

University of Pisa

Department of Chemistry and Industrial Chemistry (DCCI)
Virtual International Seminar on Theoretical Advancements



Surface hopping dynamics with Frenkel exciton model in a semiempirical framework

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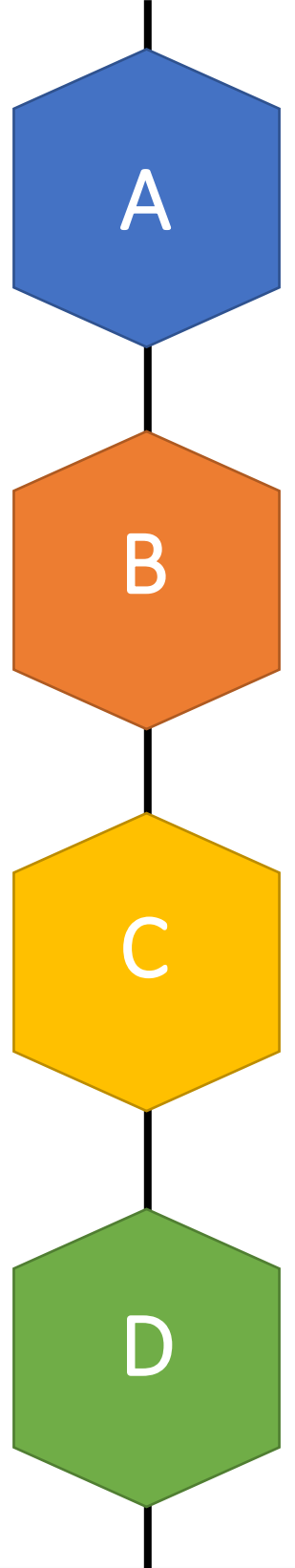
Challenges in simulating photo processes *in silico*

1. Long time scale simulations;

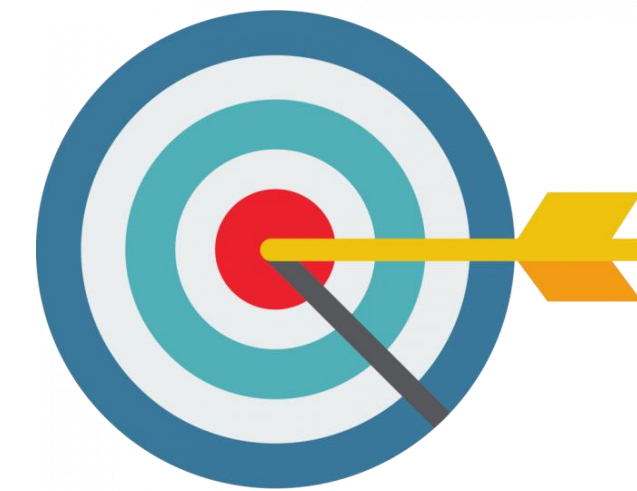
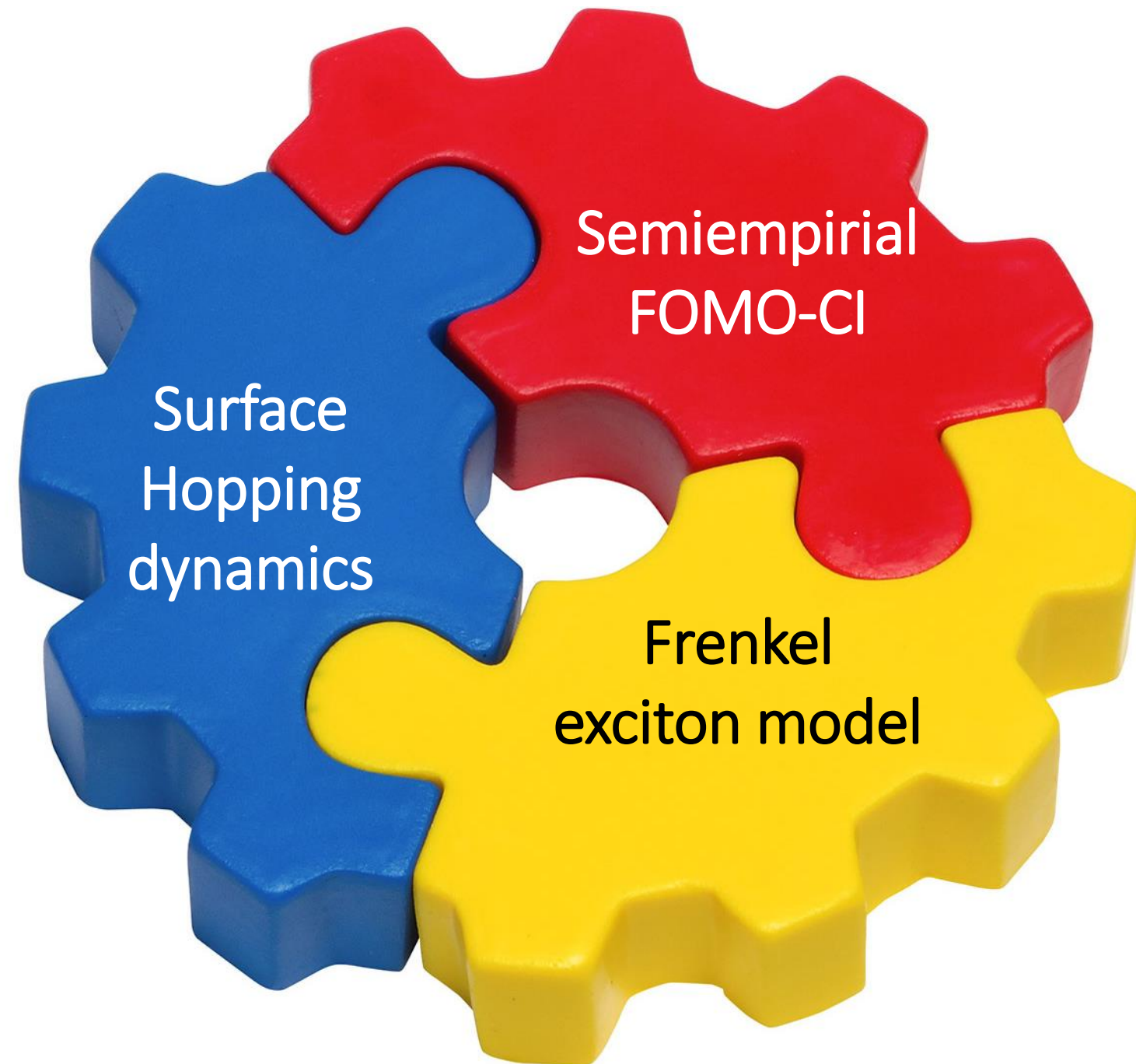
2. Simulate large systems, for instance, multichromophoric systems.

