First-Principles Study of Exciton Diffusion and Dissociation in Organic Solar Cells

Xu Zhang, Zi Li and Gang Lu

Department of Physics & Astronomy
California State University Northridge

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Advantages of organic solar cells

• Inexpensive to fabricate
• Solution-processed in a roll-to-roll fashion with high throughput
• Low weight & flexible; Compatible with plastic substrates
• High optical adsorption coefficients that permit the use of very thin films
• Based on earth-abundant & non-toxic materials

Problem: efficiency is too low (record: 5%); the goal is 10%

Major Bottlenecks of low efficiency

• Low exciton diffusion length
• Low carrier mobility
Plastic solar cell commercialized by Konarka
Bulk Heterojunction (BHJ) Donor/Acceptor Architecture


Bi-continuous donor & acceptor phases

Blue: donor (polymers)
Pink: acceptor (fullerenes)
Best material: P3HT/PCBM

1. A photon excites donor phase creating an exciton (Optimal band-gap to enhance adsorption)

2. Exciton diffuses to D/A interface where it dissociates into a bound electron and hole pair. Excitons that do not reach the interface recombine and do not contribute to photocurrent (Increase diffusion length)

3. Bound electron-hole pair separates into free carriers (enhance interfacial charge separation)

4. Carrier transport to electrodes for collection (high carrier mobility)

B. Walker (2009)
First-principles prediction of carrier mobility in disordered semiconducting polymers as a function of T, carrier concentration and electric field.


**Goal:**

1. Develop first-principles based method to predict exciton diffusion length and exciton interfacial dissociation

2. Understand physical mechanisms underlying exciton dynamics

3. Guide/accelerate experimental discovery of more efficient materials
First-principles description of exciton dynamics

Basic Ingredients:

1. Exciton states are localized due to disordered nature of amorphous polymer

2. Thermal fluctuation of molecular conformations gives rise to non-adiabatic transitions between excitonic states (phonons are important!)

   Non-adiabatic ab initio molecular dynamics is essential to capture these transitions

3. Linear response theory of time-dependent DFT (LR-TDDFT) for describing exciton states
At each *ab initio* MD step $t$:

**Exciton**

$$\Psi(t) = \sum_I C_I(t) \Phi_I(t)$$

Expressed in terms of many-body excited states $\Phi_I$ & $\omega_I$

Kohn-Sham orbital $\phi_i$ & $\varepsilon_i$

LUMO

$E_F$

HOMO

Slater determinants (SD) for single excitations

TDDFT Linear Response theory

Casida's formulation
Casida’s formulation

Pseudo-eigenvalue equation based on TDDFT linear response theory:

\[ \Omega F_I = \omega_I^2 F_I \]

matrix in the basis of KS states \( \{ij\sigma\} \) \( \text{energy of } I\text{-th excited state} \)

\[ \Omega_{ij\sigma,kl\tau} = \delta_{i,k} \delta_{j,l} \delta_{\sigma,\tau} (\epsilon_{l\tau} - \epsilon_{k\tau})^2 + 2\sqrt{(f_{i\sigma} - f_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{i\sigma})} \]

\[ \times K_{ij\sigma,kl\tau} \sqrt{(f_{k\tau} - f_{l\tau})(\epsilon_{l\tau} - \epsilon_{k\tau})} \]

occupational number \( \text{energy of KS orbital} \)

\( i \) and \( k \) run over \textbf{occupied} KS orbitals

\( j \) and \( l \) run over \textbf{unoccupied} KS orbitals

Coupling matrix describes linear response of KS effective potential to changes in charge density:

\[ K_{ij\sigma,kl\tau} = \int\int \phi^*_{i\sigma}(\vec{r}) \phi_{j\sigma}(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \phi_{k\tau}(\vec{r}') \phi^*_{l\tau}(\vec{r}') d\vec{r} d\vec{r}' \]

\[ + \int\int \phi^*_{i\sigma}(\vec{r}) \phi_{j\sigma}(\vec{r}) \frac{\delta^2 E_{xc}}{\delta \rho_{\sigma}(\vec{r}) \delta \rho_{\tau}(\vec{r}')} \phi_{k\tau}(\vec{r}') \phi^*_{l\tau}(\vec{r}') d\vec{r} d\vec{r}' \]

