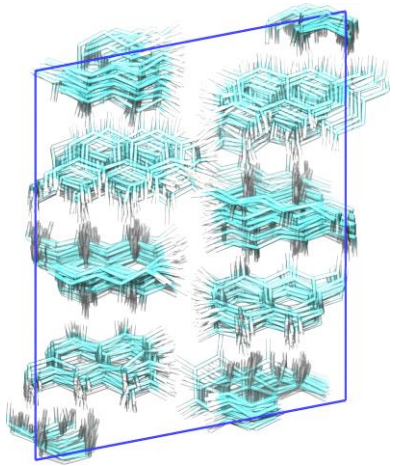


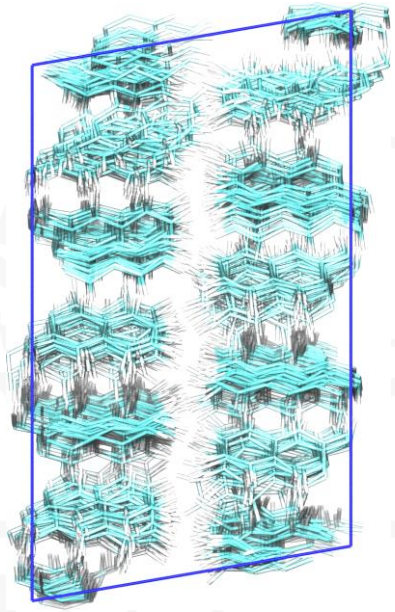

2x1x1 system
Point to left
Point to right
Energy differences, Ry
Bandgap differences, eV
FDE (x) value
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.4
0.6
0.8
1.0

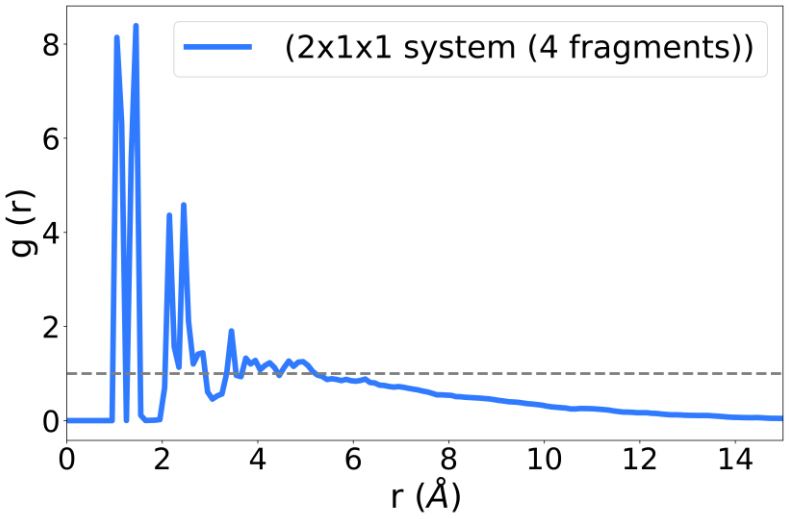

2x2x1 system
Point to left
Point to right
Energy differences, Ry
Bandgap differences, eV
FDE (x,y) value
0
20
40
60
−0.25
0.00
0.25
0.50
0.75
0.25
0.50
0.75
1.00

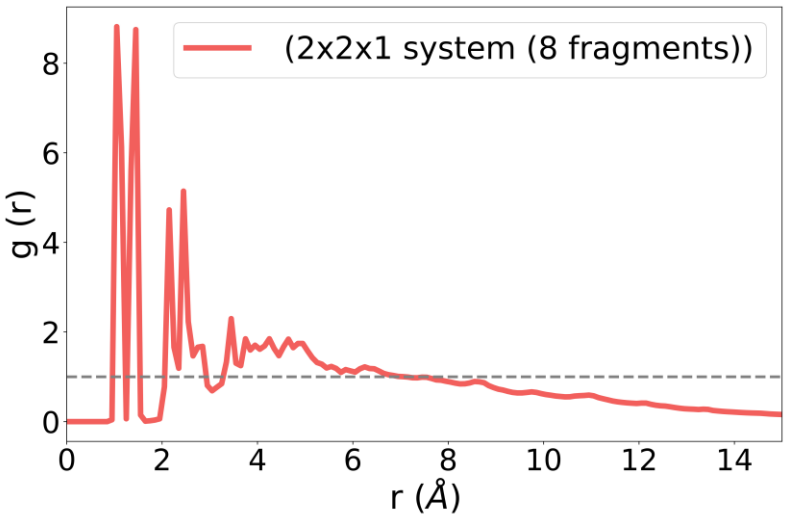

3x3x1 system
Point to left
Point to right
Energy differences, Ry
Bandgap differences, eV
FDE (x,y) value
0
50
100
150
200
250
-0.60
-0.40
-0.20
0.00
0.20
0.25
0.50
0.75
1.00