Mixed quantum-classical dynamics → Computational cost: *electronic structure method*

- The study of EET and other aspects of nonadiabatic dynamics in multichromophoric systems calls for employing some sort of **'divide and conquer'** strategy.
- **Exciton** model.



Objective

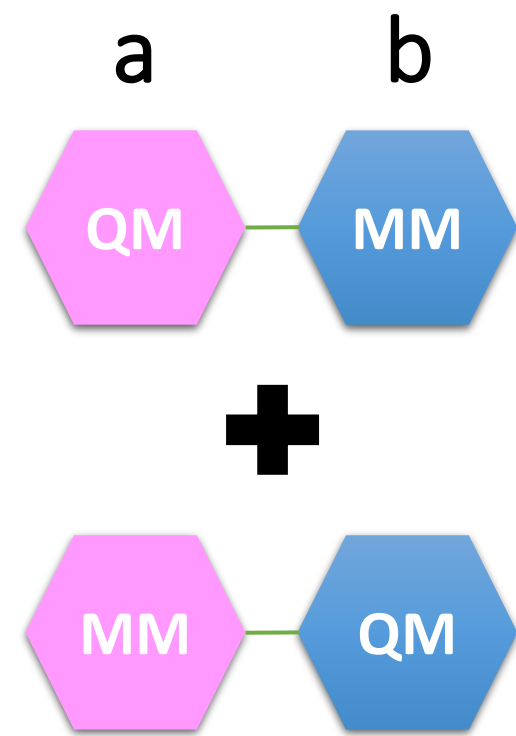


Photodynamics of multichromophoric systems

Method

Frenkel exciton model

QM/MM



$$\hat{H}^{ex} =$$

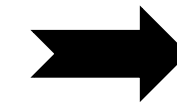
		a				b			
E^{GS}	0	...							0
0	ε_a^1	0	...	0	$V_{ab}^{1,1}$...		$V_{ab}^{1,N}$	
\vdots	0	ε_a^2	0	\vdots	\vdots	\ddots		\vdots	
	\vdots	0	\ddots	0					
	0	...	0	ε_a^N	$V_{ab}^{N,1}$...		$V_{ab}^{N,N}$	
	$V_{ba}^{1,1}$...		$V_{ba}^{1,N}$	ε_b^1	0	...	0	
	\vdots	\ddots		\vdots	0	ε_b^2	0	\vdots	
					\vdots	0	\ddots	0	
0	$V_{ba}^{N,1}$...		$V_{ba}^{N,N}$	0	...	0	ε_b^N	

+

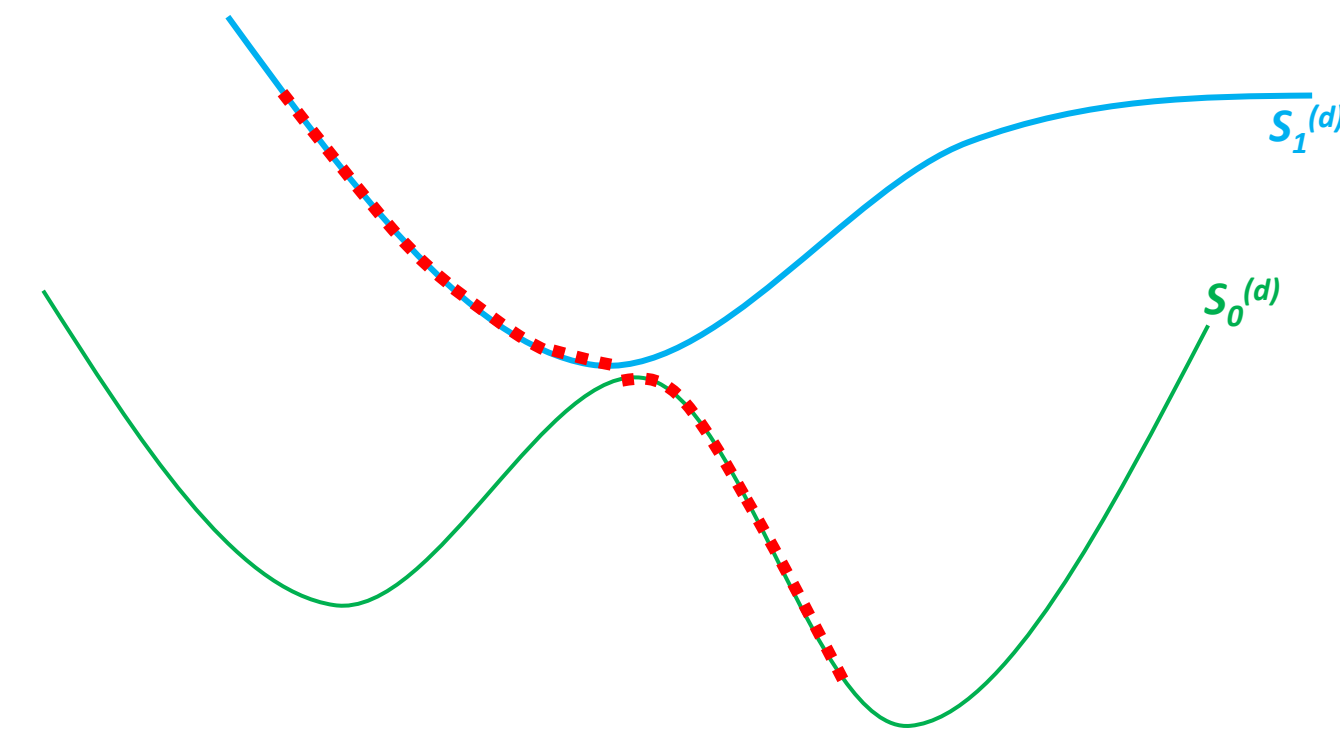
Gradients

+

Nonadiabatic couplings



Trajectory Surface Hopping



$$E^{GS} = E_{tot}^{MM} + \sum_i (E_i^{QM/MM(S_0)} - E_{tot}^{MM})$$

Method

Couplings (off-diagonal terms)

$$V_{ai,bj} \simeq \int \frac{\rho_{0i}^{(a)}(\mathbf{r}_1)\rho_{0j}^{(b)}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$$V_{ai,bj} = \sum_{A \in a} \sum_{B \in b} \sum_{\mu\nu \in A} \sum_{\sigma\tau \in B} \rho_{0i,\mu\nu}^{(a)} \rho_{0j,\sigma\tau}^{(b)} (\mu\nu|\sigma\tau) \longrightarrow \text{"Exact Coulomb" (EC)}$$

It scales quadratically with the number of chromophores.

$$V_{ai,bj} \simeq \sum_{A \in a} \sum_{B \in b} \frac{q_{A,ai} q_{B,bj}}{R_{AB}} \longrightarrow \text{"Transition charges" (TC)}$$

It scales linearly with the number of chromophores.

