Charge transfer dynamics in polymer heterojunctions

What is the reaction coordinate?

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**Central Question:** How do specific vibrational degrees of freedom tune, couple and modulate quantum energy transfer between donor and acceptor species on an ultrafast timescale?

**Topics**
- Lattice models, Quantum Chemical approaches (TD-DFT)
- Analytical methods, Statistical approximations
- Numerically exact propagation: MC-TDH
- Decoherence
- Mixed quantum/classical techniques
- Quantum trajectory/Bohmian dynamics
- Quantum thermodynamics of small clusters

**Systems:** Polymer heterojunctions, Light-harvesting systems, photoexcitons in DNA, Rare gas clusters
Theoretical Challenge: Real-time quantum dynamics

MD Simulation limit
- classical mechanics (or CPMD)
- limited to 10,000 to 100,000 atoms

Quantum Chemical limit: $H\psi = E\psi$
- (electrons)
  - Born-Oppenheimer Approx.
  - Excited states: limited technology
  - $\approx 100$ atoms

Quantum Dynamics: $i\hbar \dot{\psi} = H\psi$
- very limited technology
- $< 10$ degree of freedom
- (4 atoms = state of the art)

impossible: no masochistic: yes!
Left: image of TFB:F8BT (1:1) blend under photo luminescent electro-luminescent conditions. Right: energy level diagram of emission spectra.\(^1\)

\(^1\)Figure c/o Carlos Silva
If off-set between HOMO (or LUMO) levels at the interface is large compared to binding energy of exciton (0.5eV), interfacial charge-transfer states are energetically more stable than excitonic states. (great for PVs)

Otherwise Excitonic states are energetically favored (great for OLEDs)
In TFB:F8BT energy difference between the CT and XT states is comparable to kT at room temperature.

- possibility of back transfer and formation of secondary excitons.
- Nearly 80% of observed emission is due to 2nd-ary excitons.

Quantum Chemical Studies of Heterojunction Interfaces
General approach: MD + DFT to optimize structure, then TD-DFT/6-31G**/B3LYP + HF exchange.\(^3\)

Computationally expensive (about 1 month CPU time/calculation).

Why is the stacking (slippage) an issue?

- In excited state

\[ \cdots - F8^{\delta+} - BT^{\delta-} - \cdots \quad \& \quad \cdots - F8^{\delta-} - N\phi_3^{\delta+} - \cdots \] 

(1)

due to alternation of HOMO/LUMO levels from each monomer.

- Eclipsed (attractive)

\[ \cdots - BT^{\delta-} - F8^{\delta+} - BT^{\delta-} - \cdots \] 

(2)

\[ \cdots - N\phi_3^{\delta+} - F8^{\delta-} - N\phi_3^{\delta+} - \cdots \] 

(3)

- Staggered (repulsive)

\[ \cdots - BT^{\delta-} - F8^{\delta+} - BT^{\delta-} - \cdots \] 

(4)

\[ \cdots - N\phi_3^{\delta+} - F8^{\delta-} - N\phi_3^{\delta+} - \cdots \] 

(5)
Map of interaction energy

Figure: DFT structure/INDO descript. of PFB excited state/Coulomb interaction w/F8BT (ground state).

TFB:F8BT Heterojunction

TD/DFT energy levels for eclipsed vs staggered configurations for model solvent dielectric (toluene) vs. gas phase.  

Note: considerable exciplex stabilization due to solvent polarization

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Only eclipsed exciplex state carries appreciable oscillator strength.
**TFB:F8BT Heterojunction**

**Figure**: Projection of excited states onto monomer units

- **Eclipsed**: exciplex has considerable mixing between purely excitonic configurations and purely CT configurations.
- **Staggered Exciplex**: almost purely polaronic (CT) configurations.
Brief Summary

- TD-DFT is reliable for excitonic systems, less so for strongly charge separated ones.
- Slippage between the chains has a very profound impact on the oscillator strength, less so on the energetics.
- For TFB:F8BT: all exciplex emission is from eclipsed configurations.
- Solvent effects a red-shift on exciplex, less so on XT.
- Intermediate (dark) states certainly play a role...perhaps consistent with the field-induced dissociation measurements.
Building a site model/1

Each monomer: localized Wannier orbital for HOMO and LUMO bands + set of localized vibrations

Interactions: Coulomb ($J$), Exchange ($K$), and dipole-dipole ($D$) interactions between e/h configurations.

