Quantum Complexity in Biological and Material Systems – Where Do We Stand?

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Topics

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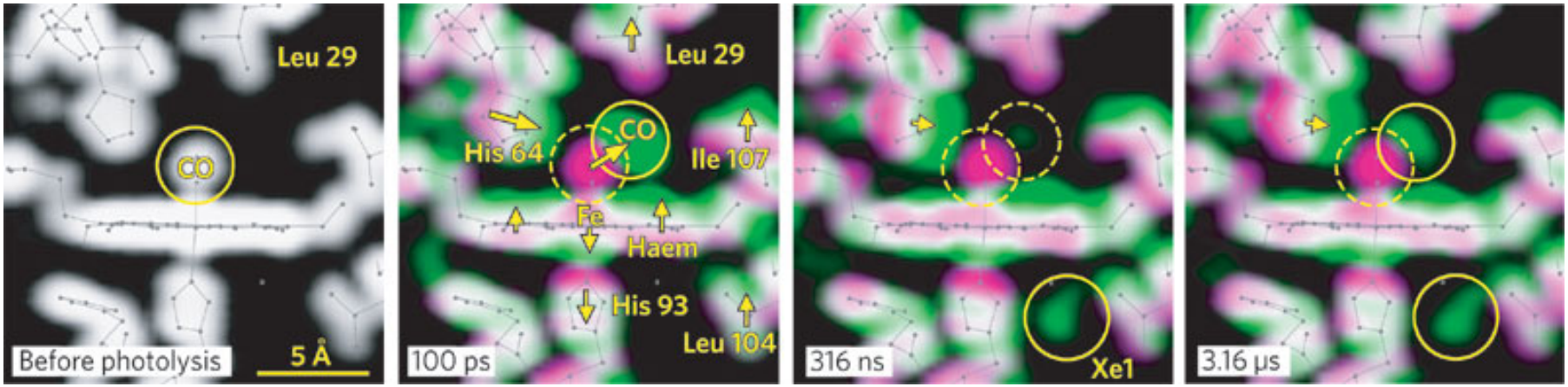
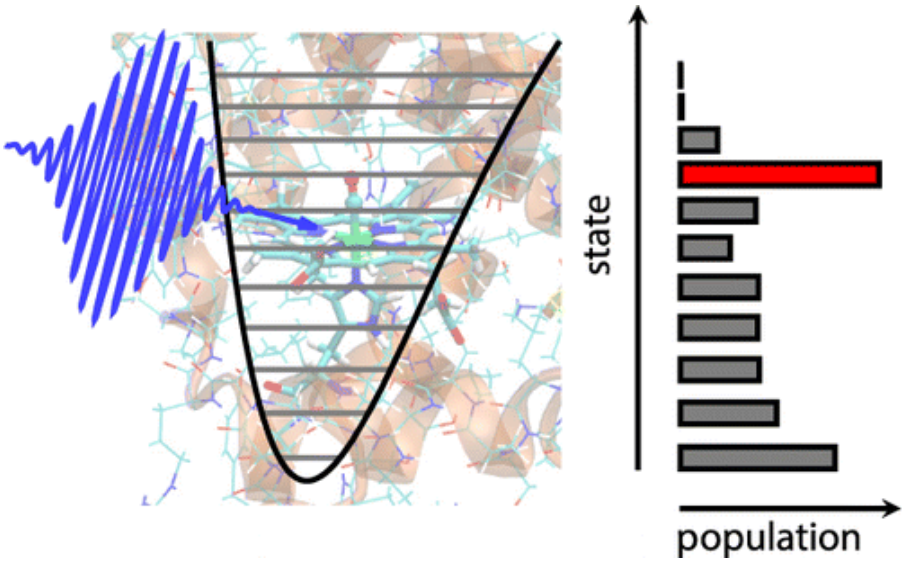
Molecular Dynamics: Quantum or Classical?

- Most properties/processes in biological & material systems can be taken to belong to the classical limit ($\lambda_{\mathrm{dB}} \ll L$, classical Wigner limit, ...)
- Hence, MD (= Molecular Dynamics) simulations are extensively used: classical-mechanical evolution of all nuclear degrees of freedom on the lowest (electronic ground state) Born-Oppenheimer (BO) surface
- However, some quantum effects are important:
  - tunneling (proton transfer, electron transfer)
  - light-induced processes: coherent superpositions
  - nonadiabatic ("non-BO") dynamics
- Methods are needed for quantum dynamics in many dimensions (E. Pollak)
  - approximate wavefunction and density operator methods
  - semiclassical approaches
  - mixed quantum-classical hybrid approaches

Quantum Oscillators in Highly Specific Environments



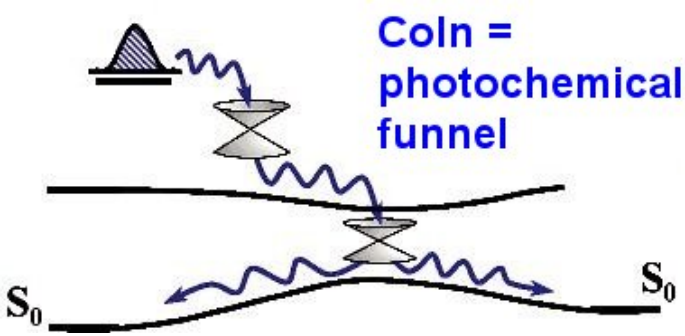


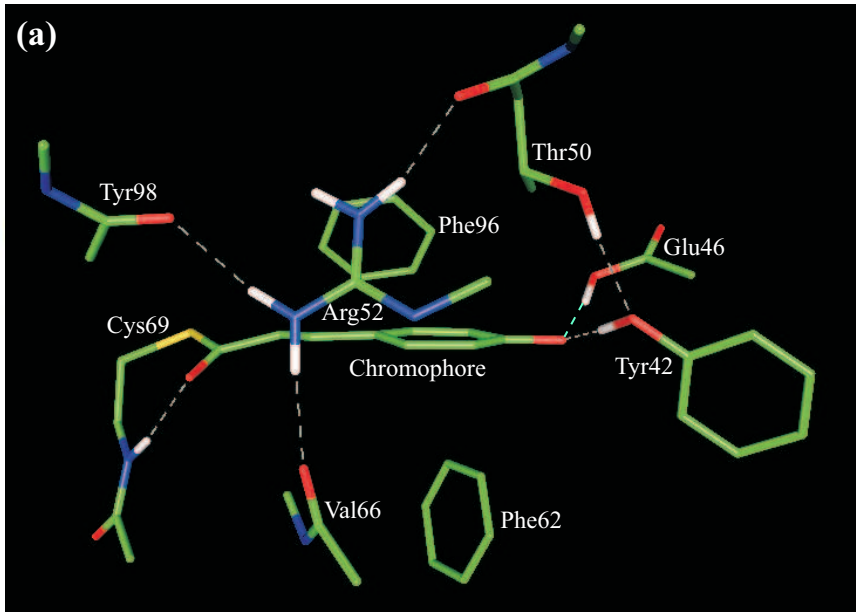
- CO-myoglobin complex
- photoinduced CO dissociation from myoglobin
- state-specific excitation feasible
- relaxation/decoherence depend critically on local environment

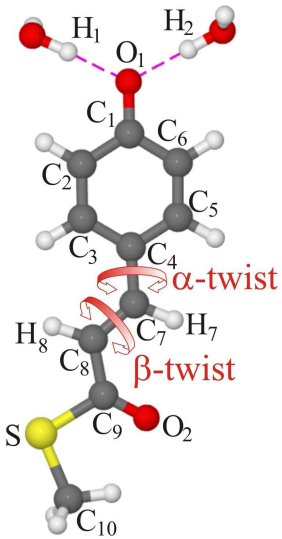
Debnath, Falvo, Meier, J. Phys. Chem. A, 117, 12884 (2013)

Photoactive Proteins: Bio-Photochemistry

Example PYP = Photoactive Yellow Protein



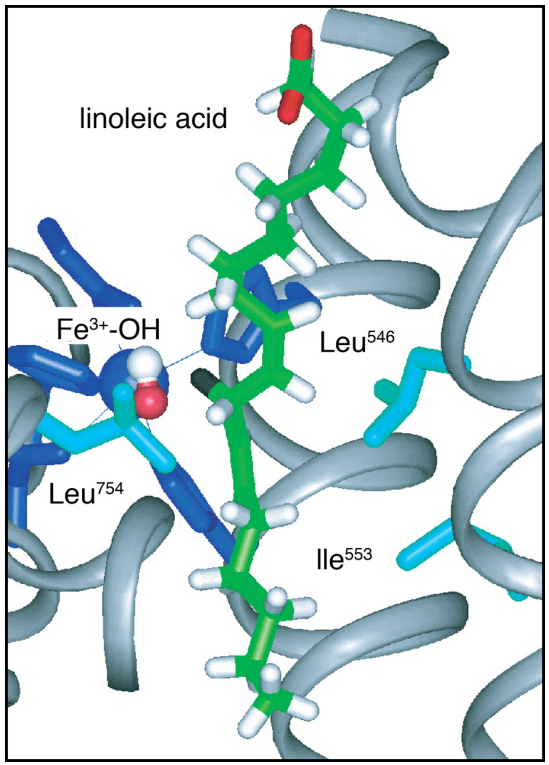


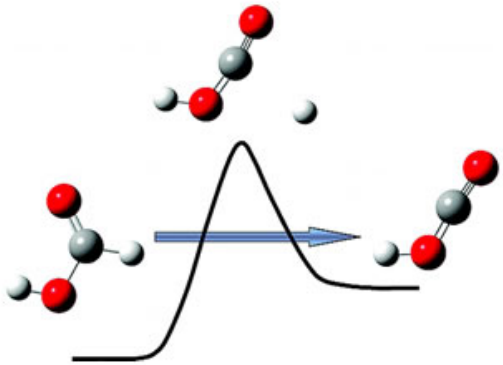


Gromov, Burghardt, Köppel, Cederbaum, J. Phys. Chem. A **115**, 9237 (2011), JACS **129**, 6798 (2007)