Method

Gradients and integration of the electronic TD Schrodinger equation

- Gradients;
- Integration of the electronic TD Schrodinger equation: Local diabaticization.

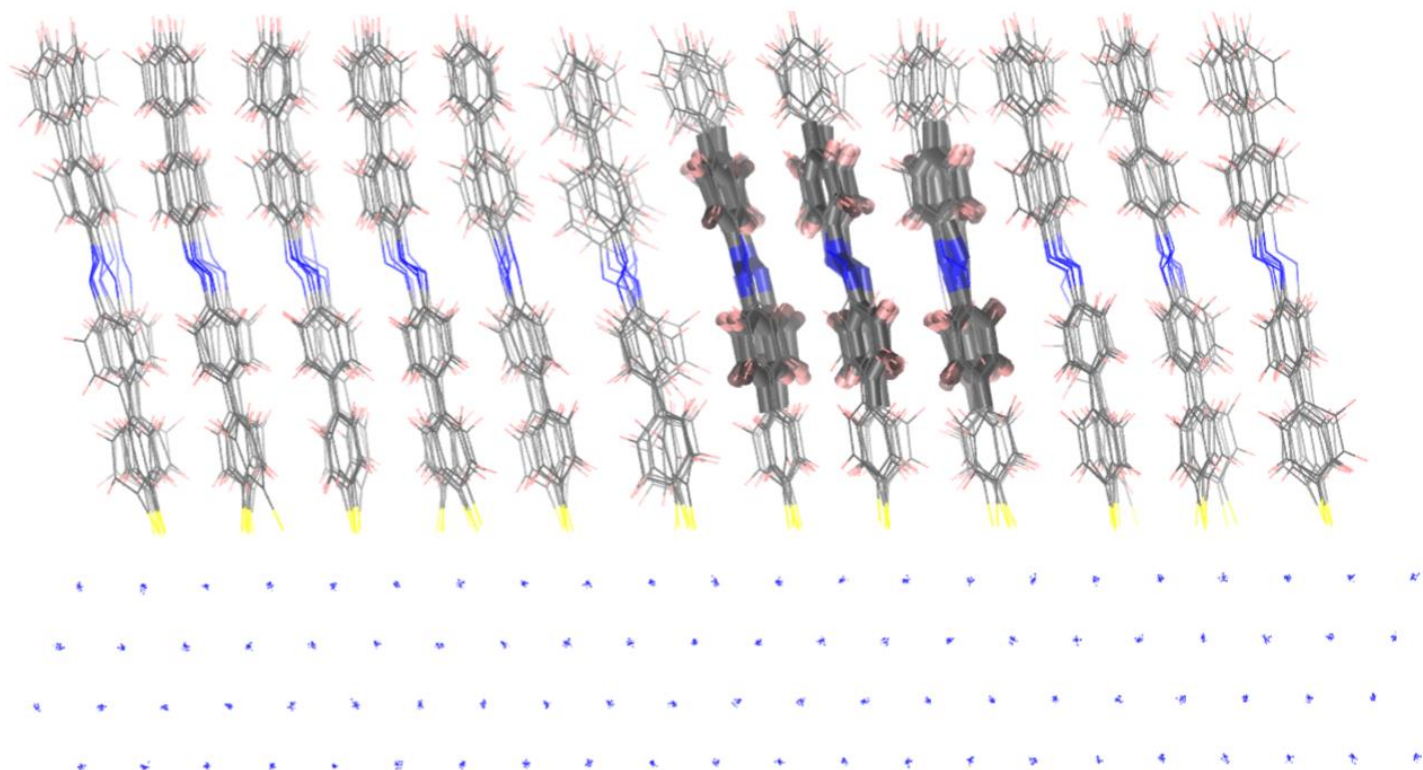
$$S_{KL} = \langle K(t) | L(t + \Delta t) \rangle$$

Sangiogo Gil, E.; Granucci, G.; Persico, M., Surface hopping dynamics with Frenkel exciton model in a semiempirical framework. *J. Chem. Theory Comput.* **2021**, *17* (12), 7373-7383.