Interchain coupling: $J, K, D + t = 0.15 t$\textsuperscript{6}

Build a site model/2

- Use either quantum chemical or spectroscopic data to parameterize a lattice model for a given polymer chain or polymer dimer.

- Each site can have an electron, hole, or both (exciton).

- Each site has localized phonons + linear coupling to neighboring (intrachain) sites.

- Diagonalize (separately) electronic and vibrational contributions...

- Taxonomy of dimer models
Heterojunction Energetics

Comparison between Lattice model and TD-DFT energies.

- Lattice model adjusted to “match” experimental values (CT-XT gap)
- Transition moments are similar
- Both lattice and TDDFT predict 2-ary CT state
- Advantage of lattice model is that we can treat far larger systems than possible with TD-DFT.

In spite of its simplicity and direct molecularity, lattice model does a good job at modeling spectra, energetics, etc.

"Strong" $t_{\perp} = 0.15t_{\parallel}$; "inter", $t_{\perp} = 0.15t_{\parallel}$ only for center F8’s; "weak" $t_{\perp} = 0$, only

Coulomb (2-body) interactions.
Quantum Dynamics
What defines our “reaction coordinate” in CT reactions?

Recall familiar Marcus picture for electron transfer

How can we relate $x$ to specific terms in our $H$?
Generic Model \( H = H_{el} + H_{ph} + V_{el/ph} \)

Diagonalize dimer hamiltonian:

- Diagonal Term defining Diabatic Potential Surfaces

\[
H_o = \sum_a |\psi_a\rangle \langle \psi_a| \left( \epsilon_a + \sum_i \hbar \omega_i (a_i^\dagger a_i + 1/2) + g_{aai}(a_i^\dagger + a_i) \right)
\]

- Relaxed (adiabatic) energies:
  \[
  \tilde{\epsilon}_a = \epsilon_a - \sum_i g_{aai}^2 \omega_i
  \]

- Diabatic couplings

\[
V = \sum_{ab} g_{abi} |\psi_a\rangle \langle \psi_b| (a_i^\dagger + a_i)
\]
Polaron transformed H

- More convenient to work in a *dressed representation*

\[ \tilde{H} = e^{-i\Omega} H e^{i\Omega} \]  

where

\[ \Omega = \sum_{ai} g_{aai} \frac{1}{\omega_i} (a_i^\dagger + a_i) |\psi_a\rangle \langle \psi_a| \]  

- Electron/phonon coupling

\[ \tilde{V} = \sum_{abi} M_{abi} |\psi_a\rangle \langle \psi_b| \]  

where

\[ M_{abi} = g_{abi} \left( a_i^\dagger + a_i - \frac{2g_{aai}}{\omega_i} \right) e^{\sum_j \frac{g_{aaj} g_{bbj}}{\omega_j} (a_j^\dagger - a_j)} \]  

In transformed representation, transitions from electronic states are accompanied by single phonon creation/annihilation + displacement in all normal coordinates.
1. Time-dependent Golden Rule

Lowest order approx: \( dW = \frac{2\pi}{\hbar} |V_{ab}|^2 \delta(E_a - E_b) \)

- written as a correlation function:  
  \[
  W_{ab} = \int_0^\infty dt \langle M_{ab}(0)M_{ab}(t) \rangle e^{i\omega_{ab}t} \quad (12)
  \]

- \( \langle M_{ab}M_{ab}(t) \rangle \) is the autocorrelation of coupling operator.  
  \[
  \langle M_{ab}(0)M_{ab}(t) \rangle = C_{\gamma}(t) \exp[A(t)] \quad (13)
  \]

Dynamical FC overlap factor:

\[
A = i \int_0^\infty J_c(\omega) \sin(\omega t) d\omega - \int_0^\infty J_c(\omega)(n(\omega) + 1)(1 - \cos(\omega t)) d\omega
\]

Position autocorrelation along diabatic coupling vector.

\[
C_{\gamma}(t) = \langle Q_{\gamma}(0)Q_{\gamma}(t) \rangle \quad (15)
\]

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7 c.f Chemical Dynamics in Condensed Phase by A. Nitzan (2007)
Figure: Structure of photosynthetic reaction center in Bacterial Rhodopsin