- photochemistry determined by conical intersection (CoIn) topology
- local environment significantly influences α vs. β twist
- interplay of steric effects / electrostatics / H-bonds / fluctuations
- excited-state lifetime: $\sim$ 700 fs (in solution: $\sim$ 10 ps)

Quantum Tunneling in Enzymes



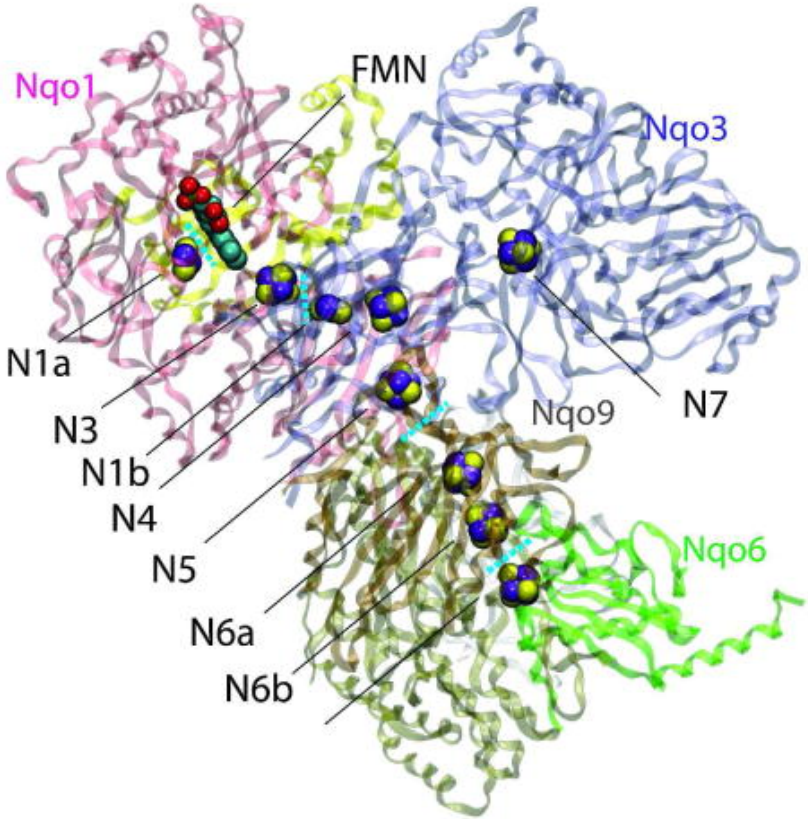


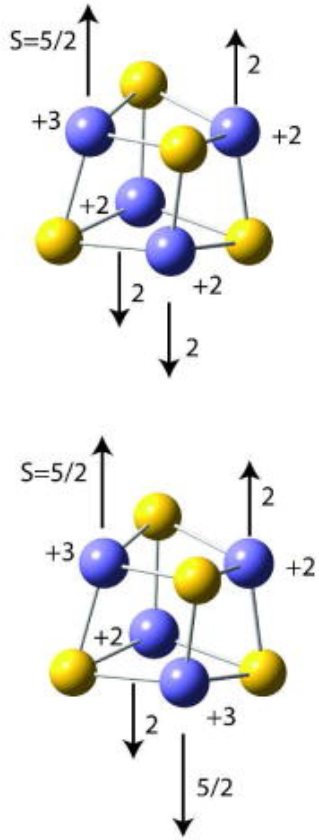
- "Did enzymes evolve to capitalize on quantum tunneling?" The Scientist, 2005
- "Our present findings on hydrogen transfer under physiological conditions cannot be explained without invoking both quantum mechanics and enzyme dynamics" Klinman, Nature 1999
- "Taking Ockham's razor to enzyme dynamics and catalysis": no need to go beyond Transition State Theory (TST) + tunneling corrections

Glowacki et al., Nature Chem. 2012

Meyer, PNAS 105, 1146 (2008)
"Enzyme structure and dynamics affect hydrogen tunneling:
The impact of a remote side chain (I553) in soybean lipoxygenase-1"

Electron Tunneling: Respiratory Chains

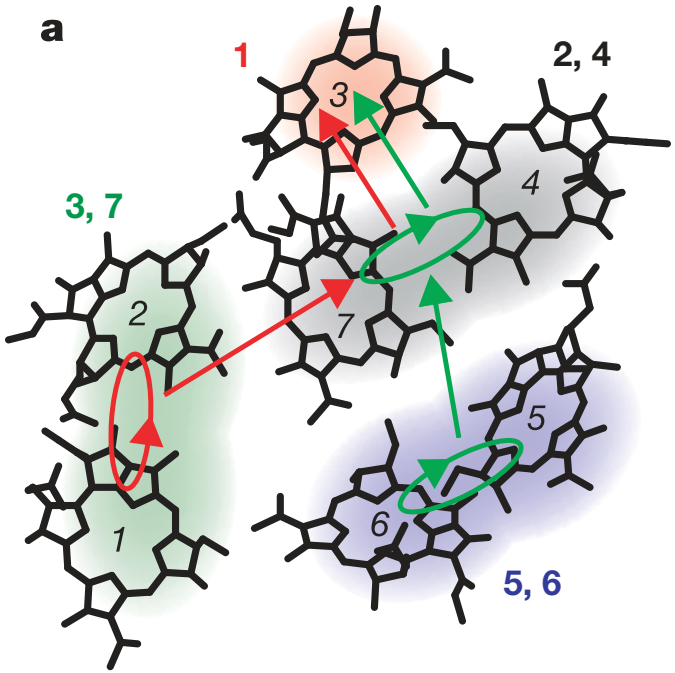




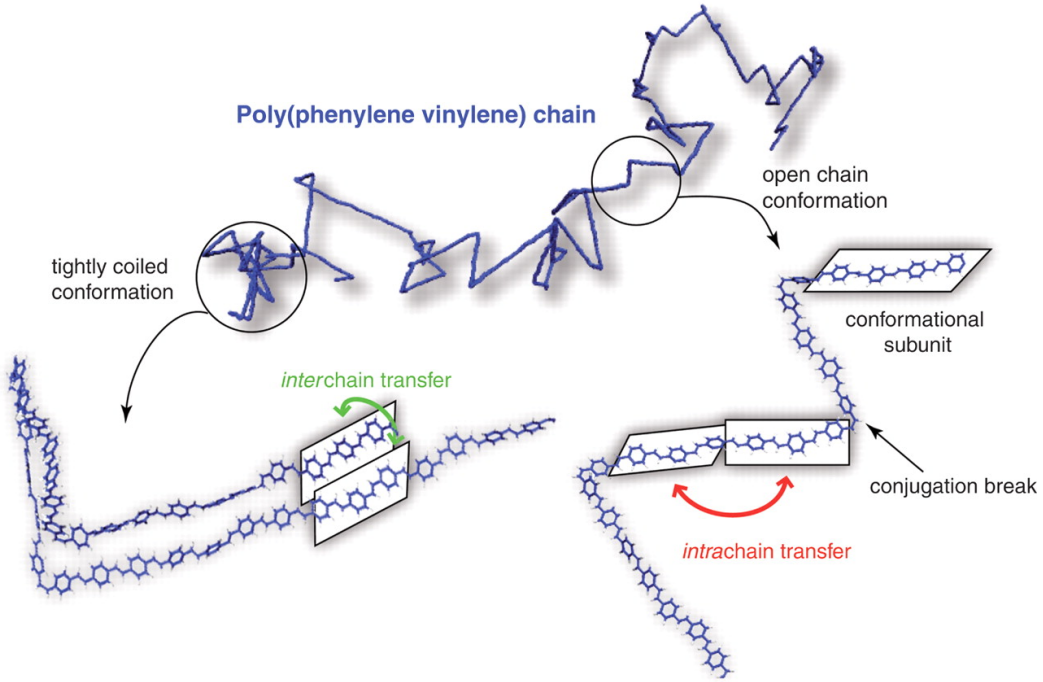
"Quantum Electron Tunneling in Respiratory Complex I1", Hayashi, Stuchebrukhov, J. Phys. Chem. B 115, 5354 (2011)

- "electronically wired" iron-sulfide (FeS) clusters
- quantum interference resulting from multiple tunneling pathways

How Coherent is Photoinduced Energy and Charge Transport in Biological and Material Light-Harvesting Systems?