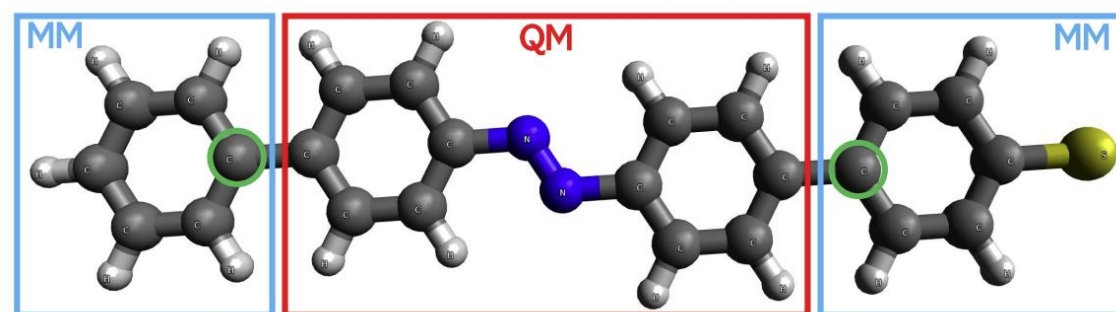
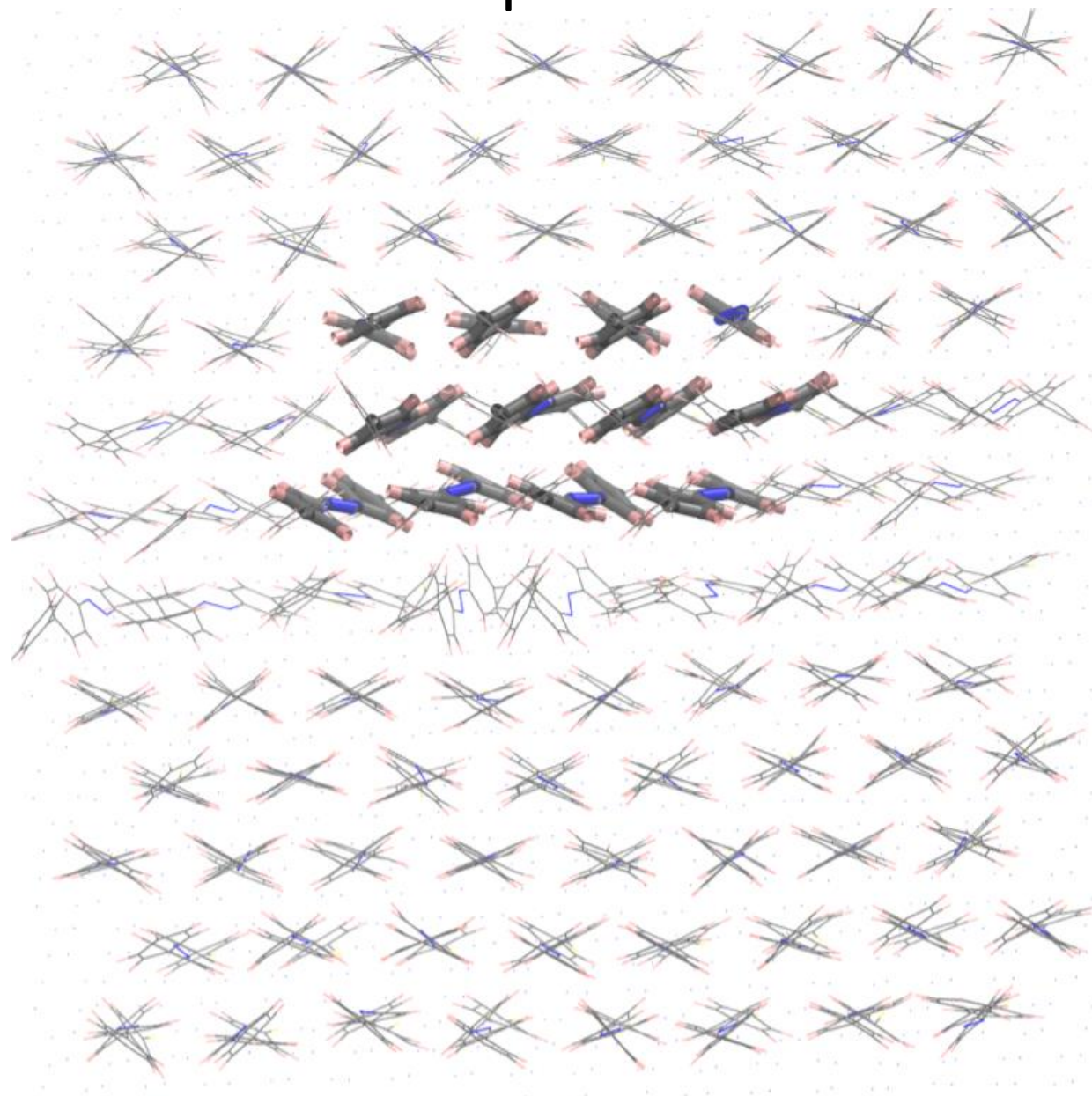
Application

Photodynamics of SAMs of ABPT

Side view:



Top view:



Link atoms

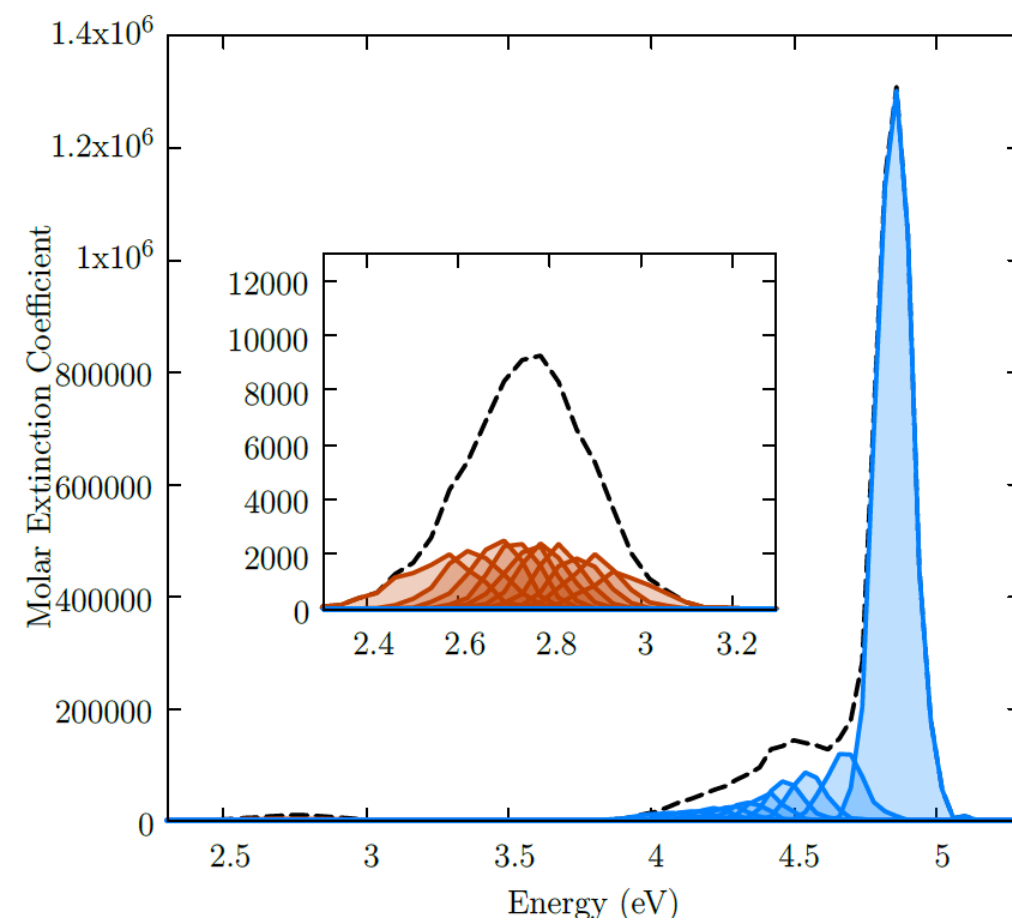
- Thermalization trajectories with **10**; **12** and **20** monomers; → Absorption Spectra;
- SH dynamics with **12** monomers;
- S_1 and S_2 state of each monomer were included in the exciton Hamiltonian.