Figure: 150 fs oscillation is due to coherent vibrational coupling between the two chromophores mediated by electronic interaction.
\[ \langle M_{ab}M_{ab}(t) \rangle \] for projected 2-mode heterodimer/2

**Figure:** Autocorrelation of the \( \langle M_{ab}M_{ab}(t) \rangle \) coupling operator vs. time for 2-phonon/2 state Bcl/Bph dimer model.

\[ \langle M_{ab}M_{ab}(t) \rangle \] gives similar behavior compared to experimental time-signals.
Model lattice dimer 1: F8BT:TFB with $2 \times 12$ sites + 12 high freq. (C=C) modes 12 low-freq torsional modes ($T = 175K$)

- Loss of coherence in $< 100$ fs due to coupling to many degrees of freedom
- Dimer model is perhaps too strongly coupled.
Model lattice dimer 2: fewer sites + 28 phonons \((T = 175K)\)

- Very little difference in general terms between coupling regimes...in terms of correlation functions.
- "Weak coupling" regime gives \(NO\) direct transition between exciton to exciplex
Recall:

\[ W_{ab} = \int_{0}^{\infty} e^{i\tilde{\omega}_{ab}t} \langle M_{ab}M_{ab}(t) \rangle dt \]  

(16)

Figure: Forward (\(XT \rightarrow CT\)) and Reverse (\(CT \rightarrow XT\)) golden-rule transition rates vs. interchain stacking and coupling
Why the slow-down for the Staggered Case??

Compare coupling vectors $Q_c = \sum_i \frac{g_{abi}}{\omega_i} q_i$

*Eclipsed Coupling*  
$\phi_1, \phi_2$  
$C=\text{C}(1), C=\text{C}(2)$

*Staggered Coupling*  
$\phi_1, \phi_2$  
$C=\text{C}(1), C=\text{C}(2)$

*Intermed Coupling*  
$\phi_1, \phi_2$  
$C=\text{C}(1), C=\text{C}(2)$

All coupling between XT and CT is from torsional motion in staggered case.
Non-Markovian Contributions

- Since transfer rates are on the order of the coherence decay, one must be concerned with the effect of memory on the predicted rate.
- Golden-rule is a Markovian limit.
- For non-Markovian dynamics, we need to integrate the Nakajima-Zwanzig eq.

\[
\frac{d\rho}{dt} = -\int_{0}^{t} \mathcal{K}(t - t')\rho(t')dt'
\]  

(17)

- Can also use non-convolutionless form

\[
\frac{d\rho}{dt} = -\int_{0}^{t} \mathcal{K}_{cl}(t')dt' \rho(t)
\]  

(18)
Non-Markovian Pauli master eq.

- Taking coupling as a perturbation and expanding in cumulants

\[ \mathcal{K}^{(2)}_{cl}(t) = \mathcal{P} \mathcal{L} e^{i \mathcal{L}_0 t} \mathcal{L} \mathcal{P} \]  \hspace{1cm} (19)

- After even more tedious algebra....

\[ \frac{dP_a}{dt} = \sum_b (W_{ab}(t)P_b(t) - W_{ba}(t)P_{ba}(t)) \]  \hspace{1cm} (20)

time-convolutionless Pauli master eq. for populations.
Taking coupling as a perturbation and expanding in cumulants:

\[ \mathcal{K}_{cl}^{(2)}(t) = \mathcal{P} \mathcal{L}_v e^{i \mathcal{L}_0 t} \mathcal{L}_v \mathcal{P} \]  \hspace{1cm} (19)

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with

\[ W_{ab}(t) = 2 \text{Re} \int_0^t \langle M_{ab}M_{ba}(t') \rangle e^{i \tilde{\omega}_{ab} t'} dt' \]  \hspace{1cm} (21)
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Model 2LS + model with couplings: $g_{ab} \propto \omega_i^p$. In GR limit, Ohmic: $p = -1/2$, super-ohmic $p = 0$

Figure: Left: Population decay from upper to lower state for ohmic = solid-line: super-ohmic = dashed lines for model 2LS +80 mode model. Right: detail of super-ohmic rates.

Note: $W_{21} < 0$ implies positivity violation in TCLME
Non-Markovian dynamics for heterojunction model

Model: 12-12 lattice + 24 phonons (12 low freq + 12 high-freq)

Figure: Left: XT → CT decay kinetics for tclme, sc-golden rule for various temperatures. Right: TCLME model eliminating either high or low freq. modes from model.