\( \text{charge density} \) \( \text{KS orbital} \)
Assignment ansatz of Casida gives many-body wave-function of $I$-th excited state:

$$\Phi_I \approx \sum_{ij}\sqrt{\frac{\varepsilon_{j\sigma} - \varepsilon_{i\sigma}}{\omega_I}} F_{I,ij} \hat{a}_{j\sigma}^+ \hat{a}_{i\sigma} \Phi_0$$

Ground state many-body wave function: Single Slater Determinant (SD) of the occupied KS orbitals

$$\hat{a}_{j\sigma}^+ \hat{a}_{i\sigma} \Phi_0 : \text{one electron is excited from occupied KS state } i \text{ to unoccupied KS state } j$$

(single excitations only)

Many-body wave function of an exciton:

$$\Psi(t) = \sum_{I=0}^{\infty} C_I(t) \Phi_I(\vec{R}(t))$$

linear combination of the adiabatic ground state ($I=0$) and excited states wave functions ($I>0$); $\{\vec{R}(t)\}$: position of ions
Expectation value of single-particle operators

N-electron system, the single-particle operator: \[ \hat{A} = \sum_{i=1}^{N} \hat{a}_i \]

Expectation value (analytic result):

\[
\langle \Phi_I | \hat{A} | \Phi_I \rangle = \langle \Phi_0 | \hat{A} | \Phi_0 \rangle + \sum_{i, jj'} z_{I,ij}^* z_{I,ij'} \langle \varphi_j | \hat{a} | \varphi_{j'} \rangle - \sum_{ii', j'} z_{I,ij}^* z_{I,i'j} \langle \varphi_{i'} | \hat{a} | \varphi_i \rangle
\]

\(i: \text{occupied orbitals; } j: \text{unoccupied orbitals}\)

- expectation value in ground state
- quasi-electron part
- quasi-hole part

E.g., for coordinate operator:

\[
\langle \Phi_I | \hat{\vec{r}} | \Phi_I \rangle = \langle \Phi_0 | \hat{\vec{r}} | \Phi_0 \rangle + \sum_{i, jj'} z_{I,ij}^* z_{I,ij'} \langle \varphi_j | \hat{\vec{r}} | \varphi_{j'} \rangle - \sum_{ii', j'} z_{I,ij}^* z_{I,i'j} \langle \varphi_{i'} | \hat{\vec{r}} | \varphi_i \rangle
\]

- sum of positions of N electrons in ground state
- quasi-electron position \(\vec{r}_e\)
- quasi-hole position \(\vec{r}_h\)
Charge density operator:

\[ \hat{\rho} = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \]

\[
\langle \Phi_I | \hat{\rho} | \Phi_I \rangle = \rho_0(\vec{r}) + \sum_{i,j,j'} z_{I,i}^* z_{I,j} \varphi_{j}(\vec{r}) \varphi_{j'}(\vec{r}) - \sum_{ii',jj'} z_{I,i}^* z_{I,j} \varphi_{i}(\vec{r}) \varphi_{i'}(\vec{r})
\]

- ground state charge density
- quasi-electron charge density
- quasi-hole charge density

Charge density of the lowest energy exciton in disordered P3HT:

Blue: quasi-electron
Red: quasi-hole

Localized states!

18 Å
Exciton diffusion

(1) Phonon-assisted transition  (2) Spontaneous emission (decay)

(1) Phonon-assisted transition

Let exciton start in an excited many-body pure state $I$ at $t=0$, i.e., $\Psi(0) = \Phi_I(\tilde{R}(0))$