Lee, Cheng, Fleming, Science 316, 1462 (2007)



Collini, Scholes, Science 323, 369 (2009)

- one would expect an extremely rapid dephasing (decoherence): $\tau_{\mathrm{dec}} < 50$ fs
- but observed coherence lifetimes are $\sim$ 300 fs to 1-2 ps (or more)

Why did Coherence Lifetimes of Several Picoseconds Come as a Surprise?

Conventional picture:

- environmental influence ubiquitous
- rapid decoherence: $\tau_{\mathrm{dec}} \sim 30$ fs
- kinetic descriptions (transfer rates, "hopping" rates) adequate

But various experiments show that decoherence times $\tau_{\mathrm{dec}} \gg 30$ fs:

- "Protein protection of excitonic coherence", Fleming and collaborators (2009)
- "Quantum coherence controls the charge separation in a prototypical organic photovoltaic system", Lienau and collaborators (2014)

The nature & role of the observed coherence remain controversial

How Fast is Electronic Decoherence?

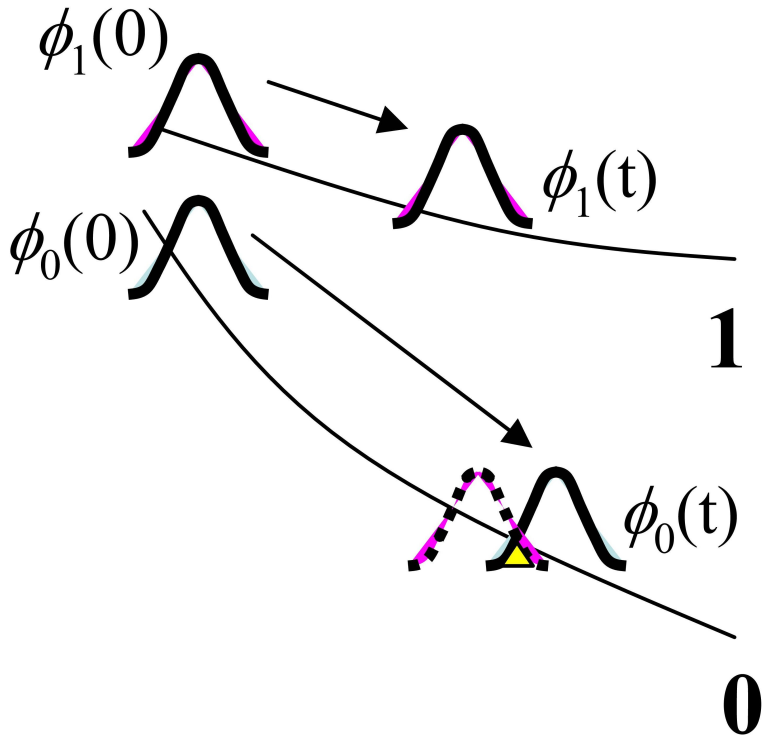
$$|\psi(t)\rangle = c_0(t)|0\rangle|\phi_0(t)\rangle + c_1(t)|1\rangle|\phi_1(t)\rangle$$

electronic (subsystem) coherence

$$\rho_{01}(t) = \mathrm{Tr}[|0\rangle\langle 1|\hat{\rho}(t)]$$
$$= \langle 1|\hat{\rho}(t)|0\rangle = c_1^*(t)c_0(t)\langle\phi_1(t)|\phi_0(t)\rangle$$

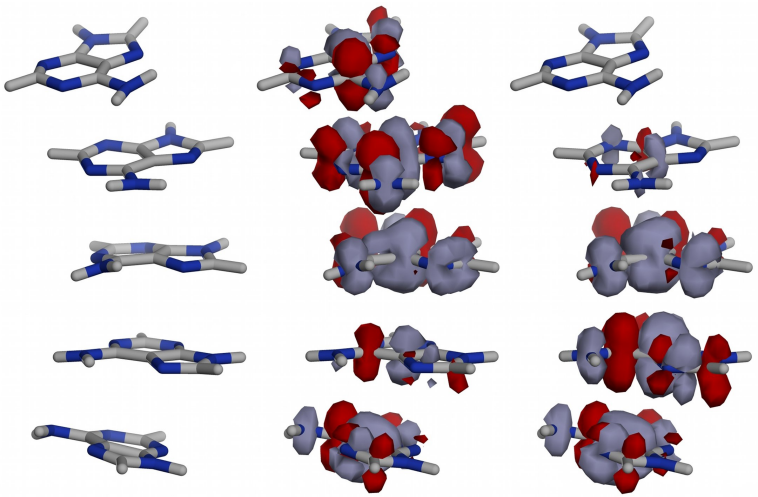
- coherence $\propto$ overlap of nuclear wavefunctions
- typical decoherence times: ~ 30 fs (estimate from $\tau_{\mathrm{dec}} \sim \tau_g(6k_BT/\lambda)^{1/2}$ or $\tau_{\mathrm{dec}} \sim \gamma^{-1}(\lambda_T/\Delta x)^2$)

  Prezdho, Rossky, PRL 81, 5294 (1998)
- loss of coherence *not* captured by classical trajectory picture



picture: P. Rossky et al.

Similar Observations: Coherent Exciton Dynamics in DNA



electronic densities of stacked adenine pentamer corresponding to two $\pi\pi^*$ states with different degrees of localisation

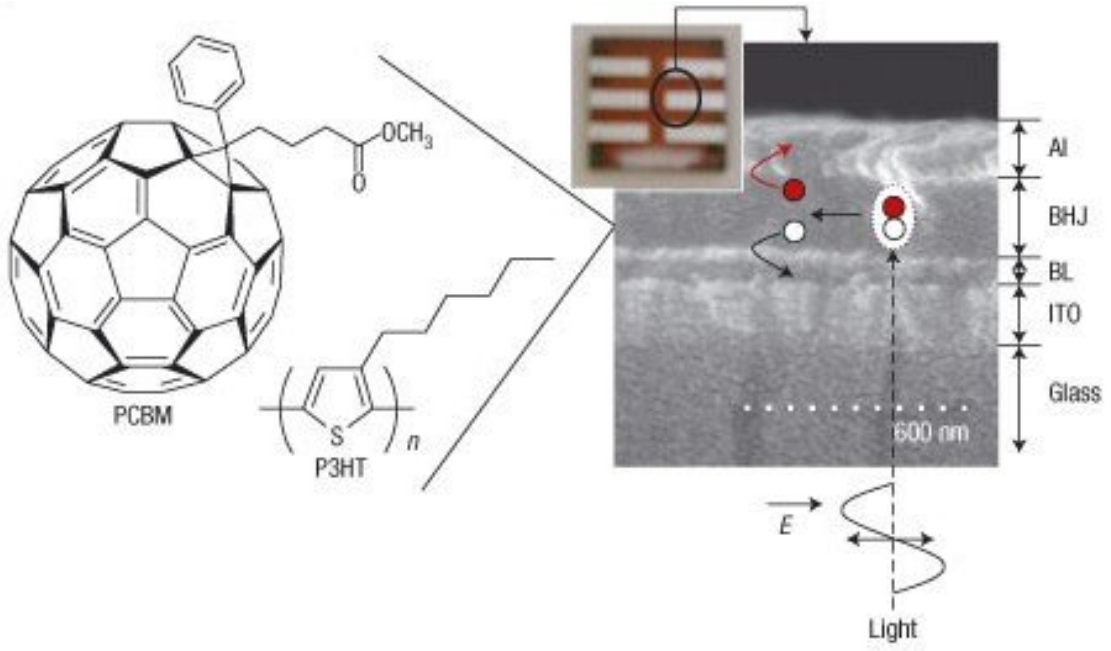
Bittner & co-workers, in: *Energy Transfer Dynamics in Biomaterial Systems*, Burghardt et al. (eds), Springer (2009).

- nonstationary photoexcited state
- collective electronic excitations
- non-perturbative el-vib coupling
- many el. states, many vib. modes

- ultrafast dynamics
- multiple curve-crossings
- non-equilibrium environment
- non-Markovian dissipation

→ It's a challenging problem ...