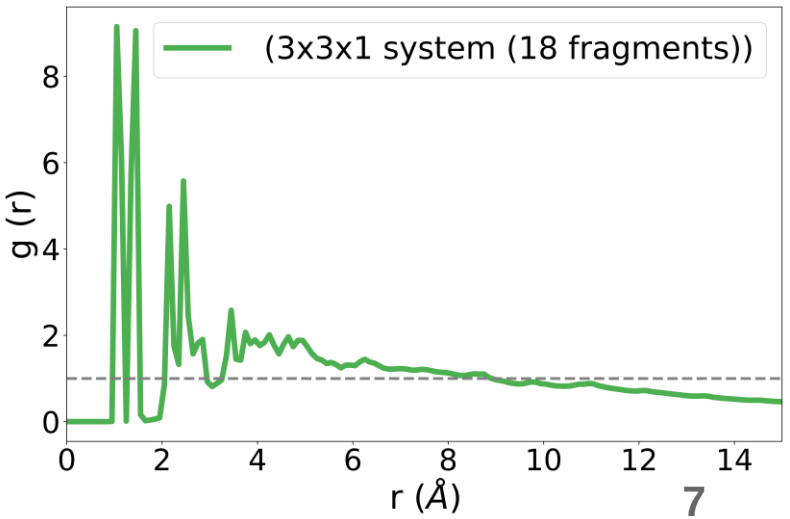


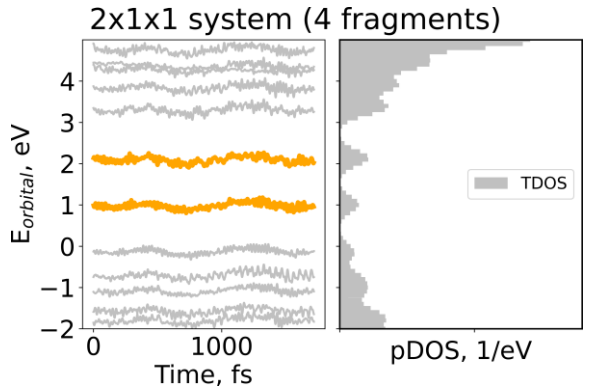


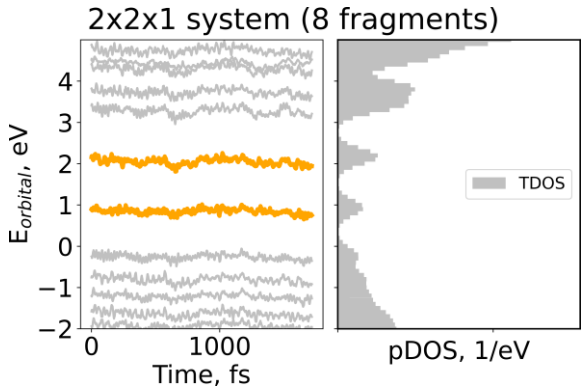


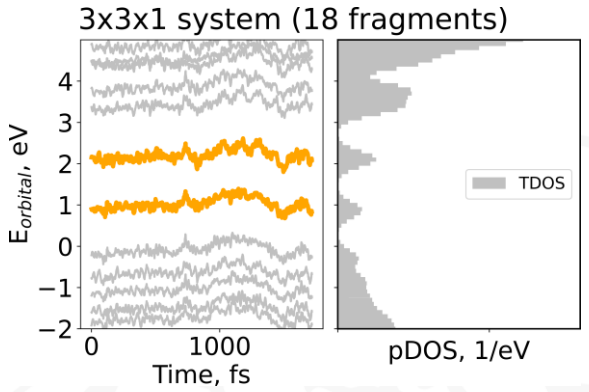

(2x1x1 system (4 fragments))
g (r)
r (Å)
0
2
4
6
8
10
12
14

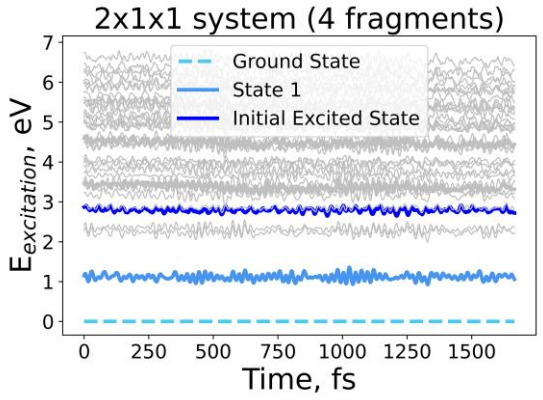

(2x2x1 system (8 fragments))
g (r)
r (Å)
0
2
4
6
8
10
12
14

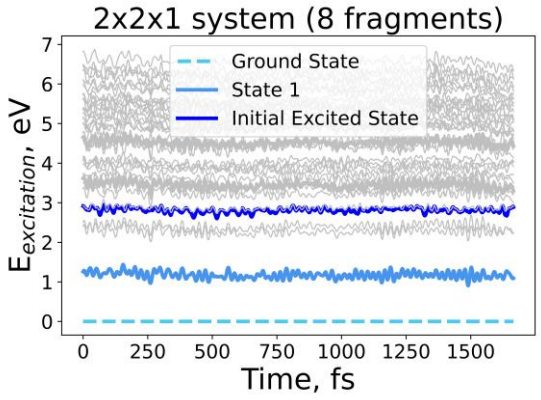

(3x3x1 system (18 fragments))
g (r)
r (Å)
0
2
4
6
8
10
12
14

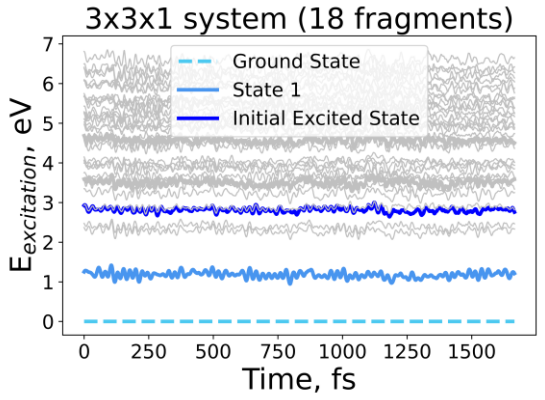

2x1x1 system (4 fragments)