$t > 0$, ions move, the exciton state becomes a mixed many-body state

Introduce $C_J^{(I)}(t)$ so that $\Psi(t) = \sum_{J=0}^{\infty} C_J^{(I)}(t) \Phi_J(\tilde{R}(t))$ \hspace{1cm} $C_J^{(I)}(t)$: probability amplitude

with $C_J^{(I)}(0) = \delta_{I,J}$

Substitute $\Psi(t)$ into time-dependent many-body Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = H(\tilde{R}(t))\Psi(t)$$

many-body Hamiltonian

Obtain dynamics of exciton transition:

$$\frac{\partial}{\partial t} C_J^{(I)}(t) = -\sum_K C_K^{(I)}(t)(\frac{i}{\hbar} \omega_K \delta_{JK} + D_{JK})$$
\[ D_{JK} = \langle \Phi_J \left| \frac{\partial}{\partial t} \right| \Phi_K \rangle = \sum_{i,j \neq j'} z_{I,ij}^* z_{J,i'j'} d_{jj'} - \sum_{i \neq i', j} z_{I,ij}^* z_{J,i'j} d_{i'i} \]

\( d_{i'i} \) : non-adiabatic coupling between Kohn-Sham state \( i \) and \( i' \)

\[ d_{i'i} = \langle \phi_i' \left| \frac{\partial}{\partial t} \right| \phi_i \rangle \approx \frac{1}{2\Delta t} \left( \langle \phi_i'(t) \left| \phi_i(t + \Delta t) \rangle \right. - \langle \phi_i'(t + \Delta t) \left| \phi_i(t) \rangle \right. \right) \]

Where \( \phi_i(t) \) is the Kohn-Sham single particle wave function.

\[ |C_J^{(I)}(t)|^2 \] exciton transition probability from state \( I \) to state \( J \) at time \( t \)

\[ \gamma_{\text{Phonon}}^{\text{Phonon}} = \left\langle \frac{|C_J^{(I)}(t)|^2}{t} \right\rangle \] transition rate (average over time interval \( [t, t + \delta t] \))
Transition rates

(2) Spontaneous emission (decay) without phonon assistance
Transition dipole moment approximation

\[ \gamma_{I,J}^{\text{Dipole}} = \frac{4(\omega_I - \omega_J)^3 |\langle \Phi_I | \vec{r} | \Phi_J \rangle|^2}{3c^3} \]

(3) Transition rate satisfying detailed balance:

\[
\gamma_{I,J} = \begin{cases} 
\gamma_{I,J}^{\text{Phonon}} \exp(-\frac{\omega_J - \omega_I}{k_B T}), & \text{if } \omega_J \geq \omega_I \\
\gamma_{I,J}^{\text{Phonon}} + \gamma_{I,J}^{\text{Dipole}}, & \text{if } \omega_J < \omega_I 
\end{cases}
\]

- Phonon assisted transition contributes to both the downhill and uphill transitions
- Spontaneous emission only contributes to the downhill transitions
Exciton diffusion in real and energy space

Real space

Many-body energy space

\[ \vec{r}_{ex} = \frac{\vec{r}_e + \vec{r}_h}{2} \]

Binding energy: 0.16 eV (disordered P3HT)
0.53 eV (single P3HT chain)

Phonon-assisted exciton transition (rate: \(10^9 \sim 10^{12} \text{ s}^{-1}\), ps to ns)

Spontaneous emission (from high energy to low energy, \(\leq 10^7 \text{ s}^{-1}\), microsecond)

Exciton annihilation (from excited states to GS, \(10^9 \text{ s}^{-1}\), ps)

Transition between exciton states ➔ Exciton diffusion in real space
Construction of macroscopic system

Two daunting challenges: (1) to model macroscopic system with microns dimensions (2) to model amorphous disordered system

“Macroscopic” system: \( l_x \times l_y \times l_z \) cubes

1. Cube \( n \): home box in which transition rates have been calculated (5 excitons here)
2. KS states in each cube are randomly selected and rotated from MD snap-shots (to model amorphous structure)
3. Determine exciton position in each box

To determine inter-cube transition rate:
E.g. considering exciton \( n_1 \):

Translate cube \( n \) so that \( n_1 \) is at the center of the cube (dashed cube); etc. The transition rate \( \gamma_{n_1,m_2} \) is replaced by \( \gamma_{n_1,n_2} \) or \( \gamma_{n_1,n_2'} \)

\( n_1 \) can only hop to 4 neighboring excitons
Monte Carlo Calculation

Maximum distance of exciton diffusion: **diffusion length**

- **Step 1:** select an exciton $I$
- **Step 2:** list event table with transition probability
  - Annihilation: $P_1 = \gamma_{I,0} \times \Delta t$
  - Inter-state transition: $P_{J=2,3,...,N} = \gamma_{I,J} \times \Delta t$
  - Stay in the same state: $P_{N+1} = 1 - (P_1 + P_2 + \cdots + P_N)$