Related Issues Appear in Organic Photovoltaics



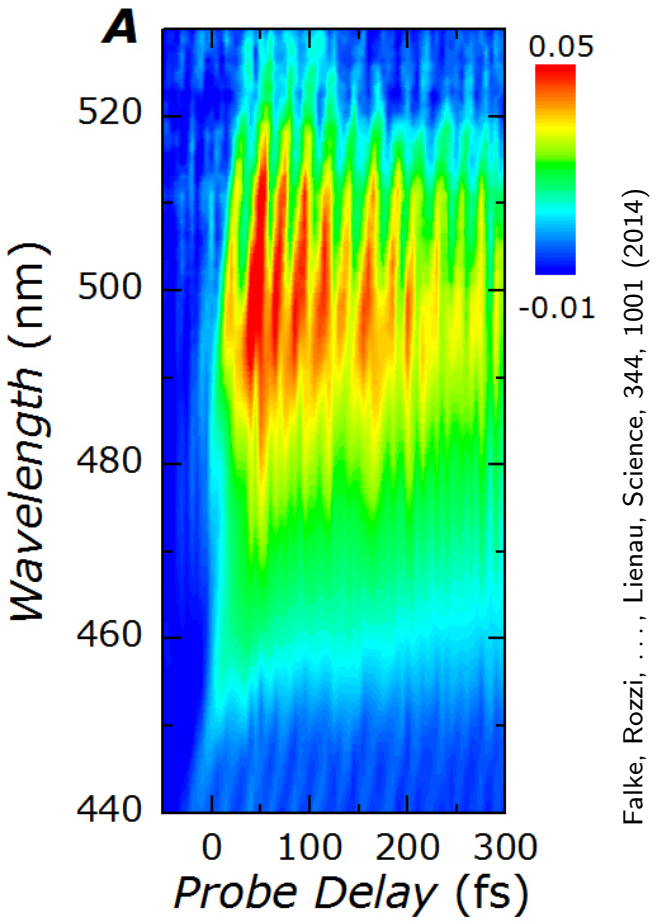
Kim et al., Nature Materials, 5, 197 (2006)

elementary steps:

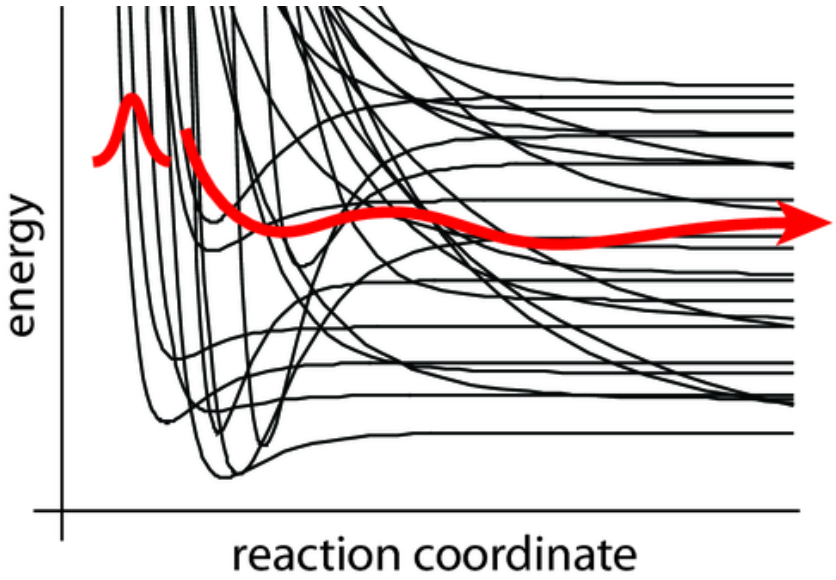
- creation of electron-hole pairs (excitons)
- exciton dissociation at donor-acceptor junctions (here, PCBM-P3HT)[1]
- capture of charge carriers at electrodes
- potentially competing process: electron-hole recombination!

[1] PCBM = phenyl-C_{61}-butyric acid methyl ester, P3HT = poly(3-hexylthiophene)

Initial Charge Separation is often Ultrafast & Coherent



Falke, Rozzi, . . . , Lienau, Science, 344, 1001 (2014)

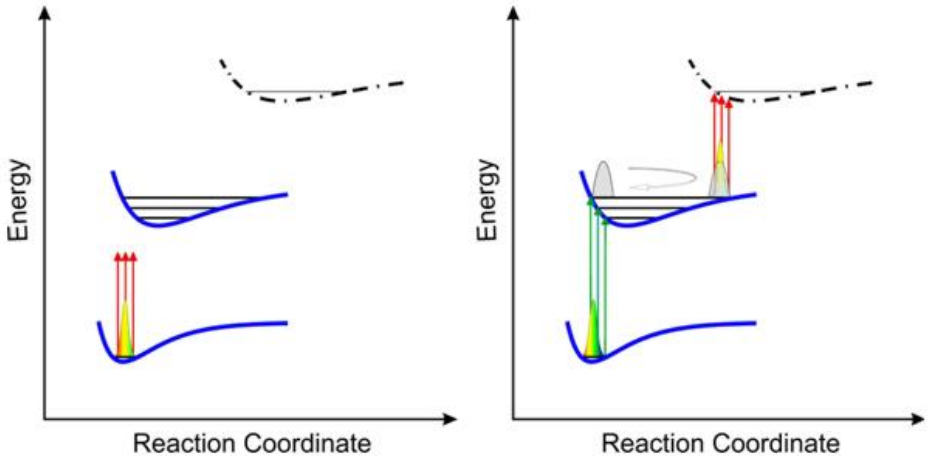


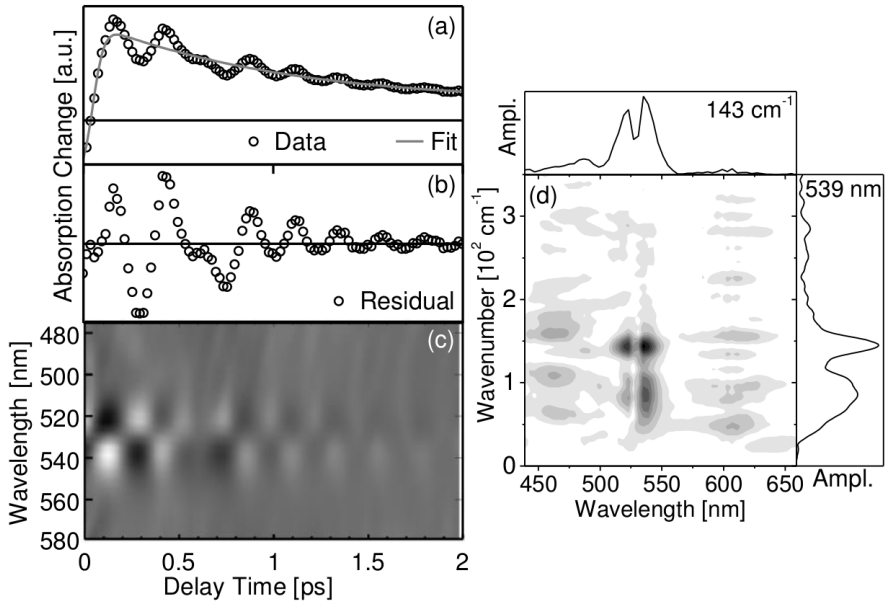
www.wag.caltech.edu/home/jsu/Thesis/node9.html

- exciton breakup in P3HT/PCBM
- coherent, oscillatory transients
- possibly "hot" vibronic states

- nonadiabatic wavepacket dynamics
- many states, many coordinates
- static and dynamic disorder

Vibrational Coherence & Coherence Transfer





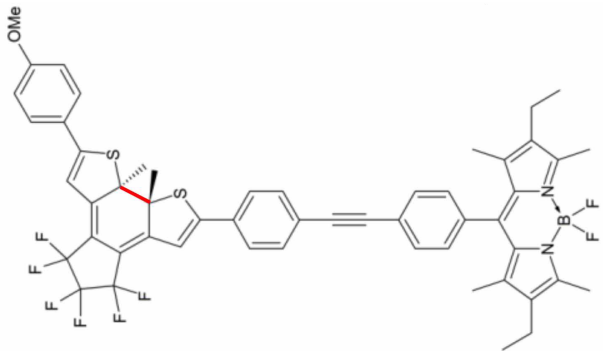
Pump-Probe spectroscopy

http://www.uni-heidelberg.de/fakultaeten
/chemgeo/pci/motzkus/research/wavepackets.html

- vibrational coherence
  ◂▸ wavepacket motion
- coherence transfer due to coupled vibrations

Vibrational coherence transfer in an electronically decoupled molecular dyad

Schweighöfer et al., Scientific Reports (2015)



Where Do We Stand?

- Is "quantum-driven" functionality a robust feature, or rather an accidental occurrence?
- Does nature capitalize on quantum coherence, such as to optimize efficiency?
- To what extent does quantum entanglement "scale up" into these systems that are at the border between the microscopic and macroscopic world?
- Do specific environments act so as to protect low-dimensional subsystems from decoherence?
- To what extent can effective descriptions of these systems be found?

