Surface hopping dynamics with Frenkel exciton model in a semiempirical framework

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March 2nd, 2022
Challenges in simulating photo processes *in silico*

1. Long time scale simulations;

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

Mixed quantum-classical dynamics $\Rightarrow$ 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

Semiempirical FOMO-CI

Surface Hopping dynamics

Frenkel exciton model

Photodynamics of multichromophoric systems

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# Method

**Frenkel exciton model**

\[
\hat{H}^{ex} = \begin{array}{c|c|c|c|c}
\hline
E^{GS} & 0 & \cdots & 0 & V_{ab}^{1,1} & \cdots & 0 & 0 \\
\hline
0 & \varepsilon_a^1 & 0 & \cdots & 0 & V_{ab}^{1,1} & \cdots & V_{ab}^{1,N} \\
\vdots & 0 & \varepsilon_a^2 & 0 & \vdots & \vdots & \vdots & \vdots \\
\vdots & 0 & \vdots & \vdots & 0 & \varepsilon_a^N & \cdots & \varepsilon_a^N \\
\hline
0 & \cdots & 0 & \varepsilon_b^N & V_{ab}^{N,1} & \cdots & 0 & 0 \\
\hline
V_{ba}^{1,1} & \cdots & V_{ba}^{1,N} & \varepsilon_b^1 & 0 & \cdots & 0 & 0 \\
\vdots & \vdots & \vdots & 0 & \varepsilon_b^2 & 0 & \vdots & \vdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\hline
0 & V_{ba}^{N,1} & \cdots & V_{ba}^{N,N} & 0 & \cdots & 0 & \varepsilon_b^N \\
\hline
\end{array}
\]

\[E^{GS} = E^{tot\ MM} + \sum_i (E_i^{QM/MM (S0)} - E_i^{MM})\]

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Method

Couplings (off-diagonal terms)

\[ V_{ai,bj} \approx \int \frac{\rho^{(a)}_{0i}(r_1)\rho^{(b)}_{0j}(r_2)}{r_{12}} dr_1 dr_2 \]

\[ V_{ai,bj} = \sum_{A \in a} \sum_{B \in b} \sum_{\mu \nu \in A} \sum_{\sigma \tau \in B} \rho^{(a)}_{0i,\mu \nu} \rho^{(b)}_{0j,\sigma \tau} (\mu \nu | \sigma \tau) \]

"Exact Coulomb" (EC)

It scales quadratically with the number of chromophores.

\[ V_{ai,bj} \approx \sum_{A \in a} \sum_{B \in b} \frac{q_{A,ai} q_{B,bj}}{R_{AB}} \]

"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 diabatization.

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

Application

Photodynamics of SAMs of ABPT

- Thermalization trajectories with 10; 12 and 20 monomers; \( \rightarrow \) 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 ($n\pi^{*}$)

Lifetime: 4.00 ps.

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

Lifetime: 3.41 ps.

Lifetime: 0.27 ps.

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

\[
\hat{H}_{\text{ex}} =
\]

<table>
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<tr>
<th></th>
<th>ABC</th>
<th>A*BC</th>
<th>AB*C</th>
<th>ABC*</th>
<th>A'BC</th>
<th>A'B'C</th>
<th>AB'C</th>
<th>AB*C</th>
<th>A'BC</th>
<th>A'BC*</th>
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<tr>
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<td>(E_{GS})</td>
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<tr>
<td>A*BC</td>
<td>0</td>
<td>(\varepsilon_A^1)</td>
<td>(\varepsilon_{AB}^{1,1})</td>
<td>(\varepsilon_{AC}^{1,1})</td>
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<td>(\Delta_{CT}^{A})</td>
<td>(\Delta_{CT}^{A*})</td>
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<tr>
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<td>0</td>
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<tr>
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<td>0</td>
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<td>(\Delta_{CT}^{C*})</td>
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<tr>
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- 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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