$E_{orbital}$, eV
Time, fs
pDOS, 1/eV
TDOS

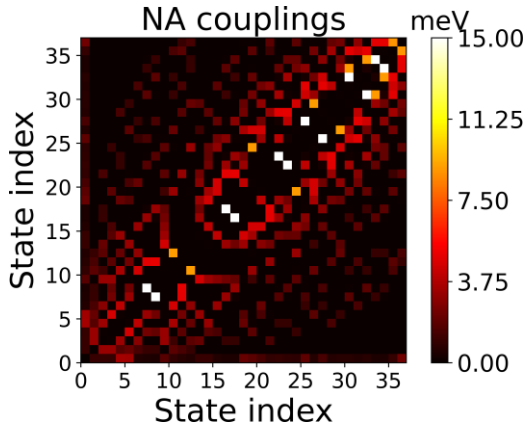

2x2x1 system (8 fragments)
$E_{orbital}$, eV
Time, fs
pDOS, 1/eV
TDOS

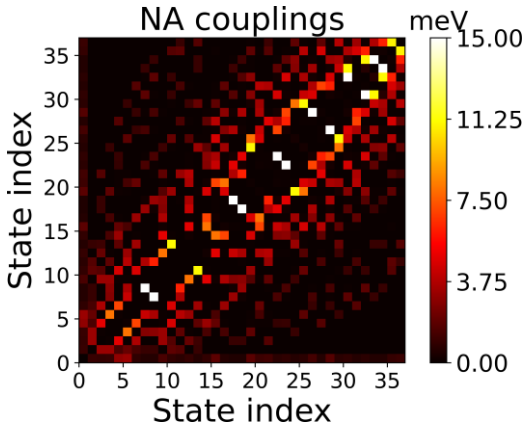

3x3x1 system (18 fragments)
$E_{orbital}$, eV
Time, fs
pDOS, 1/eV
TDOS

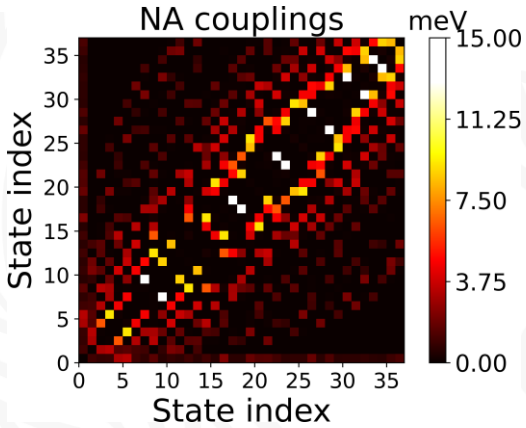

2x1x1 system (4 fragments)
Ground State
State 1
Initial Excited State
$E_{excitation}$, eV
Time, fs


2x2x1 system (8 fragments)
Ground State
State 1
Initial Excited State
$E_{excitation}$, eV
Time, fs