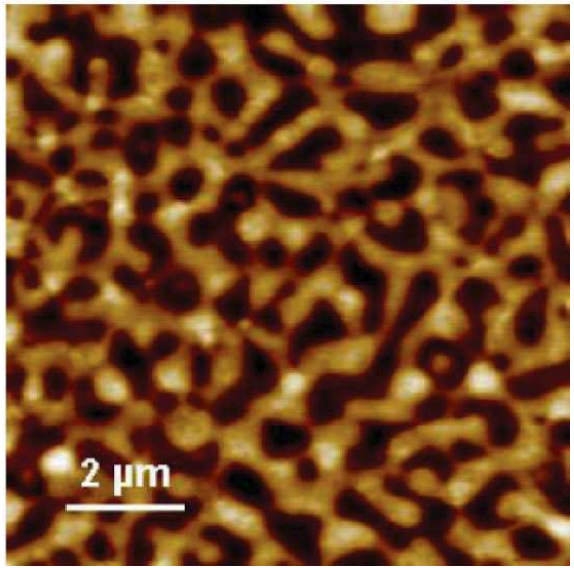
Excitonic Transport in Molecular Aggregates – Where Do We Stand?

"Have photosynthetic systems adopted interesting quantum effects to improve their efficiency in the course of evolution, as suggested by the experiments? In this article, we provide a first step to answer this question by characterizing the protein environment of the FMO photosynthetic system to identify the microscopic origin of the long-lived quantum coherence." (A. Aspuru-Guzik & coll., 2012)

"*Despite the fact that experiments show signatures of coherent dynamics at short times, such features play little role in controlling the energy transfer rate. We show that the presence of coherent beating in chromophore network populations, which matches closely with features observed in nonlinear 2D spectroscopy signals, is strongly dependent on the way the excitation is injected into the multichromophore network. The articial initial conditions employed in the experiments enhance the coherence and with more realistic initialization the coherent features are signicantly diminished. We show that a simple kinetic model can be used to understand the population dynamics and relaxation to thermal equilibrium in these systems."* (Huo, Coker (2015))

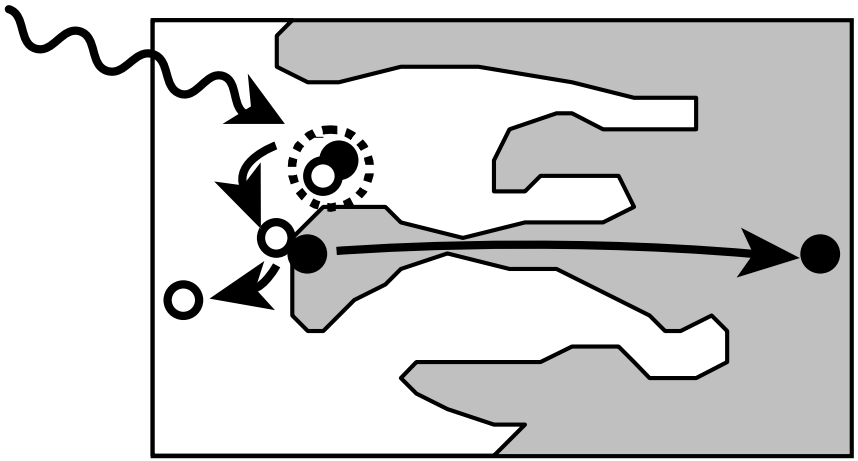
"The presence of quantum coherence, and therefore entanglement, in the system does not seem to be enhancing the excitation transfer. This suggests that entanglement that may be present in bio-molecules, though interesting, may not be a universal functional resource." (Plenio, Huelga (2008))

Excursion: Organic Materials for Optoelectronics



AFM image of d-F8:F8BT blend

McNeill & Greenham, Adv. Mater. 21, 1 (2009)



Schematic of exciton dissociation

Peumans, Uchida, Forrest, Nature **125**, 8098 (2003)

- so-called bulk heterojunction technology led to breakthrough in $\sim$ 1995
- maximization of interface area $\longrightarrow$ increase likelihood that excitons encounter interface within diffusion length $\sim$ 10 nm

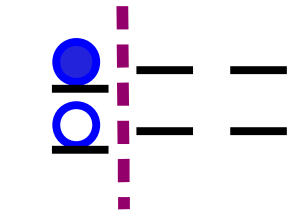
Molecular-Level Model Hamiltonians & Quantum Dynamics$^{(*)}$

1. electron-hole (e-h) lattice models including vibronic interactions
2. *ab initio* (typically CC2, ADC(2)), TD-DFT or semi-empirical parametrization; diabatization procedures to generate electronic couplings
3. selection of "most important" modes:
   - by intuition
   - by exploration of PES (geometry optimization, on-the-fly dynamics)
   - by sampling over spectral densities
   - by reduction *via* effective-mode schemes
4. efficient quantum dynamics using multi-configurational methods (MCTDH)
   - $\psi(\boldsymbol{x},t)$ including *all* phonon modes, for discretized environments[2]
   - $\rho(\boldsymbol{x},\boldsymbol{x}';t)$ including a subset of effective modes + dissipative terms
   - strong electron-phonon coupling necessitates non-perturbative treatment

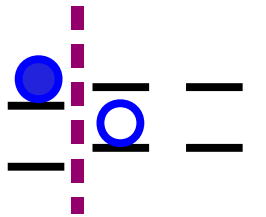
$^{(*)}$Alternative/complementary approach: on-the-fly dynamics

[2] subsequently construct $\rho(\boldsymbol{x},\boldsymbol{x}';t) = \sum_n p_n \, \psi_{\boldsymbol{n}}(\boldsymbol{x},t)\,\psi^*_{\boldsymbol{n}}(\boldsymbol{x}',t)$

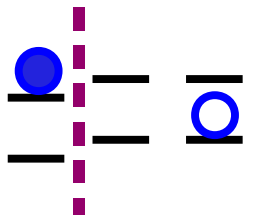
Electron-Hole Lattice Model



$|1_e\rangle_C \otimes |1_h\rangle_V$



$|1_e\rangle_C \otimes |2_h\rangle_V$



$|1_e\rangle_C \otimes |3_h\rangle_V$

- electron-hole (e-h) configurations:
  $|\mathbf{n}\rangle = |n_e n'_h\rangle = |n_e\rangle_C \otimes |n'_h\rangle_V$
- Hamiltonian in this basis:

$$\hat{H} = \sum_{\mathbf{mn}} (\hat{h}^{eh}_{\mathbf{mn}} + \hat{h}^{eh\text{-}ph}_{\mathbf{mn}}(\mathbf{x}))|\mathbf{m}\rangle\langle\mathbf{n}| + \hat{H}^{ph}_0(\mathbf{x})$$

Merrifield, J. Chem. Phys. 34, 1835 (1961)
Wang and Mukamel, Chem. Phys. Lett. 192, 417 (1992)
Karabunarliev and Bittner, J. Chem. Phys. 118, 4291 (2003)
Binder, Wahl, Römer, Burghardt, Faraday Discuss, 163, 205 (2013)

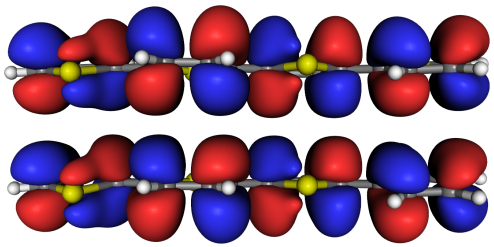
- includes Frenkel-type exciton (XT) states and charge transfer (CT) states
- oligomer (fragment) calculations: obtain diabatic couplings & vibronic couplings
- e-h representation connects to fragment-based single-particle transition density analysis

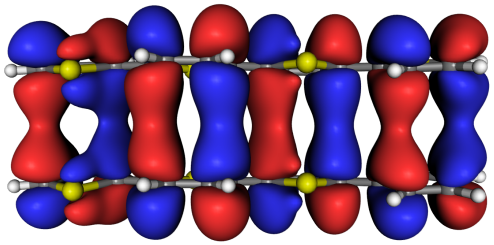
Plasser, Lischka, JCTC 8, 2777 (2012)
Panda, Plasser, Aquino, Burghardt, Lischka, JPCA, 117, 2181 (2013)

Special Case: Frenkel Exciton Model

- Frenkel model ($n_e = n'_h$) often a good approximation to describe EET
- exact analytic mapping of oligomer PES's to Frenkel model

  Binder, Römer, Wahl, Burghardt, J. Chem. Phys. 141, 014101 (2014)





stacked oligothiophene $(OT4)_2$: "HJ aggregate"

- delocalized states

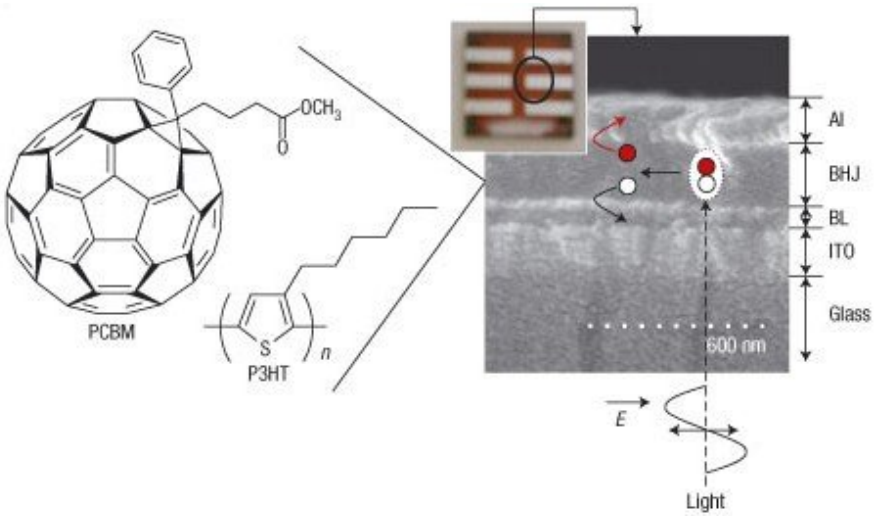
$$|\Psi_{\text{exciton}}\rangle = \sum_{n}^{n_{\text{exc}}} c_n |\Phi_n\rangle$$