Application

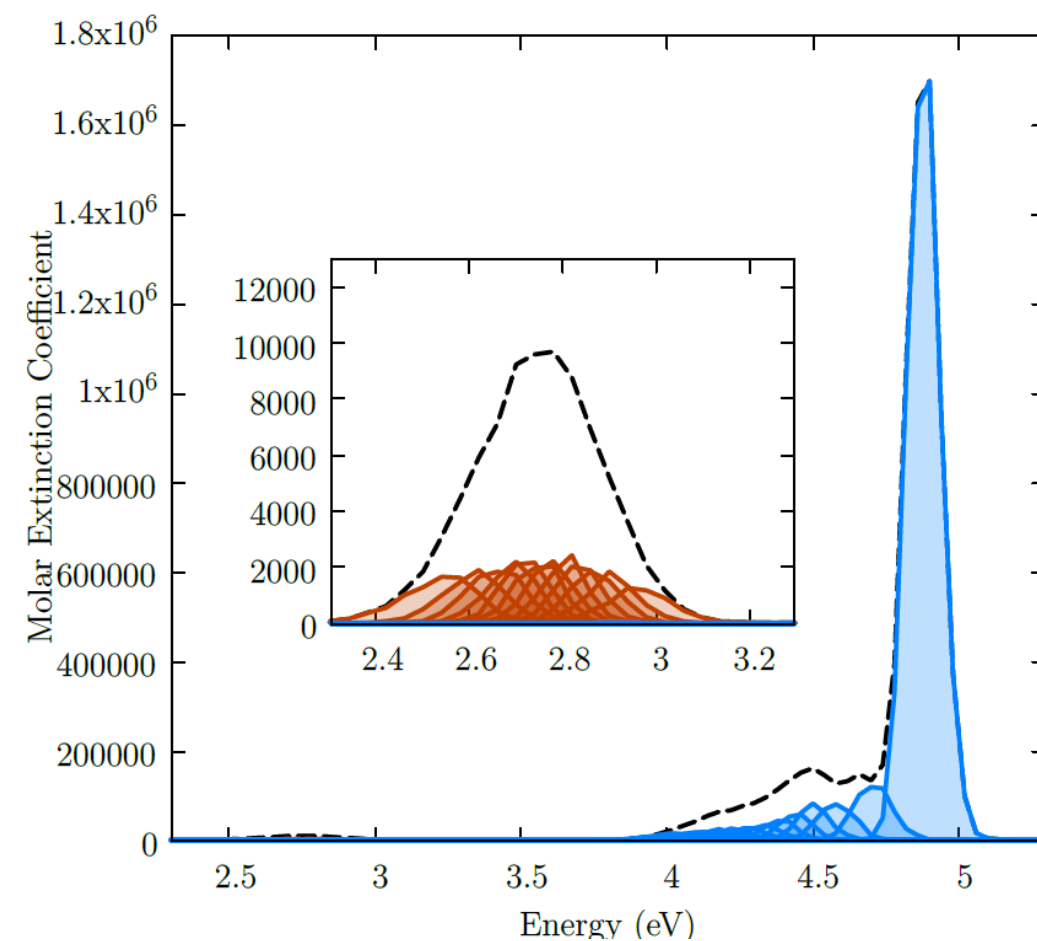
Photodynamics of SAMs of ABPT

Absorption Spectra

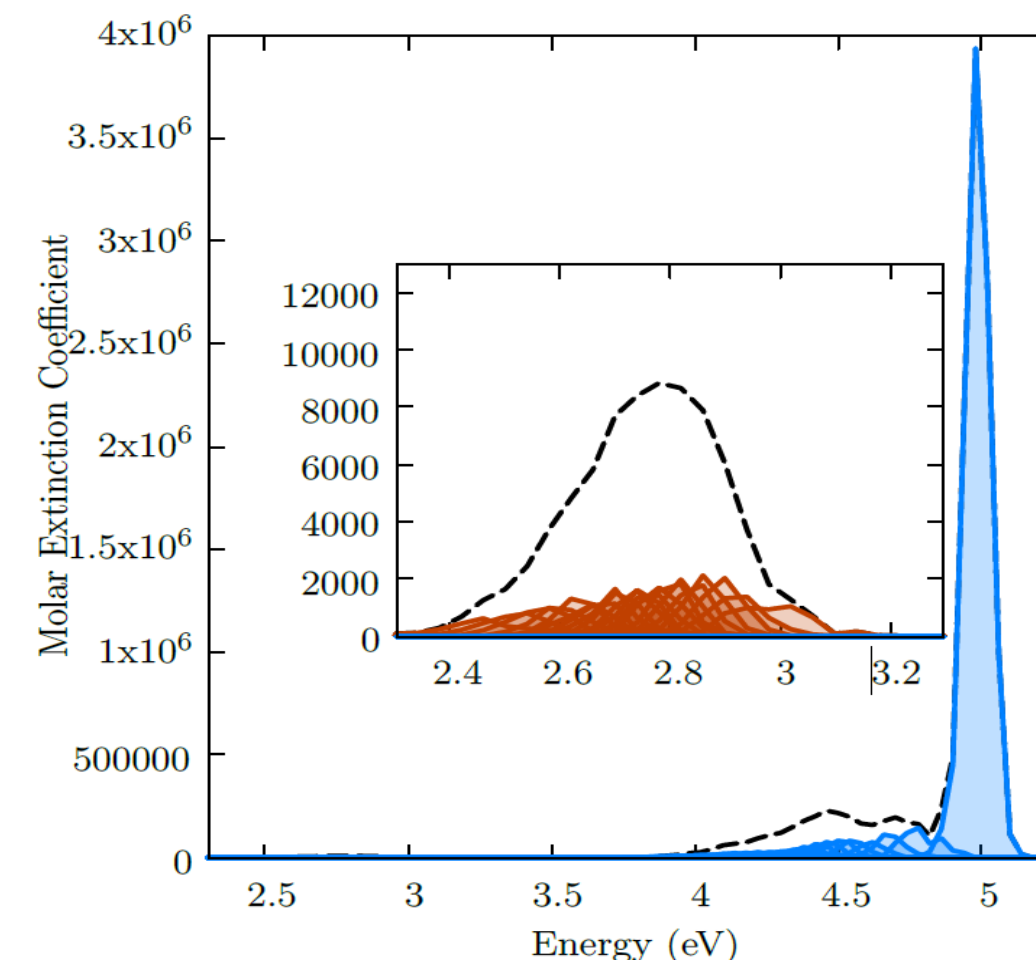
10 monomers:
21 states



12 monomers:
25 states