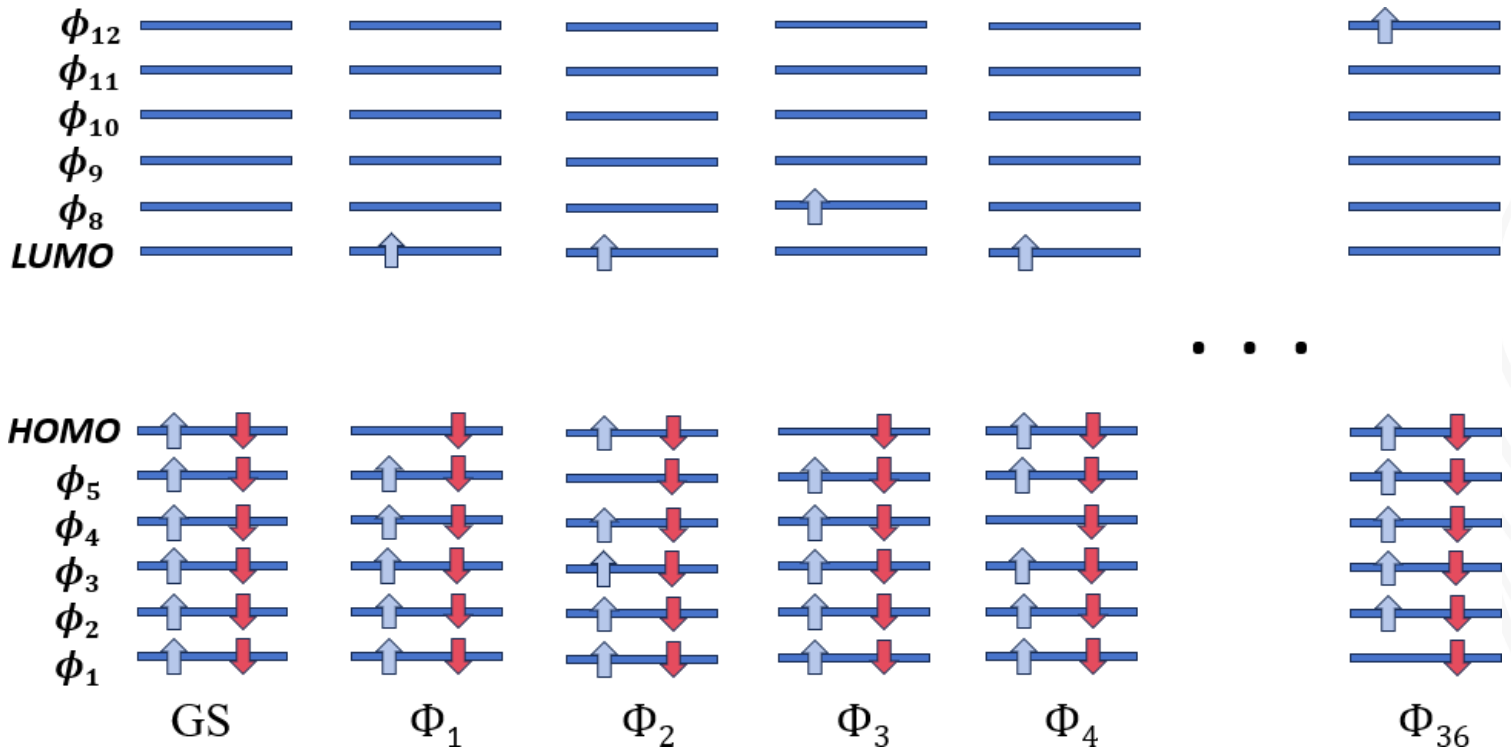

3x3x1 system (18 fragments)
Ground State
State 1
Initial Excited State
$E_{excitation}$, eV
Time, fs