Transfer requires participation between both high and low frequency modes
Fully dynamic model: MCTDH

\[ \text{MCTDH} = \text{MultiConfigurational Time-Dependent Hartree} \]

- **Nuclear** wavepacket is expanded in time-dependent basis

\[
\Psi(Q_i \cdots, Q_f, t) = \sum_{j_1=1}^{n_i} \sum_{j_f=1}^{n_f} A_{j_1 \cdots j_n}(t) \prod_{\kappa=1}^{f} \phi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \]

- Dirac-Frenkel variation principle

\[
\langle \delta \Psi | H - i \partial_t | \Psi \rangle = 0
\]

- Solve MCTDH equations of motion within a mean-field approx

\[
\langle H \rangle_{jl}^{(\kappa)} = \langle \psi_{j}^{(\kappa)} | H | \psi_{l}^{(\kappa)} \rangle
\]

where \( | \psi_{j}^{(\kappa)} \rangle \) denote quasi-particle wavefunctions.

- huge savings in both memory and cpu usage for high-dimensional systems

Comparing ME to MCTDH

effect of mode-mode coupling is consistent with numerically exact treatment\textsuperscript{10}

\textbf{Figure:} Left: TCLME population decay ($T = 175 \text{K}$). Right: MCTDH results ($T = 0 \text{K}$).

Figure: Left: Coupled potential energy surfaces for model heterojunction. Right: $\langle x(t) \rangle$ on upper (blue) and lower (red) surfaces following excitation.
In MCTDH treatment, the $Q_a(t)$, $Q_b$ vectors taken over a mean-field to define an effective Hamiltonian

**a-d** Evolution of adiabatic potentials projected onto branching plane ($Q_a(t)$, $Q_b$) at 2 time slices, $t = 0$ (left) and $t = 150$fs (right).

**e,f** $\langle X \rangle$ for wave packet for $t = 0$ to 50fs (left) and for 150 to 200 fs (right).

The intersection seam and crossing surfaces become dynamical quantities as well.
Effect of Electric Field

- No effect on exciton nor exciplex lifetime.
- Pronounced enhancement of photocurrent.

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**FIG. 1.** Potential energy diagram describing the energetics and kinetics at type II polymer heterojunctions. The energetic order of $|A^{-}\tilde{D}^+\rangle_{r=\infty}$ and $|A^+D\rangle_{r=\infty}$ may be reversed for PFB:F8BT vs TFB:F8BT. The inset shows the band offsets at a type II heterojunction (see also [7]).

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![Potential energy diagram](image)

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Coherent transfer via intermediate\textsuperscript{12}

MCTDH calculations on model 12/12 dimer.

(a) 12/12 model fully coupled: nearly 50% of $XT \rightarrow CT$ transfer occurs in 150 fs.

(b) $XT \rightarrow IS \rightarrow CT$ transfer only. Here we have set coupling matrix elements $g_{13i} = 0$ to force the $3 \rightarrow 2 \rightarrow 1$ indirect transfer.

\textsuperscript{12}See Irene Burghardt’s talk next month!
Complex and dynamical systems requiring both state of the art computational techniques \textit{and} new theoretical approaches to study their dynamics.

Very strong mixing between electronic and vibrational quantum dynamics $\Rightarrow$ very interesting dynamics!

Numerically exact treatments of dynamics coupled with accurate electronic structure of interface are required to fully capture the details of charge-transfer in these systems.

Eventually want to include continuum for charge-separation dynamics, higher order tclme methods, etc...
Thanks!

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Andrey Pereverzev: UH
John Ramon: UH
Carlos Silva: U. Montreal
Laura Herz: Oxford

Group info: http://k2.chem.uh.edu

Thanks also: Richard Friend and OE group for hospitality during my sabbatical.
the end!
misc. technical and/or formal details....
Interacting Dimer Model
Interactions between molecular dimers

Molecular dimer model: Start with isolated chains and allow to interact. \(^{13}\)

\[
H = \left( \epsilon_A + \sum_n g_{An} (a_n^\dagger + a_n) \right) \lambda + \left( \epsilon_B + \sum_n g_{Bn} (a_n^\dagger + a_n) \right) + \sum_n \hbar \omega_n (a_n^\dagger a_n)
\]

- \(\lambda\) interaction between chains (—)
- \(\epsilon_{A,B}\) excitation energies of isolated chains
- \(\{a_n, a_n^\dagger\} = \) phonons-normal modes localized on either A or B chain.