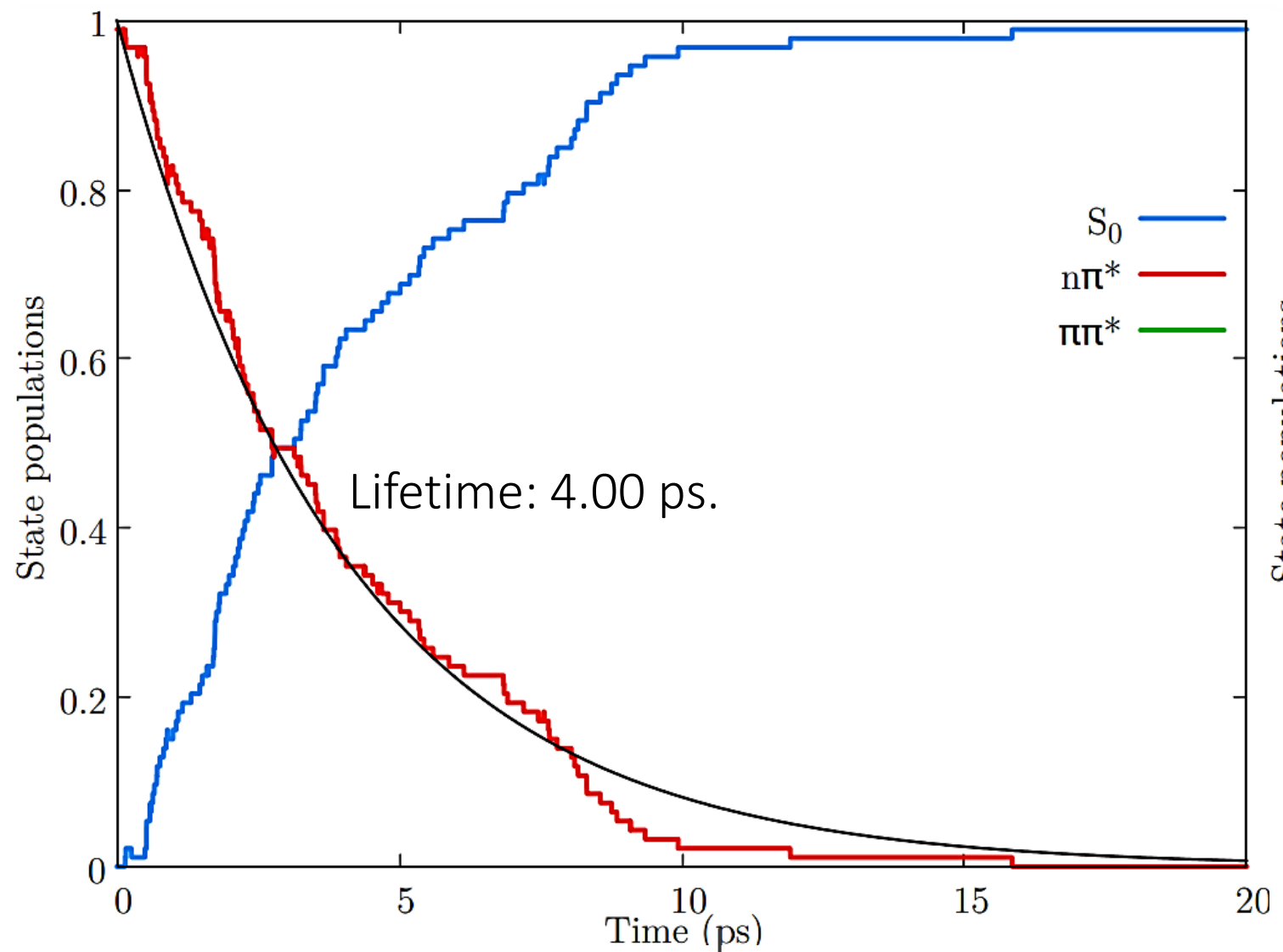
20 monomers:
41 states



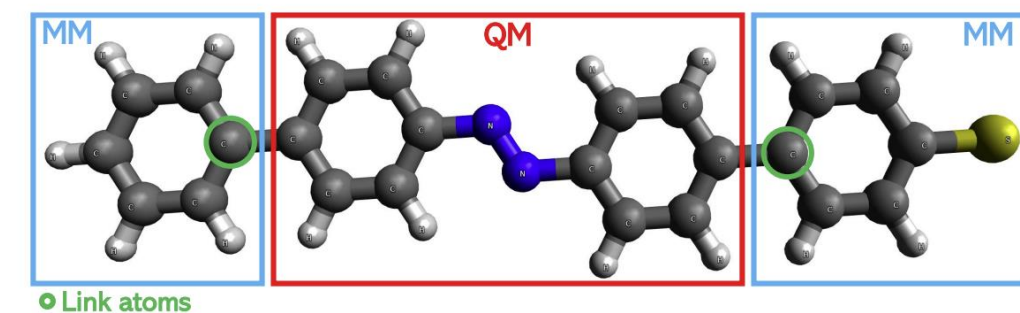
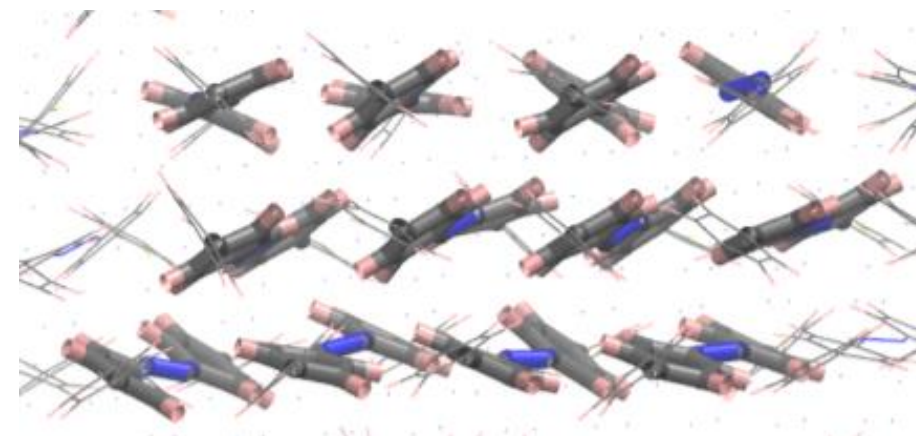
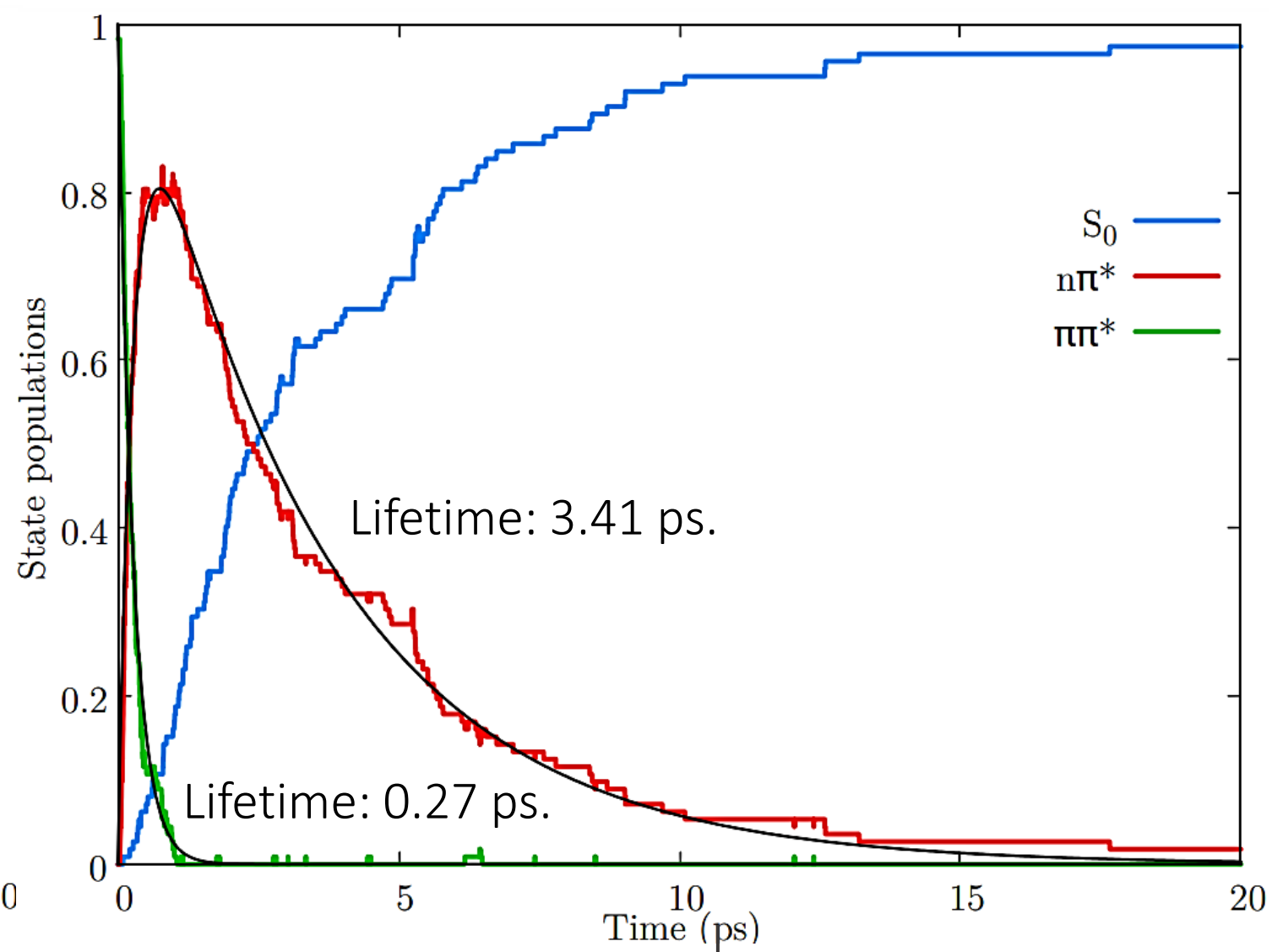
Application