NA couplings
meV
State index
State index

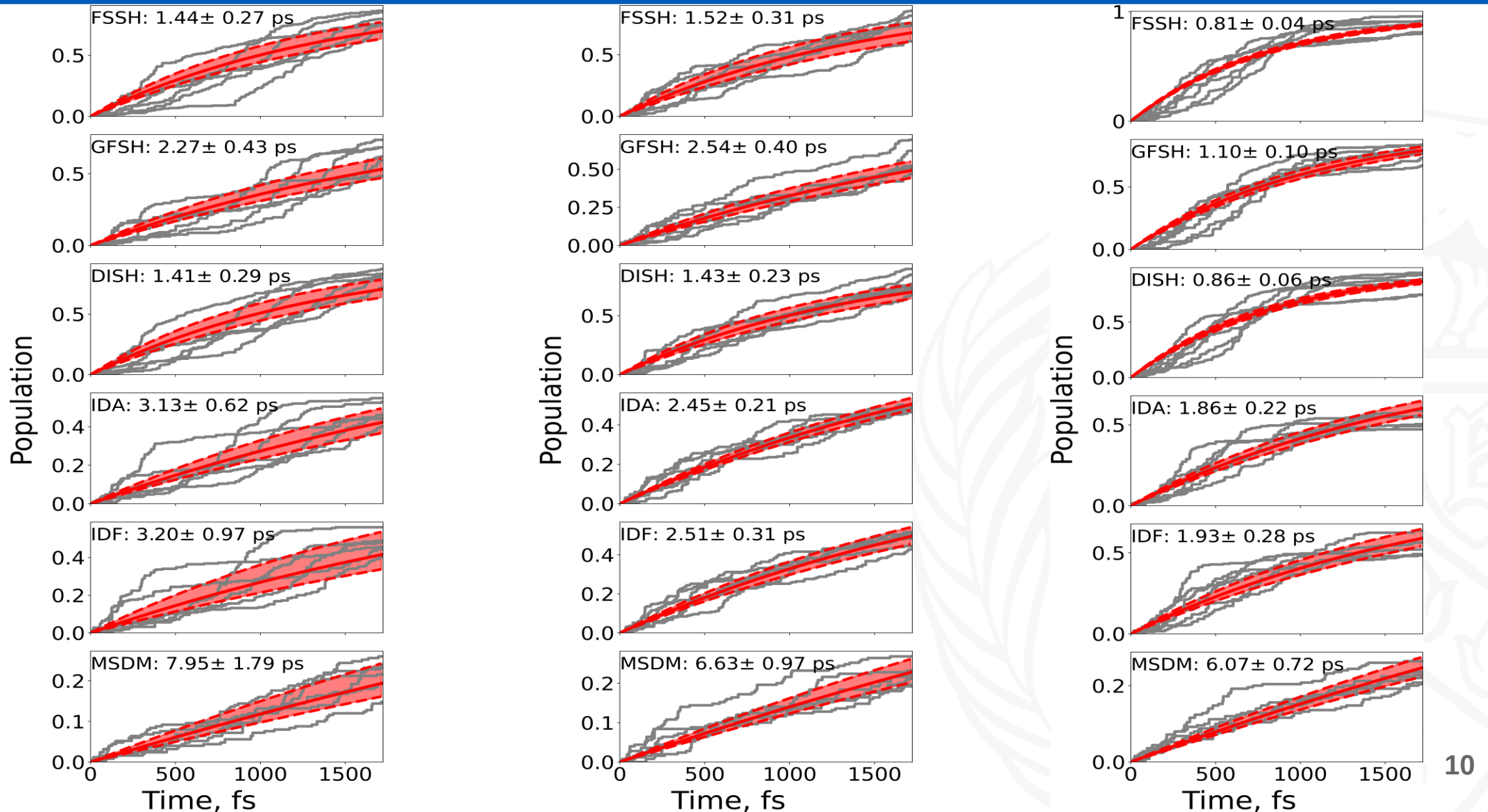

NA couplings
meV
State index
State index

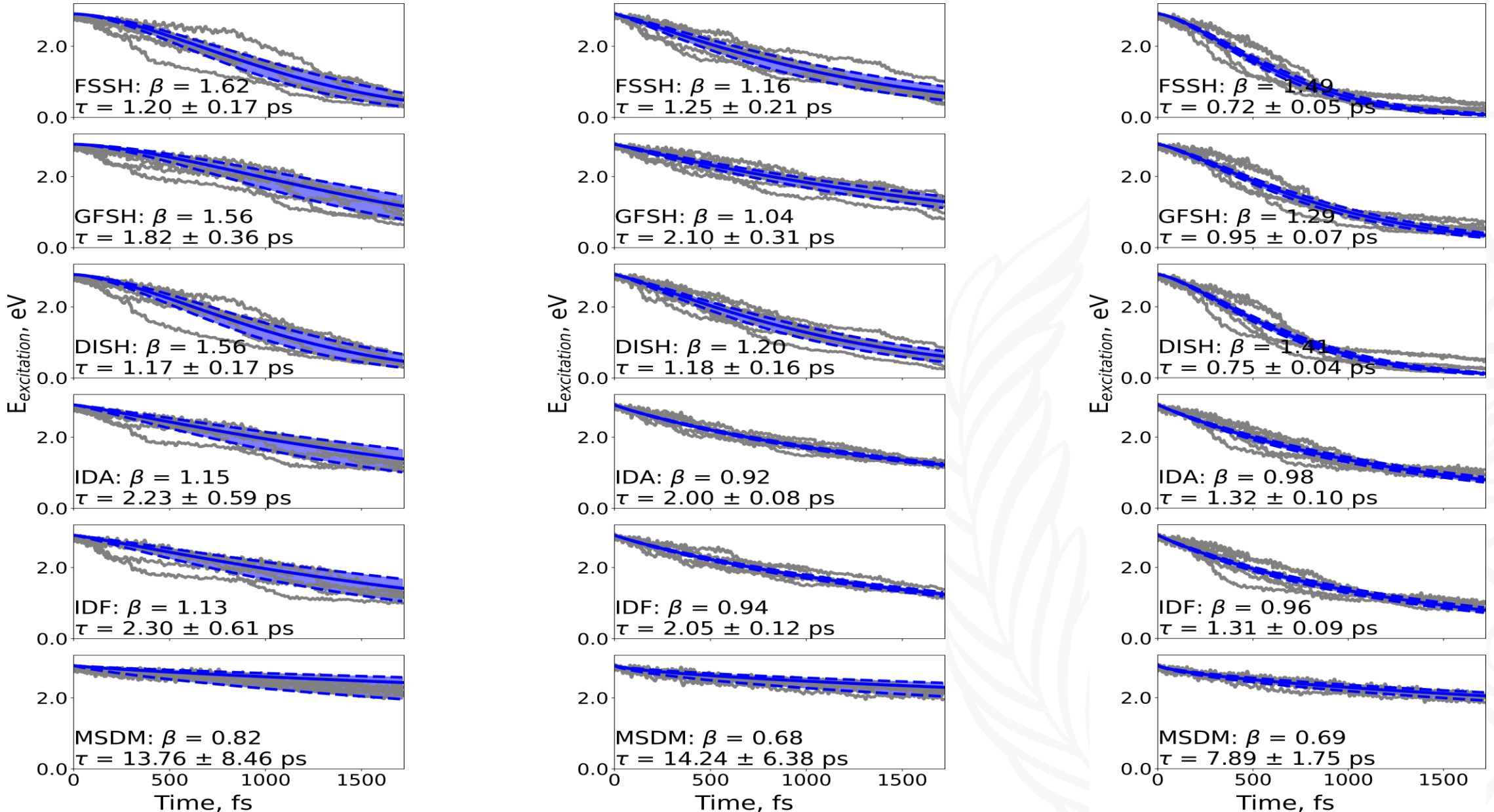

NA couplings
meV
State index
State index

Single-particle excited states basis. ϕ and Φ stand for KS orbitals and Slater determines, respectively.