\(^{13}\)E. R. Bittner, A. Pereverzev, A. M. Goj, and I. Burghardt, in preparation
Example: 2-state system

For a two state system, \( E_{a,b} = \tilde{E} \pm \sqrt{\lambda^2 + \Delta^2} \) and freq. scaled coordinate \( q_i = \omega_i x_i \)

\[
H = \begin{bmatrix}
  E_a + V_a & V_c \\
  V_c & E_b + V_b 
\end{bmatrix} + H_{\text{phonons}}
\]

(26)

with

\[
V_a = \sum_i q_i \frac{g_{Ai}}{\omega_i} \cos^2 \theta + \sum_j q_j \frac{g_{Bj}}{\omega_j} \sin^2 \theta = g_a Q_a
\]

(27)

\[
V_b = \sum_i q_i \frac{g_{Ai}}{\omega_i} \sin^2 \theta + \sum_j q_j \frac{g_{Aj}}{\omega_j} \cos^2 \theta = g_b Q_b
\]

(28)

\[
V_{ab} = V_c = - \cos \theta \sin \theta \left( \sum_i q_i \frac{g_{Ai}}{\omega_j} - \sum_j q_j \frac{g_{Bj}}{\omega_i} \right) = g_c Q_c
\]

(29)

where \( \tan 2\theta = \lambda / \Delta \) is the mixing angle between the electronic states.

\( \{Q_a, Q_b, Q_c\} \) define non-orthogonal unit vectors and \( g_{a,b,c} \) are linear coupling vectors.
Significance of coupling vectors

- Taking $q_i = \omega_i x_i$, polaron-transform translates each well to new diabatic minima located along $Q_a$ and $Q_b$.

- Motion along $Q_a$ or $Q_b$ will not induce any further mixing of the electronic states.

- Only motion along $Q_c \propto Q_a - Q_b$ directly couples the diabatic states.

- $Q_c \perp$ seam of intersection between diabatic curves.
$Q_c$ defines our “reaction coordinate”

Recall familiar Marcus picture for electron transfer
Further Implications of $Q_\gamma$ mode: A-B dimer model

- $Q_a$ and $Q_b$ can define a 2D plane imbedded in the $N$ dimensional space of normal coordinates with $Q_c$ lying in this plane connecting the diabatic minima.
- For any $n$ level electronic system: $\exists$ an $O(n)$ dim. subspace embedded amongst the $N$ normal modes that encapsulates all electronic coupling.
- Can project out orthogonal $P$ and $Q$ subspaces

\[
P = \sum_{a \neq b} S_{ab}^{-1} Q_a \otimes Q_b \tag{30}
\]

\[
Q = 1 - P \tag{31}
\]

Using the projection ops and block-diagonalization, can determine coupling and residual modes + their bi-linear coupling.
Deriving Time-convolutionless Master Eq.
Since not all phonons are created equal, we partition total system into $P \supseteq Q_a, Q_b, (\& Q_c)$ modes + electronic states + treat remainder $\exists Q$ as an external bath.

$$\rho = (P + Q)\rho \quad (32)$$

Nakajima/Zwanzig Eq.

$$\frac{d}{dt} P\rho(t) = -i\mathcal{L}_{PP} P\rho(t) - \int_{t_0}^{t} dt' \mathcal{L}_{PQ} e^{-i\mathcal{L}_{QQ}(t-t')} \mathcal{L}_{QP} P\rho(t')$$

$$- i\mathcal{L}_{PQ} e^{-i\mathcal{L}_{QQ}(t-t_o)} Q\rho(t) \quad (33)$$

$$= -\int_{t_0}^{t} dt' \mathcal{K}_{NZ}(t-t') P\rho(t') \quad (34)$$

so far this is exact...
Quantum Dynamics (2)

**Standard Assumptions**

- Work in the interaction representation of decoupled system/bath.
- Assume at t=0, bath is at thermal eq. and density matrix is separable.

\[
\frac{\partial \tilde{\rho}}{\partial t} = - \sum_{0}^{t} dt' \sum_{ij} C_{ij}(t - t')[\tilde{S}_i(t), [\tilde{S}_j(t'), \tilde{\rho}(t')]]
\]  (35)

where

\[
C_{ij} = \langle B_i(t)B_j(t') \rangle
\]  (36)

taken to be real.
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- Any explicitly treated phonons are coupled to a thermal bath held at thermal eq.