$N$: number of excitons in a cube (54)
$\Delta t$: time step in MC (10 fs)

- **Step 3:** for a given random number, execute an MC move

  0 1
  
  P_1  P_{J=2,...,N}  P_{N+1}

- **Step 4:** continue Step 3 until exciton annihilates for one MC trajectory.
- **Step 5:** continue for many trajectories.
- **Step 6:** take average of all trajectories
- **Step 7:** continue for different excitons

**Diffusion length** $L_D = \langle d_{\text{max}} \rangle$
**Diffusion time** $\tau = \langle t \rangle$
**Diffusivity** $D = \frac{\langle d_{\text{max}}^2 \rangle}{3 \langle t \rangle}$

- Annihilation site
Simulation Flowchart

1. Static relaxation of initial structure (636 atoms); heat up to desired temperatures; stay at the desired temperature with 500 MD steps to reach thermal equilibrium. MD step size 1 fs. Simulation performed by VASP.

2. Run a micro-canonical MD for 1000 fs. Determining $\omega_I$ & $\Phi_I$ and spontaneous emission rate at each MD step. 6 occupied KS orbitals and 9 unoccupied KS orbitals are considered to produce 54 excited states.

3. To calculate phonon-assisted transition rate $\gamma_{I,J}^{\text{phonon}}(t)$ at time $t$, TDDFT is run from $t$ to $t+\delta t$ ($\delta t=100$ fs) with the KS states determined from MD.

4. Construct macroscopic system using $l_x \times l_y \times l_z$ cubes.

5. Perform Monte Carlo calculation.
Results for disordered P3HT

Statistics (percentage) of exciton diffusion distance for $10^4$ trajectories

Three exciton states are examined:
- S1: lowest energy exciton state
- S2: exciton state $\sim 0.6$ eV higher than S1
- S3: exciton state $\sim 1.2$ eV higher than S1

- Higher energy excitons diffuse farther
- S2 & S3 have (almost) the identical diffusion behavior
- Diffusion length increases with temperature; particularly so for lower energy excitons
Calculated diffusion length $L_D$ (nm), lifetime $\tau$ (ns), and diffusivity $D$ ($10^{-9} \text{m}^2/\text{s}$)

<table>
<thead>
<tr>
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<th>300K</th>
<th>200K</th>
<th>100K</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>s1</td>
<td>s2</td>
<td>s3</td>
</tr>
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<td>3.0</td>
<td>3.1</td>
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<td>$\tau$</td>
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<td>1.8</td>
<td>1.7</td>
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<tr>
<td>$D$</td>
<td>4.1</td>
<td>5.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Experimental results at 300K:

$L_D = 4 \text{ nm} \quad [1]$

$L_D = 2.6 \sim 5.3 \text{ nm} \quad [2]$

Exciton diffusion (S3) in real and energy space at 300K
Exciton diffusion mechanisms

Exciton energy vs. diffusion distance

- **Downhill migration**: quickly dumps energy, but has minor contribution to diffusion length - doesn’t need phonons

- **Thermally activated migration**: dominate exciton diffusion without significant change of exciton energy - need phonon assistance

- At low temperature, downhill migration dominates

- At higher temperature, downhill migration followed by thermally activated migration
Two regimes for exciton diffusion*

(1) Downhill migration, temperature regime 4 - 150 K
(2) Thermally activated migration, temperature regime > 150 K

Interfacial Exciton Dissociation

Simplified Fewest switch surface hopping (FSSH)

In original FSSH [1], an electron (exciton) always stays at one excited state at any given time, but it can hop from one state to another. Here, we use a simplified FSSH method [2], in which a hop-rejection in the original FSSH is replaced by multiplying the hop probability with Boltzmann factor for an energetic upward transition. The probability from state \( J \) to \( K \) during the time-step \( \delta t \) is

\[
g_{JK} = \begin{cases} 
\left[ \max(0, \frac{b_{KJ}\delta t}{a_{JJ}}) \right] \cdot \exp\left( -\frac{(\varepsilon_K - \varepsilon_J)}{kT} \right), & \varepsilon_K > \varepsilon_J \\
\left[ \max(0, \frac{b_{KJ}\delta t}{a_{JJ}}) \right], & \varepsilon_K \leq \varepsilon_J
\end{cases}
\]

where

\[
a_{KJ} = C^*_K(t)C_J(t) \\
b_{KJ} = -2\text{Re}(a_{KJ}D_{KJ})
\]