- Six occupied and six unoccupied orbitals
- Thirty-seven states
- two numbers stand for each state


FSSH: 1.44± 0.27 ps
GFSH: 2.27± 0.43 ps
DISH: 1.41± 0.29 ps
IDA: 3.13± 0.62 ps
IDF: 3.20± 0.97 ps
MSDM: 7.95± 1.79 ps
FSSH: 1.52± 0.31 ps
GFSH: 2.54± 0.40 ps
DISH: 1.43± 0.23 ps
IDA: 2.45± 0.21 ps
IDF: 2.51± 0.31 ps
MSDM: 6.63± 0.97 ps
FSSH: 0.81± 0.04 ps
GFSH: 1.10± 0.10 ps
DISH: 0.86± 0.06 ps
IDA: 1.86± 0.22 ps
IDF: 1.93± 0.28 ps
MSDM: 6.07± 0.72 ps
Population
Time, fs


FSSH: β = 1.62
τ = 1.20 ± 0.17 ps
GFSH: β = 1.56
τ = 1.82 ± 0.36 ps
DISH: β = 1.56
τ = 1.17 ± 0.17 ps
IDA: β = 1.15
τ = 2.23 ± 0.59 ps
IDF: β = 1.13
τ = 2.30 ± 0.61 ps
MSDM: β = 0.82
τ = 13.76 ± 8.46 ps
FSSH: β = 1.16
τ = 1.25 ± 0.21 ps
GFSH: β = 1.04
τ = 2.10 ± 0.31 ps
DISH: β = 1.20
τ = 1.18 ± 0.16 ps
IDA: β = 0.92
τ = 2.00 ± 0.08 ps
IDF: β = 0.94
τ = 2.05 ± 0.12 ps
MSDM: β = 0.68
τ = 14.24 ± 6.38 ps
FSSH: β = 1.49
τ = 0.72 ± 0.05 ps
GFSH: β = 1.29
τ = 0.95 ± 0.07 ps
DISH: β = 1.41
τ = 0.75 ± 0.04 ps
IDA: β = 0.98
τ = 1.32 ± 0.10 ps
IDF: β = 0.96
τ = 1.31 ± 0.09 ps
MSDM: β = 0.69
τ = 7.89 ± 1.75 ps
E_excitation, eV
Time, fs
0.0
2.0
0
500
1000
1500

Conclusion

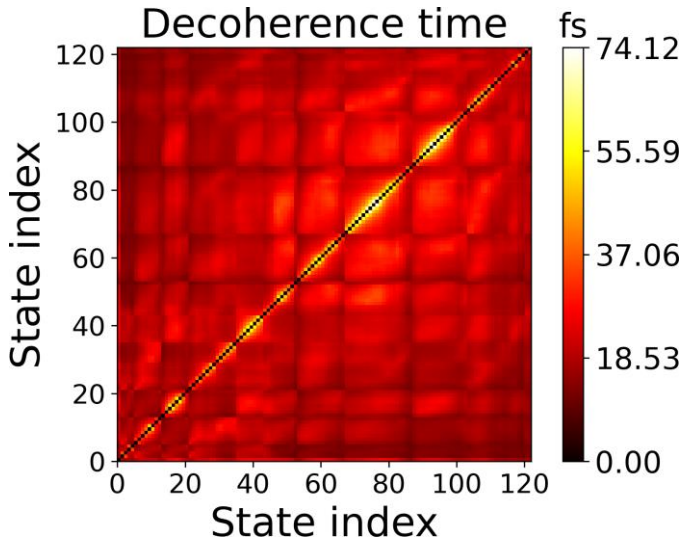
- Increased structural disorder observed in larger supercell models induces larger nonadiabatic couplings of electronic states and accelerates the relaxation dynamics of excited states

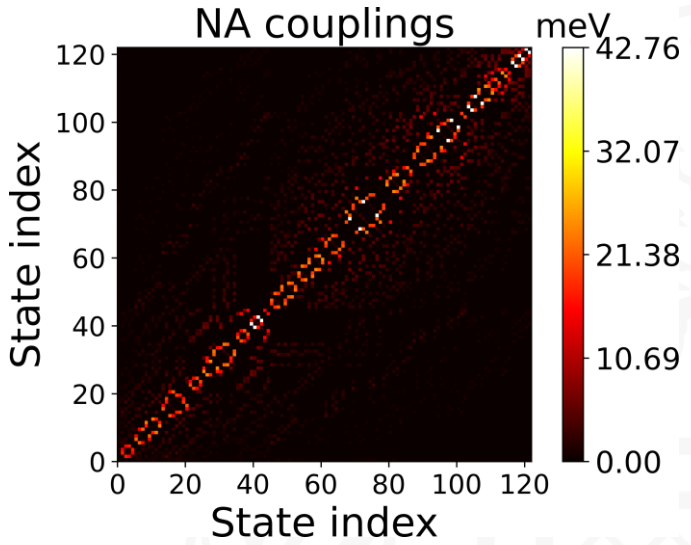
- Most of the tested schemes suggest fast energy relaxation occurring with the timescales in the 0.7 – 2.0 ps range, but they significantly overestimate the ground state recovery rates.

- Only the modified simplified decay of mixing approach yields a notably slower relaxation timescales of 8 – 14 ps, with a significantly inhibited ground state recovery.