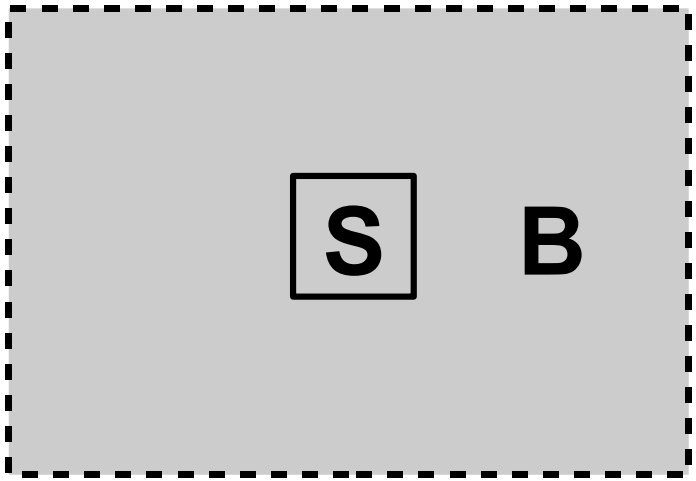
  where $n_{\text{exc}} \sim$ 5-10; $|\Phi_n\rangle =$ configuration with single excitation on nth monomer
- trapping due to exciton-phonon interactions

- J-aggregate: end-to-end alignment of monomer units; lowest state of the exciton manifold is the bright state
- H-aggregate: plane-to-plane stacked geometry; highest state of the exciton manifold is the bright state
- HJ-aggregate: combination of both, as in stacked oligomers

  Yamagata, Spano, JCP **136**, 184901 (2012)

System-Bath Models





S region: e.g., electronic degrees of freedom (electron-hole states)

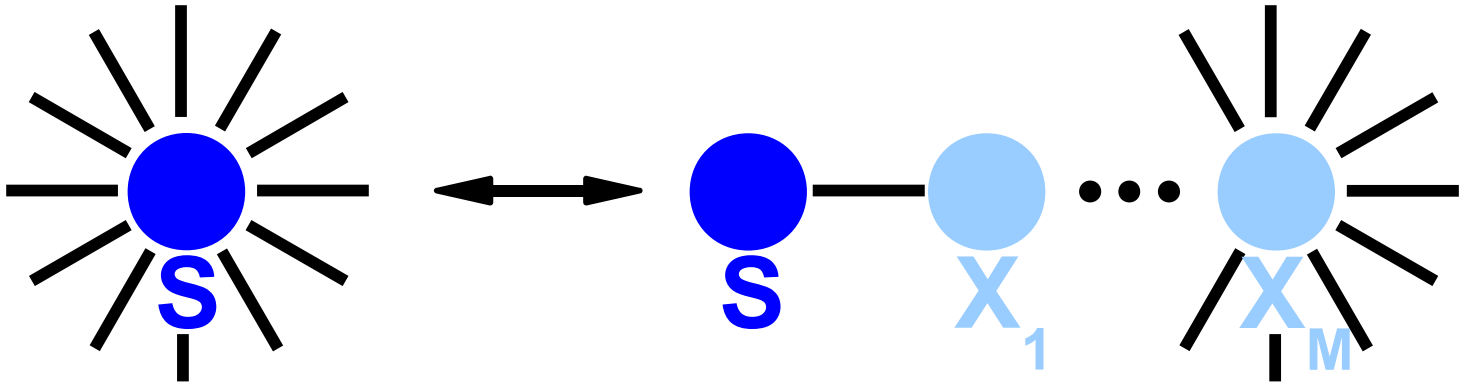
B region: all vibrations (phonons) mapped to harmonic oscillator model

$$\hat{H}_B + \hat{H}_{SB} = \sum_n \frac{1}{2}(\hat{p}_n^2 + \frac{1}{2}\omega_n^2 \hat{x}_n^2) + \hat{s}\sum_n c_n \hat{x}_n$$

$$J(\omega) = \pi/2 \sum_n c_n^2/\omega_n \delta(\omega - \omega_n)$$

spectral density

Reduced-dimensional Models: Collective Modes



Martinazzo, Vacchini, Hughes, Burghardt, J. Chem. Phys. 134, 011101 (2011), Hughes, Christ, Burghardt, J. Chem. Phys. 131, 024109 (2009)
Tamura, Bittner, Burghardt, J. Chem. Phys. 126, 021103 (2007), Gindensperger, Köppel, Cederbaum, J. Chem. Phys. 126, 034106 (2007)
Cederbaum, Gindensperger, Burghardt, Phys. Rev. Lett., 94, 113003 (2005), Garg, Onucic, Ambegaokar, J. Chem. Phys. 83, 4491 (1985)

$$\hat{H}_{SB} + \hat{H}_B = \hat{s} \sum_i c_n \hat{x}_n + \hat{H}_B \longrightarrow D\hat{s}\hat{X}_1 + d_{12}\hat{X}_1\hat{X}_2 + \ldots + \hat{X}_M\text{–residual bath}$$

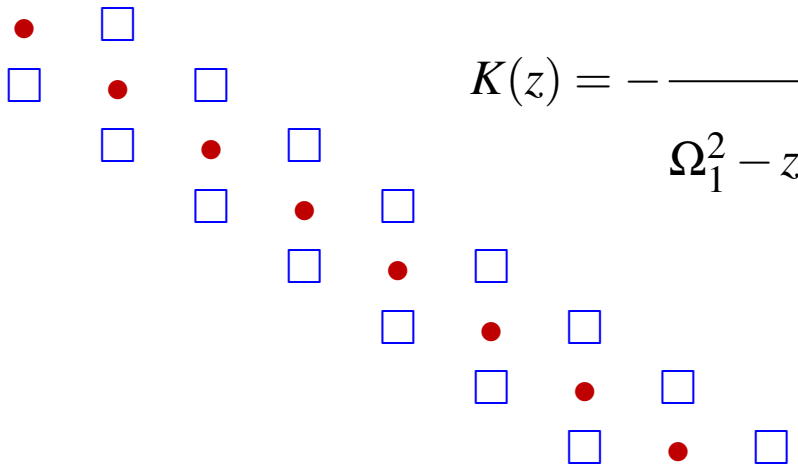
- orthogonal coordinate transformation $\hat{\boldsymbol{X}} = \mathbf{T}\hat{\boldsymbol{x}}$
- short-time dynamics captured by first few effective modes
- truncate the chain – with a (quasi-)Markovian closure – to define an approximate, reduced-dimensional model

Spectral Densities as Continued Fractions

- map spectral densities onto the transformed representation
- "Mori-chain" continued fraction (CF):