Photodynamics of SAMs of ABPT

Simulation of the photodynamics ($n\pi^$)*



Simulation of the photodynamics ($\pi\pi^$)*



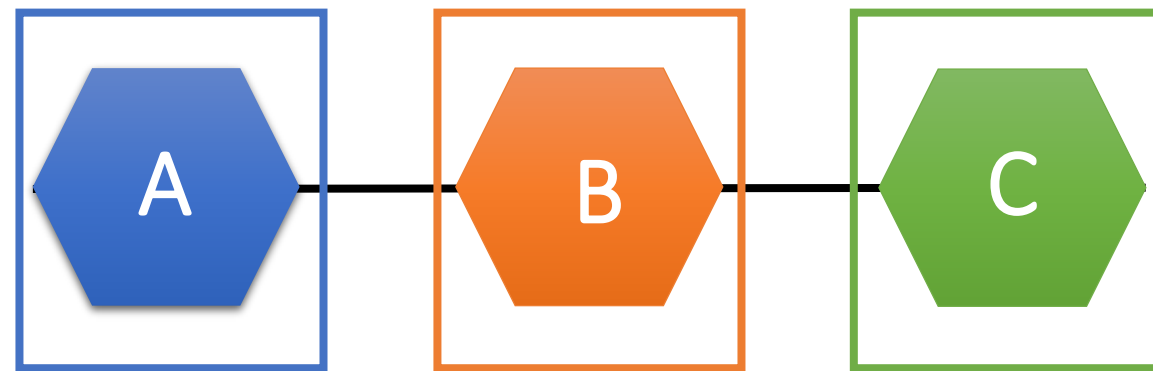
Very low photoisomerization quantum yield