With FSSH, we know precisely which state the exciton is at in any time. We can determine the position and charge density of the exciton (and quasi-electron and quasi-hole). Examine electron-hole (e-h) distance and charge distribution as a function of time

1. Static relaxation of initial structure; heating system to desired temperature; stay at the desired temperature with 500 MD steps to reach thermal equilibrium. MD step size 1 fs. The simulation performed by VASP.

2. Run a micro-canonical MD for 1000 fs. Determining $\omega_i$ & $\Phi_i$ at each MD step. 3 occupied KS orbitals and 9 unoccupied KS orbitals are used to obtain 27 excited states. The non-adiabatic coupling and position of Kohn-sham states are also determined.

3. Choose different (~100) initial structures from the MD trajectory, each with 200 fs long.

4. For each selected short trajectory, FSSH evolution of the exciton state is performed. (1) choose the initial exciton with the shortest e-h distance (2) evolve $C_f(t)$ and calculate the hopping probability (3) generate different (~100) random number sequences to determine the exciton trajectories and the corresponding position and charge density (4) average over different random number sequences.

5. Take ensemble average of the different trajectories
Exciton dissociation at P3HT/PCBM interface

Simulation box:  48.0Å x 16.2Å x 15.7Å

Lowest interfacial exciton state energy: 0.20 eV
Band gap by $\Delta$SCF: 0.55 eV

Interfacial exciton binding energy: 0.35 eV

Experimental estimate of binding energy: 0.1-1 eV
**Exciton dissociation process**

Distribution of initial exciton states:
- e-h distance: 7-11 Å
- Exciton energy: 0.5-0.8 eV

**Interfacial** electron moves faster than hole, similar to the case in **bulk**, in which electron mobility is larger than hole.

Energy decreases from 0.64 to 0.5 eV, providing a driving force for dissociation.

**e-h distance (black solid line) and exciton energy (black dash line) vs. time**
**Estimate of dissociation timescale**

According to Onsager theory [1], Coulomb capture radius $r_c$ is defined as the distance at which the Coulomb attraction energy equals the thermal energy $k_B T$.

$$ r_c = \frac{e^2}{4\pi \varepsilon_r \varepsilon_0 k_B T} $$

With $\varepsilon_r = 4$ and $T = 300$ K, we have $r_c = 13.9$ nm

We assume that (i) once the e-h distance is larger than $r_c$, the dissociation process completes; (ii) the electron and hole dissociate with a constant velocity (3.1 nm/ps for $e^-$ and 0.5 nm/ps for $h^+$), we can estimate dissociation time of 3.9 ps, consistent with experimental result 4.0 ps [2].

Charge separation

Quasi-electron:
At beginning, charge mainly localized on PCBM-1.
In time, the population on PCBM-1 decreases, but the population on PCBM-2 and PCBM-3 increases

Quasi-hole:
At beginning, delocalized on all three P3HT. The farther the molecule, the smaller the population.
In time, the population on P3HT-1 decreases, population on P3HT-2 and P3HT-3 increases

Clear evidence of charge separation across interface
Exciton dissociation from one MD trajectory

In this example, e-h distance increases with time

t=0, e⁻ on the PCBM-1 and h⁺ delocalized on the first and second P3HT.

t=200 fs, significant charge separation

Exciton could have different dissociation behaviors as shown in trajectory 1-4 (charge trapped in 4)
Other processes at P3HT/PCBM interface

Exciton relaxation from higher to lower excited states:

- Estimated time scale: 2.2 ps
- Time scale similar to exciton dissociation, competition of the two processes

Exciton from the lowest excited state to ground state (recombination process):

- Estimated time scale: 2.8 ns
- Time scale much longer than dissociation, negligible influence on dissociation process