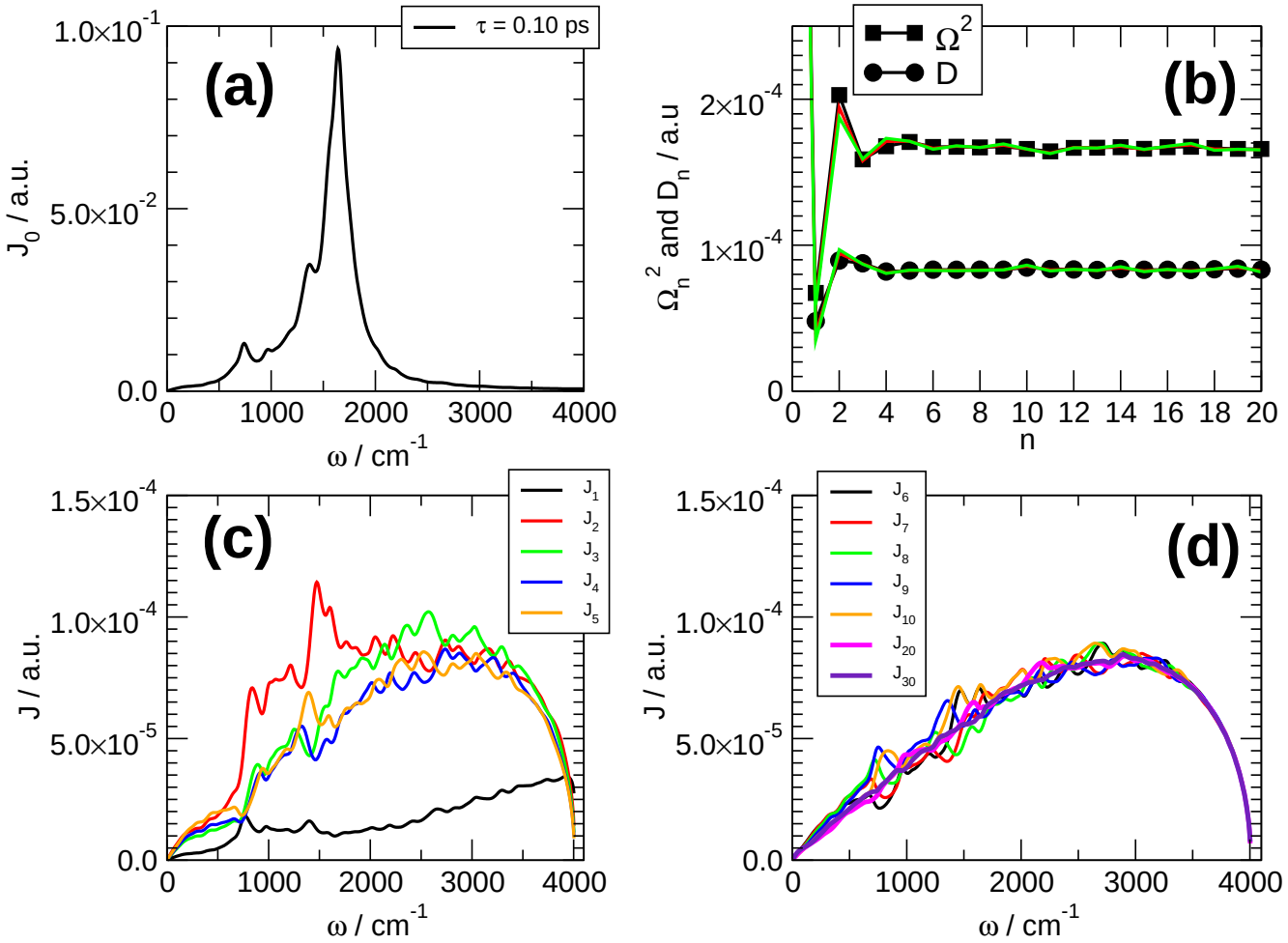
$$J(\omega) = \frac{\pi}{2} \sum_n \frac{c_n^2}{\omega_n} \delta(\omega - \omega_n) \quad \longleftrightarrow \quad J(\omega) = \lim_{\varepsilon \to 0^+} \mathrm{Im}\, K(z)\Big|_{z=\omega - i\varepsilon}$$

Hughes, Christ, Burghardt, JCP 131, 024109 (2009), Garg, Onuchic, Ambegaokar, JCP 83, 4491 (1985), Leggett, Phys. Rev. B 30, 1208 (1984)



$$K(z) = -\cfrac{D^2}{\Omega_1^2 - z^2 - \cfrac{d_{1,2}^2}{\Omega_2^2 - z^2 - \cdots \cfrac{d_{M-2,M-1}^2}{\Omega_{M-1}^2 - z^2 - \cfrac{d_{M-1,M}^2}{\Omega_M^2 - z^2 - \ldots}}}}$$

Effective Mode Chains – Convergence to an Ohmic SD



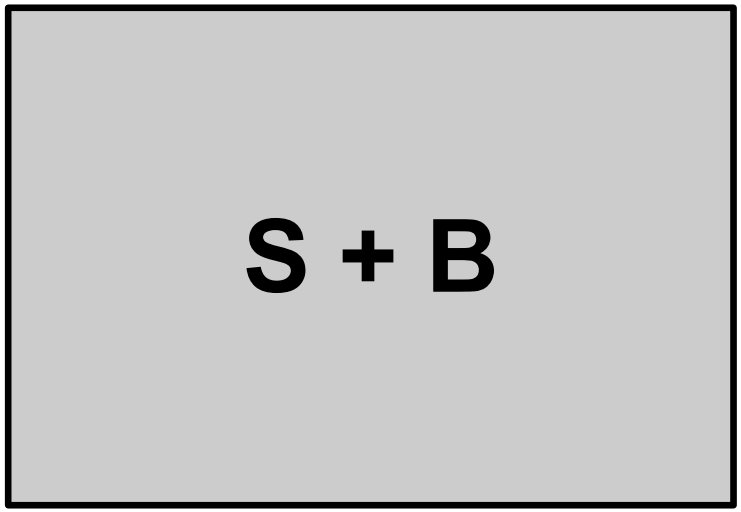
Martinazzo, Vacchini, Hughes, Burghardt, J. Chem. Phys. 134, 011101 (2011)

- residual SD's tend towards a quasi-Ohmic limit (i.e., with cutoff)

Quantum Dynamics in Many Dimensions

$$i\frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

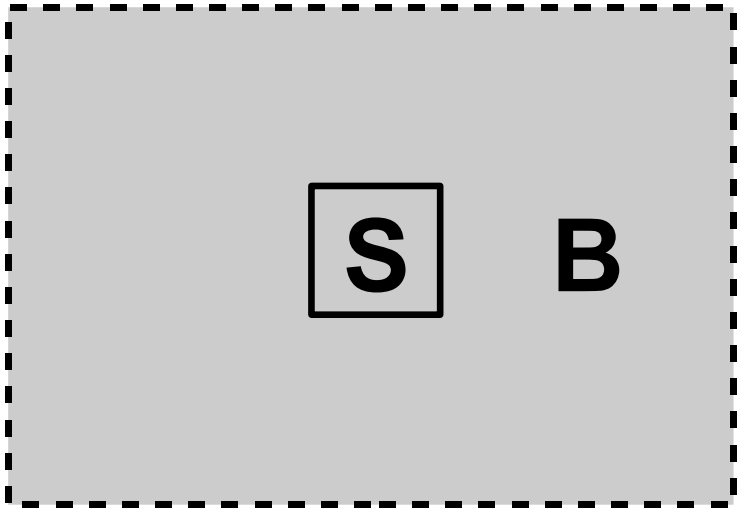
- initial value problem
- full eigenstate resolution
  may not be necessary/feasible



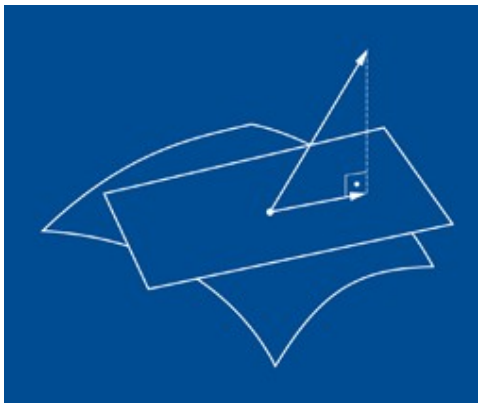
also, for mixed states:

$$i\frac{\partial \hat{\rho}}{\partial t} = \left[\hat{H}, \hat{\rho}\right] + \hat{\hat{L}}_{\text{diss}}\hat{\rho}$$

- generally non-Markovian



Approximate Wavefunctions from the Dirac-Frenkel Variational Principle



C. Lubich, From Quantum to Classical Molecular Dynamics: Reduced Models and Numerical Analysis, Zürich (2008)

Dirac-Frenkel (DF) variational principle:

$\langle \delta\Psi | \hat{H} - i\frac{\partial}{\partial t} | \Psi \rangle = 0 \quad \longrightarrow$ dynamical equation for $\dot{\Psi}$

where $\delta\Psi \in \mathscr{T}_\Psi \mathscr{M}$ (tangent space wrt the approximate manifold $\mathscr{M}$ on which the wavefunction is defined)

Dirac 1930, Frenkel 1934, McLachlan 1964

- the time derivative is then given by
  $\dot{\Psi} = \mathscr{P}(\Psi)\frac{1}{i}\hat{H}\Psi$
  where $\mathscr{P}(\Psi)$ projects onto the tangent space
- the residual is minimized: $||\dot{\Psi} - \frac{1}{i}\hat{H}\Psi|| = \min$
- norm conservation, energy conservation
- symplectic flow

Multi-Configuration Time-Dependent Hartree (MCTDH)

- standard basis set methods do not go beyond 5-6 dimensions ($\sim f N^{f+1}$)
- approximate Ψ by an *ansatz*: linear combination of Hartree products

$$\begin{aligned}\Psi(r,t) &= \sum_J A_J(t)\ \Phi_J(r,t) \\ &= \sum_{j_1=1}^{n_1} \dots \sum_{j_N=1}^{n_N} A_{j_1 \dots j_N}(t)\, \varphi_{j_1}^{(1)}(r_1,t) \dots \varphi_{j_N}^{(N)}(r_N,t)\end{aligned}$$

- orthogonal, time-evolving single particle functions (spf's) $\varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$
- the spf's can be multi-dimensional ("combined modes")
- configurations $\Phi_J(r,t) = \prod_{\kappa=1}^{N} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$
- obtain time evolution of the coefficients and spf's from DF principle