Extended exciton model

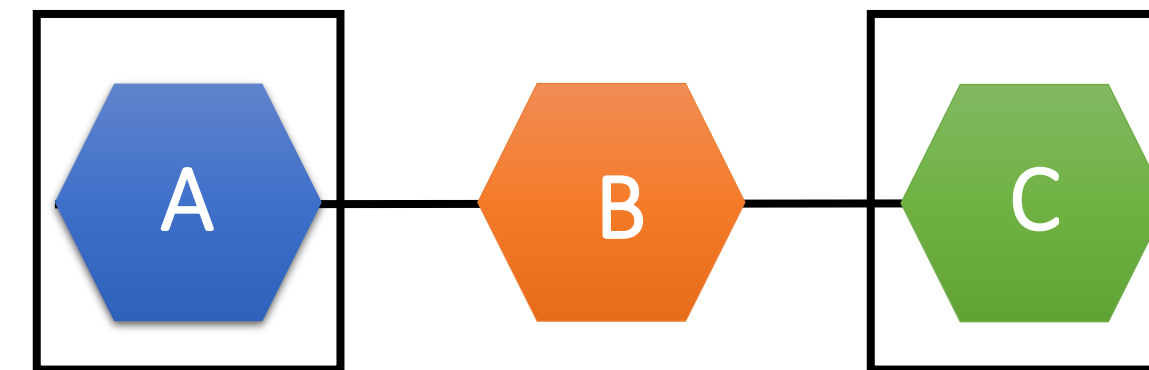
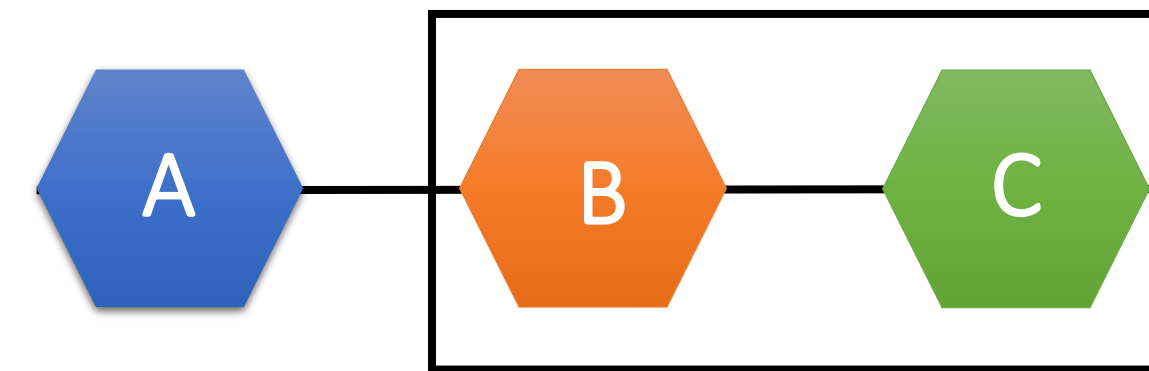
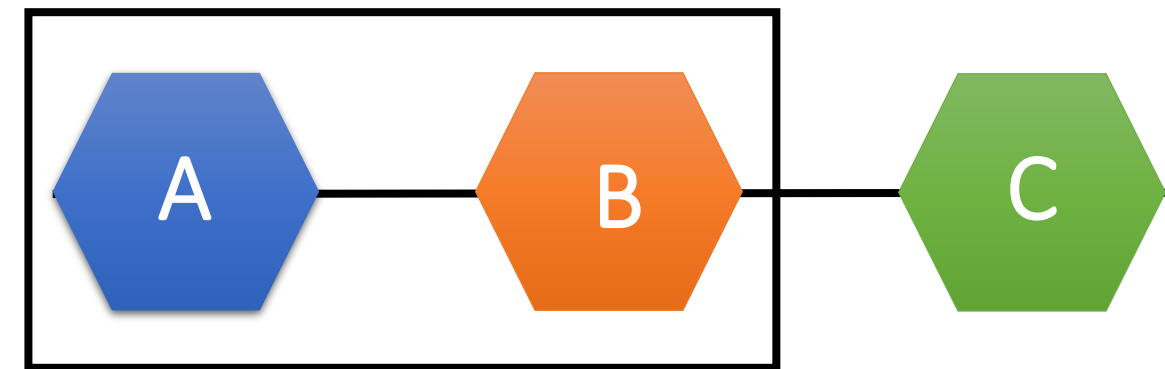
LIMITATION OF THE FRANKEL EXCITON MODEL:

It can only describe local excitation

Monomers:



Dimers:



Extended exciton model

$$\hat{H}^{ex} =$$

	ABC	A*BC	AB*C	ABC*	A+B-C	A-B+C	AB+C-	AB-C+	A+BC-	A-BC+
ABC	E^{GS}	0	0	0	0	0	0	0	0	0
A*BC	0	ε_A^1	$C_{AB}^{1,1}$	$C_{AC}^{1,1}$	D_{CT}^{A*}	D_{CT}^{A*}	0	0	D_{CT}^{A*}	D_{CT}^{A*}
AB*C	0		ε_B^1	$C_{BC}^{1,1}$	D_{CT}^{B*}	D_{CT}^{B*}	D_{CT}^{B*}	D_{CT}^{B*}	0	0
ABC*	0			ε_C^1	0	0	D_{CT}^{C*}	D_{CT}^{C*}	D_{CT}^{C*}	D_{CT}^{C*}
A+B-C	0				ε_{CT}^1	D_{CT}^{CT}	0	0	0	0
A-B+C	0					ε_{CT}^2	0	0	0	0
AB+C-	0						ε_{CT}^3	D_{CT}^{CT}	0	0
AB-C+	0							ε_{CT}^4	0	0
A+BC-	0								ε_{CT}^5	D_{CT}^{CT}
A-BC+	0									ε_{CT}^6

- The *null terms* are coupled via NAD;
- Gradients;
- Overlap matrix (local diabatization).

Conclusions

- Overall, the two Frenkel exciton approaches (EC and TC) showed very close matching results in terms of absorption spectra, lifetimes, and photoisomerization quantum yields;
- The Frenkel exciton model combined with SH dynamics makes possible the study of EET in multichromophoric systems;
- The extended exciton model can open up new scenarios for the study of more complex systems.

Remarks

- The Frenkel exciton model was implemented in Newton-X program within:
 - ✓ Semiempirical FOMO-CI – MOPAC
 - ✓ TDDFT - Gaussian



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