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- Since transfer rates are on the order of the coherence decay, one must be concerned with the effect of memory on the predicted rate.
- Golden-rule is a Markovian limit.
- For non-Markovian dynamics, we need to integrate the Nakajima-Zwanzig eq.

$$\frac{d\rho}{dt} = -\int_{0}^{t} \mathcal{K}(t - t')\rho(t')dt'$$  \hspace{1cm} (37)

- Can also use non-convolutionless form

$$\frac{d\rho}{dt} = -\int_{0}^{t} \mathcal{K}_{cl}(t')dt'\rho(t)$$  \hspace{1cm} (38)
Taking coupling as a perturbation and expanding in cumulants

\[ \mathcal{K}_{cl}^{(2)}(t) = \mathcal{P} \mathcal{L} e^{i \mathcal{L} \cdot t} \mathcal{L} \mathcal{P} \]  

After even more tedious algebra,…

\[ \frac{dP_a}{dt} = \sum_b (W_{ab}(t)P_b(t) - W_{ba}(t)P_{ba}(t)) \]  

time-convolutionless Pauli master eq. for populations.
Non-Markovian Pauli master eq.

- Taking coupling as a perturbation and expanding in cumulants

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- with

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Note: $W_{21} < 0$ implies positivity violation in TCLME
Removing Time-convolution

- Take Laplace x-form of the NZ equation

\[ \mathcal{L}(\tilde{\rho})(s) - \rho(0) = -\mathcal{K}_{NZ}(s)\mathcal{L}(\tilde{\rho}(s)) \quad (42) \]

- Rearrange:

\[ \mathcal{L}(\tilde{\rho})(s) = \frac{\rho(0)}{s + \mathcal{K}(s)} \quad (43) \]
Removing Time-convolution

- Take Laplace x-form of the NZ equation

\[ \mathcal{L}(\tilde{\rho})(s) - \rho(0) = -K_{NZ}(s)\mathcal{L}(\tilde{\rho}(s)) \]  \hspace{1cm} (42)

- Rearrange:

\[ \mathcal{L}(\tilde{\rho})(s) = \frac{\rho(0)}{s + \mathcal{K}(s)} \]  \hspace{1cm} (43)

- Inverse LP (closing contour over poles)

\[ \mathcal{U}(t) = \frac{1}{2\pi i} \int_{\eta-i\infty}^{\eta+i\infty} \frac{e^{st}}{s + \mathcal{K}(s)} ds \]  \hspace{1cm} (44)
Removing Time-convolution

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- Rearrange:
  \[ \mathcal{L}(\tilde{\rho})(s) = \frac{\rho(0)}{s + \mathcal{K}(s)} \quad (43) \]

- Inverse LP (closing contour over poles)
  \[ U(t) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} e^{st} ds \quad (44) \]

- Time-evolution eq:
  \[ \tilde{\rho}(t) = U(t)\rho(0) \quad (45) \]
Removing Time-convolution

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Convolutionless NZ equation

- Inverting:
  \[ \rho(0) = U(t) \tilde{\rho}(t) \]  \hspace{1cm} (46)

- Taking time-deriv.
  \[ \frac{d}{dt} \tilde{\rho}(t) = \left( \frac{d \log U}{dt} \right) \tilde{\rho}(t) \]  \hspace{1cm} (47)


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  \[ \frac{d}{dt} \tilde{\rho}(t) = \left( \frac{d \log \mathcal{U}}{dt} \right) \tilde{\rho}(t) \]  
  \[ (47) \]

- Convolutionless kernel
  \[ K_{cl}(t) = -\frac{d^2}{dt^2} \log \mathcal{U} \]  
  \[ (48) \]

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  (48)

- Do perturbative expansion on \(U(t)\),

Quantum Chemical Studies
Electronic Structure at Heterojunction Interface

- $\pi$-stacked systems are very challenging: dispersion interaction charge-separation is also difficult: requiring good description of both exchange and correlation effects.

