Surface hopping dynamics with Frenkel exciton model in a semiempirical framework

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Challenges in simulating photo processes \textit{in silico}

1. Long time scale simulations;

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

Mixed quantum-classical dynamics $\rightarrow$ Computational cost: \textit{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.

- \textit{Exciton} model.
Objective

Semiempirical FOMO-CI

Surface Hopping dynamics

Frenkel exciton model

Photodynamics of multichromophoric systems
Method
Frenkel exciton model

\[
\hat{H}^{ex} = H^a + H^b
\]

\[
\begin{align*}
E_{\text{GS}} & = 0 & \cdots & 0 & V_{a1}^{1,1} & \cdots & V_{a1}^{1,N} \\
\vdots & \ddots & \ddots & \vdots & \vdots & \ddots & \vdots \\
0 & \cdots & 0 & e_{a1}^N & V_{a1}^{N,1} & \cdots & V_{a1}^{N,N} \\
\vdots & \ddots & \ddots & \vdots & \vdots & \ddots & \vdots \\
0 & \cdots & 0 & \cdots & \cdots & \cdots & 0
\end{align*}
\]

\[
E_{\text{GS}} = E_{\text{tot}}^{\text{MM}} + \sum_i (E_i^{\text{QM/MM}}(S_0) - E_{\text{tot}}^{\text{MM}})
\]
Method

Couplings (off-diagonal terms)

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

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

"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.

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

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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 (nπ*)**

- Lifetime: 4.00 ps.

**Simulation of the photodynamics (ππ*)**

- Lifetime: 3.41 ps.
- Lifetime: 0.27 ps.

Very low photoisomerization quantum yield
Extended exciton model

LIMITATION OF THE FRANKEEL EXCITON MODEL: 
*It can only describe local excitation*

Monomers:

Dimers:
Extended exciton model

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

|       | ABC | A*BC | AB*C | ABC* | A'B'C | A'B'C* | AB'C | AB'C* | A'BC | A'BC* |
|-------|-----|------|------|------|-------|--------|------|-------|------|-------|
| ABC   | 0   | 0    | 0    | 0    | 0     | 0      | 0    | 0     | 0    | 0     |
| A*BC  | 0   | \(\epsilon_{A}^{1}\) | \(\epsilon_{A}^{1}\) | \(\epsilon_{A}^{1}\) | \(D_{C}^{A*}\) | \(D_{C}^{A*}\) | 0    | 0     | \(D_{C}^{A*}\) | \(D_{C}^{A*}\) |
| AB*C  | 0   | \(\epsilon_{B}^{1}\) | \(\epsilon_{B}^{1}\) | \(\epsilon_{B}^{1}\) | \(D_{C}^{B*}\) | \(D_{C}^{B*}\) | \(D_{C}^{B*}\) | \(D_{C}^{B*}\) | 0    | 0     |
| ABC*  | 0   | 0    | \(\epsilon_{C}^{1}\) | 0    | 0      | \(D_{C}^{C*}\) | \(D_{C}^{C*}\) | \(D_{C}^{C*}\) | \(D_{C}^{C*}\) | 0    |
| A'B'C | 0   | \(\epsilon_{C}^{1}\) | \(\epsilon_{C}^{1}\) | \(\epsilon_{C}^{1}\) | \(D_{C}^{2}\) | \(D_{C}^{2}\) | 0    | 0     | 0    |
| A'B'C*| 0   | 0    | \(\epsilon_{C}^{2}\) | \(\epsilon_{C}^{2}\) | \(\epsilon_{C}^{2}\) | \(D_{C}^{C*}\) | 0    | 0     | 0    |
| AB'C  | 0   | 0    | 0    | \(\epsilon_{C}^{3}\) | \(D_{C}^{3}\) | \(D_{C}^{3}\) | 0    | 0     | 0    |
| AB'C* | 0   | 0    | 0    | 0    | \(\epsilon_{C}^{4}\) | \(\epsilon_{C}^{4}\) | 0    | 0     | 0    |
| A'BC  | 0   | 0    | 0    | 0    | 0      | \(\epsilon_{C}^{5}\) | \(D_{C}^{5}\) | \(D_{C}^{5}\) | 0    |
| A'BC* | 0   | 0    | 0    | 0    | 0      | 0      | \(\epsilon_{C}^{6}\) | \(\epsilon_{C}^{6}\) | 0    |

- The null terms are coupled via NAD;
- Gradients;
- Overlap martix (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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