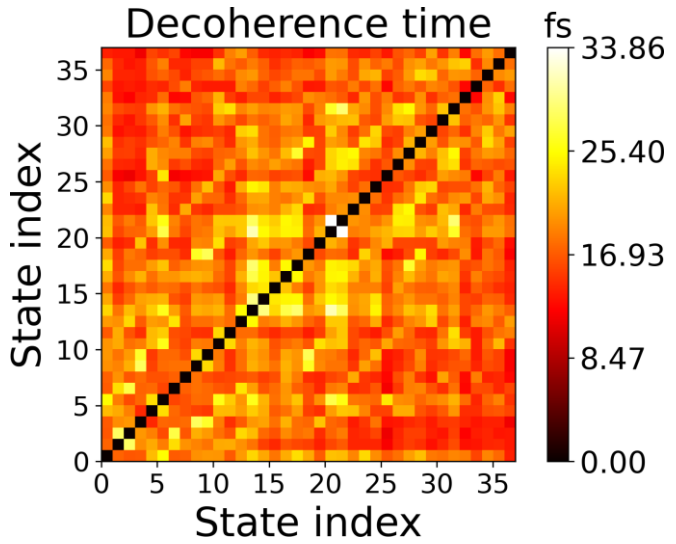
- 2x2x1 system (288 atoms) → (7 fragments) ---------- Just for fun

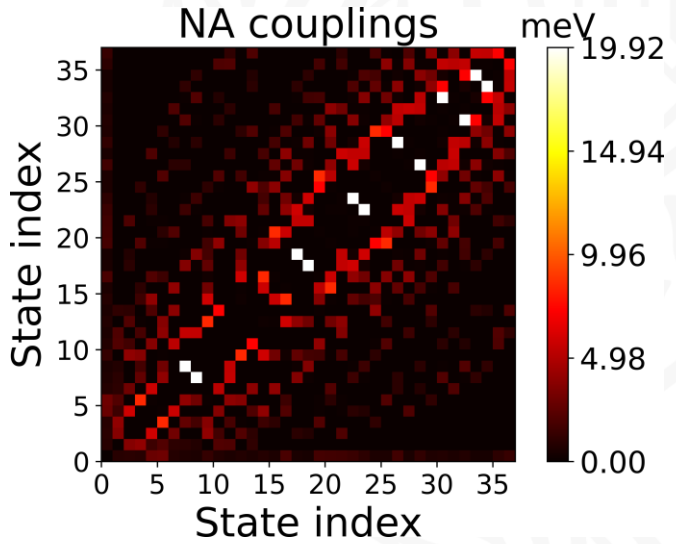
A fragment of 72 atoms



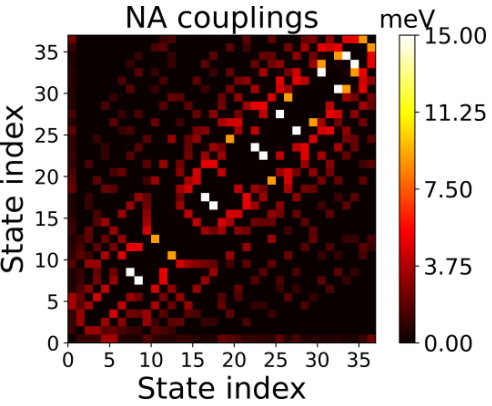


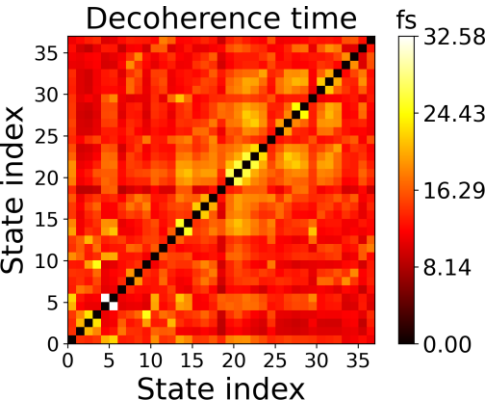
A fragment of 36 atoms



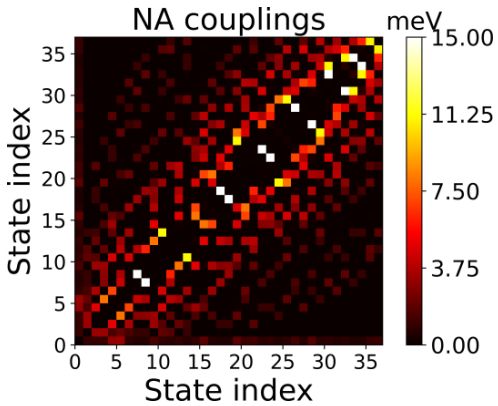


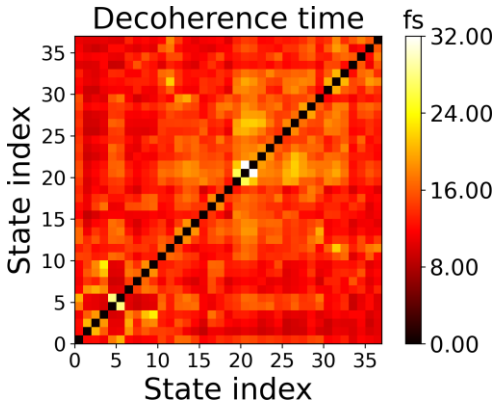
A fragment (36 atoms) of the 2x1x1 system