- Time-dependent Density Functional Theory + hybrid exchange/correlation functions problematic..but currently the best choice for large-scale systems (300 atoms)

- Why TD-DFT? Considers the response of the KS ground state to an excitation. Formally, equivalent to RPA since it includes back-polarization of ground state due to excitation.

- Need to have reliable parameters before we can do any sort of dynamics (GIGO)
TFB:F8BT Heterojunction

- General approach: MD + DFT to optimize structure, then TD-DFT/6-31G**/B3LYP + HF exchange.
- Computationally expensive (about 1 month CPU time/calculation).

Why is the stacking (slippage) an issue?

- In excited state

\[ \cdots - F8^{\delta+} - BT^{\delta-} - \cdots & \cdots - F8^{\delta-} - N\phi_3^{\delta+} - \cdots \]

F8BT* & TFB*

(49)

due to alternation of HOMO/LUMO levels from each monomer.

- Eclipsed (attractive)

\[ \cdots - BT^{\delta-} - F8^{\delta+} - BT^{\delta-} - \cdots \]

\[ \cdots - N\phi_3^{\delta+} - F8^{\delta-} - N\phi_3^{\delta+} - \cdots \]

(50) & (51)

- Staggered (repulsive)

\[ \cdots - BT^{\delta-} - F8^{\delta+} - BT^{\delta-} - \cdots \]

\[ \cdots - N\phi_3^{\delta+} - F8^{\delta-} - N\phi_3^{\delta+} - \cdots \]

(52) & (53)
Map of interaction energy\textsuperscript{16}

**Figure:** DFT structure/INDO descript. of PFB excited state/Coulomb interaction w/F8BT (ground state).

CI theory grossly overestimates the excitation energy.

CI: F8BT exciton is lowest energy state since interchain coupling is weak.
TFB:F8BT Heterojunction

TD/DFT energy levels for eclipsed vs staggered configurations for model solvent dielectric (toluene) vs. gas phase.

Note: considerable exciplex stabilization due to solvent polarization.
Only eclipsed exciplex state carries appreciable oscillator strength.
Comparison of transition densities:

For XT, most oscillator strength is localized on the F8BT with some mixing with the TFB chain.
Comparison of transition densities: Eclipsed Exciplex States

Eclipsed CT

Eclipsed CT2

most of transition density is on 2nd CT state
Comparison of transition densities: Staggered Exciplex states

Stag. CT1 & CT2
Figure: Projection of excited states onto monomer units

- **Eclipsed**: exciplex has considerable mixing between purely excitonic configurations and purely CT configurations.
- **Staggered Exciplex**: almost purely polaronic (CT) configurations.
Brief Summary

- TD-DFT is reliable for excitonic systems, less so for strongly charge separated ones.
- Slippage between the chains has a very profound impact on the oscillator strength, less so on the energetics.
- For TFB:F8BT: all exciplex emission is from eclipsed configurations.
- Solvent effects a red-shift on exciplex, less so on XT.
- Intermediate (dark) states certainly play a role...perhaps consistent with the field-induced dissociation measurements.
Building a site model/1

each monomer: localized
Wannier orbital for HOMO and LUMO bands + set of localized vibrations
Interactions: Coulomb (J), Exchange (K), and dipole-dipole (D) interactions between e/h configurations.
Interchain coupling: \( J, K, D + t_\perp = 0.15t_\parallel \)

Building a site model/2

- Use either quantum chemical or spectroscopic data to parameterize a lattice model for a given polymer chain or polymer dimer.

  ![Polymer Lattice Diagram]

- Each site can have an electron, hole, or both (exciton)

  ![Electron, Hole, and Exciton Diagrams]

- Each site has localized phonons + linear coupling to neighboring (intrachain) sites.

- Diagonalize (separately) electronic and vibrational contributions...

- Taxonomy of dimer models
Heterojunction Energetics

Comparison between Lattice model and TD-DFT energies.

- Lattice model adjusted to “match” experimental values (CT-XT gap)
- Transition moments are similar
- Both lattice and TDDFT predict 2-ary CT state
- Advantage of lattice model is that we can treat far larger systems than possible with TD-DFT.

"Strong" $t_\perp = 0.15 t_\parallel$; "inter", $t_\perp = 0.15 t_\parallel$
only for center F8’s; "weak" $t_\perp = 0$, only

Coulomb (2-body) interactions.

In spite of its simplicity and direct molecularity, lattice model does a good job at modeling spectra, energetics, etc.