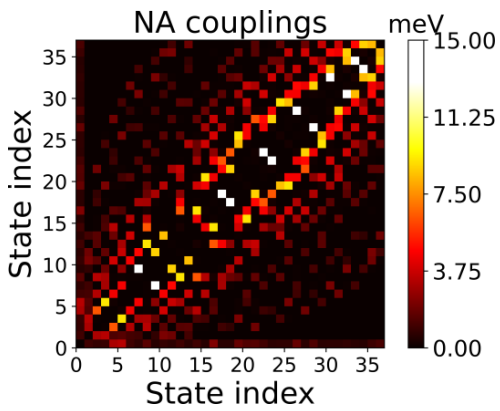


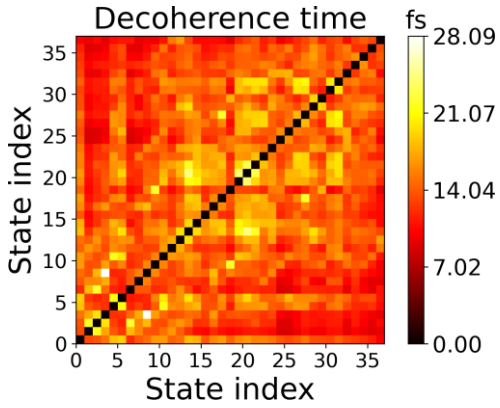
A fragment (36 atoms) of the 2x2x1 system



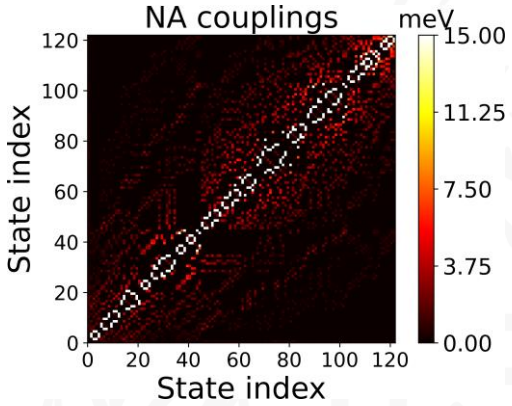


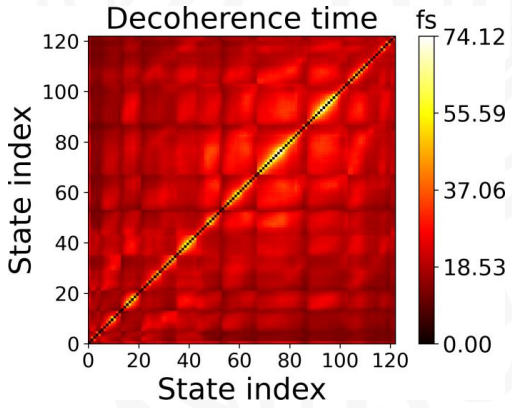
A fragment (36 atoms) of the 3x3x1 system



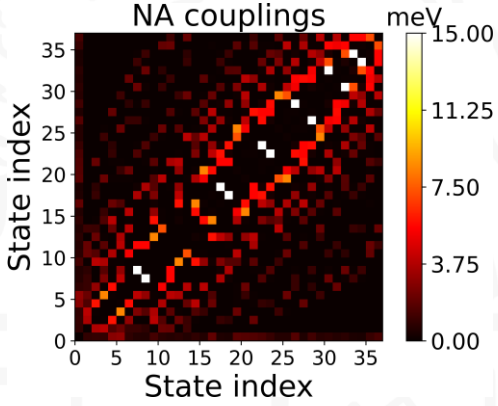


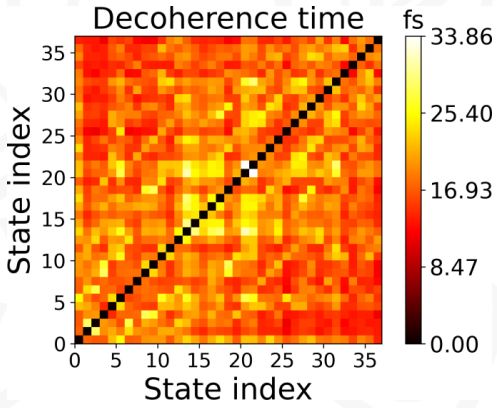
A fragment* (72 atoms) of the 2x2x1 system





A fragment* (36 atoms) of the 2x2x1 system





(*represents cell split from a special way)

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Nonadiabatic Molecular Dynamics with Subsystem Density Functional Theory: Application to Crystalline Pentacene

Qingxin Zhang,[1] Xuecheng Shao,[2] Wei Li,[3] Wenhui Mi,[4,5] Michele Pavanello,[2] and Alexey V Akimov[1]

Michele Pavanello @MikPavane... · 6/13/24

Thanks to a fun collaboration led by @AkimovLab, now subsystem DFT can even do nonadiabatic dynamics!
Learn it all in this nice JPCM:...

5 41 1607

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Our group：

Collaborators：

Miguel Recio Poo(Universitat de Barcelona)
Wei Li (Hunan Agricultural University)
Xuecheng Shao (Jilin University)
Michele Pavanello (Rutgers University)
Wenhui Mi (Jilin University)