Meyer et al., CPL **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)

MCTDH – Equations of Motion

Coupled system of coefficient equations and low-dimensional non-linear equations for the spf's:

coefficients:
$$i\frac{dA_J}{dt} = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L$$

spf's:
$$i\rho^{(\kappa)} \frac{\partial \varphi^{(\kappa)}}{\partial t} = \left(\hat{1} - \hat{P}^{(\kappa)} \right) \hat{H}^{(\kappa)} \varphi^{(\kappa)}$$

- $\rho^{(\kappa)}$ is the reduced density matrix in the κth subspace
- $\hat{P}^{(\kappa)} = \sum_j |\varphi_j^{(\kappa)}\rangle\langle\varphi_j^{(\kappa)}|$ is the time-dependent projector on the κth subspace
- $\hat{H}^{(\kappa)}$ is a mean-field Hamiltonian matrix
- simplest case: Time-Dependent Hartree = TDH[3] (single configuration)

Meyer, Manthe, Cederbaum, CPL **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)

[3] also denoted Time-Dependent Self-Consistent Field = TDSCF

Scope and Extensions

- MCTDH takes one to 50-100 modes
- exponential scaling ($\sim f N^{f+1}$) not broken but alleviated
- restriction on the form of the potential: sums over products

- related multi-layer variant (ML-MCTDH) goes up to 1000 modes

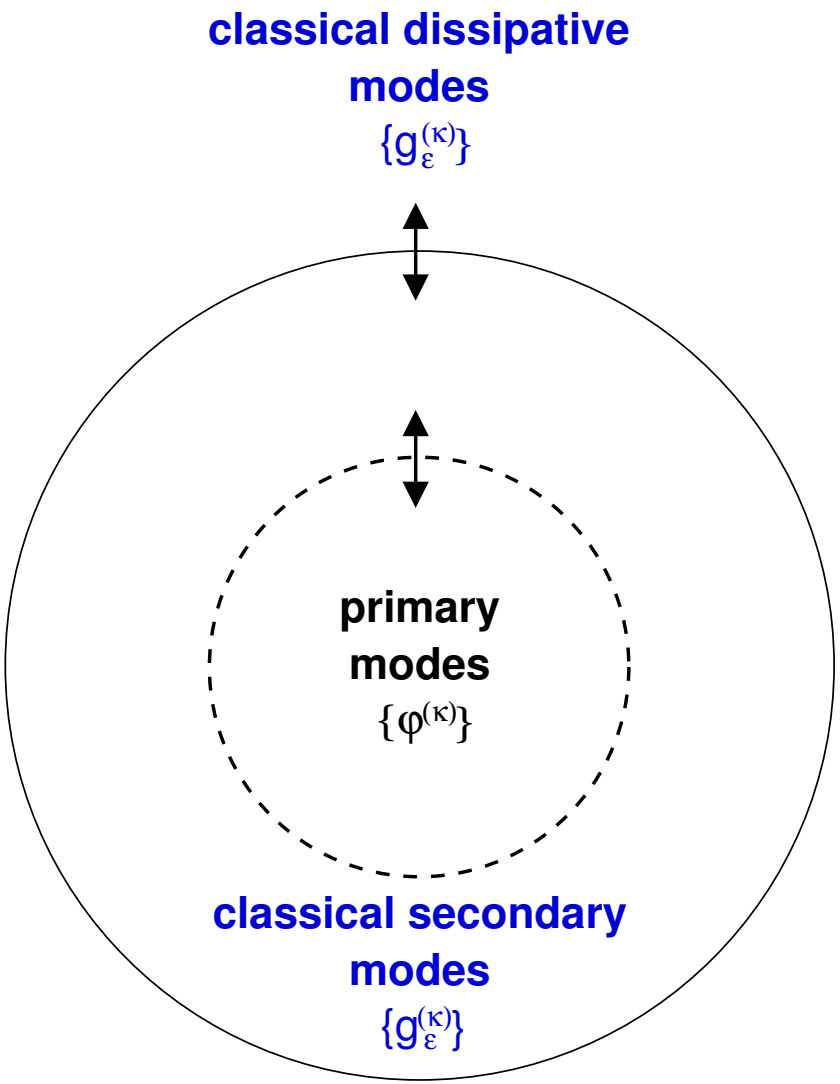
  Wang, Thoss, J. Chem. Phys. 119, 1289 (2003)
- related MCTDH-F (fermion) and MCTDH-B (boson) methods

  Kato, Kono, Chem. Phys. Lett. 392, 533 (2004), Nest, Klamroth, Saalfrank, J. Chem. Phys. 122, 124102 (2005)
  Alon, Streltsov, Cederbaum, Phys. Lett. A 362, 453 (2007)
- density matrix variant

  Raab, Burghardt, Meyer, J. Chem. Phys. 111, 8759 (1999)
- hybrid approaches: e.g., Gaussian-based variant (G-MCTDH, vMCG)

  Burghardt, Meyer, Cederbaum, J. Chem. Phys. 111, 2927 (1999), Worth, Burghardt, Chem. Phys. Lett. 368, 502 (2003)

Quantum-Classical Limit of (G-)MCTDH



take GWP subspace to classical limit:

$$\Psi^{\mathrm{qc}}(r,t) = \sum_J A_J(t)\ \Phi_J^{\mathrm{qc}}(r,t)$$

$$\Phi_J^{\mathrm{qc}}(r,t) = \underbrace{\prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{primary nodes}}\ \underbrace{\prod_{\kappa=M+1}^{P} g_{\varepsilon,j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{secondary modes}}$$

Römer, Burghardt, Mol. Phys. 111, 3618 (2013)

use "narrow" semiclassical GWPs:

$$g_{\varepsilon,j_\kappa}^{(\kappa)}(r_\kappa) = N_\varepsilon \exp\left[-\frac{1}{2\varepsilon}(r_\kappa - q_{j_\kappa})\cdot a(r_\kappa - q_{j_\kappa}) + \frac{i}{\varepsilon} p_{j_\kappa}^{(\kappa)}(t)\cdot(r_\kappa - q_{j_\kappa})\right]$$

Pure-State vs. Mixed-State Propagation

1. explicit, multidimensional dynamics for the full system + bath space: wavefunction $\psi_{SB}(t)$ or density operator $\hat{\rho}_{SB}(t) = \sum_n p_n |\psi_{n,SB}(t)\rangle\langle\psi_{n,SB}(t)|$

   ⟶ typically MCTDH

   Beck et al., Phys. Rep. **324**, 1 (2000)

2. reduced dynamics (master equation) methods: $\hat{\rho}_S(t) = \mathrm{Tr}_B \hat{\rho}_{SB}(t)$

   ⟶ typically Hierarchy Equations of Motion (HEOM)

   Tanimura, J. Phys. Soc. Jpn. **75**, 082001 (2006)

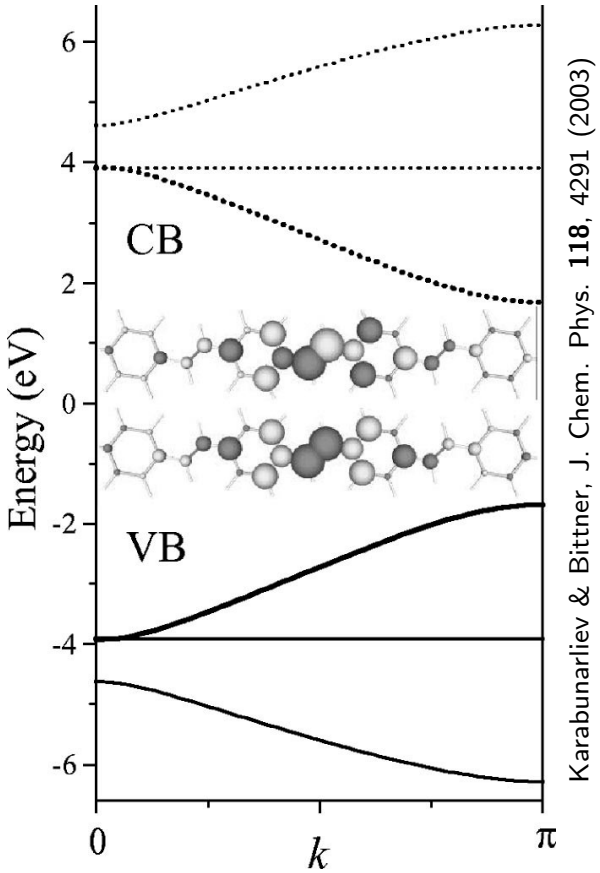
3. intermediate methods: explicit treatment of subsystem + effective-mode (E) part of the bath + master equation for residual (B') bath:[4]

$$\frac{\partial \hat{\rho}_{SE}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{SE}, \hat{\rho}_{SE}(t)] + \hat{\hat{L}}^{(B')}_{\mathrm{diss}} \hat{\rho}_{SE}(t) \quad ; \quad \hat{\rho}_{SE}(t) = \mathrm{Tr}_{B'} \hat{\rho}_{SEB'}(t)$$

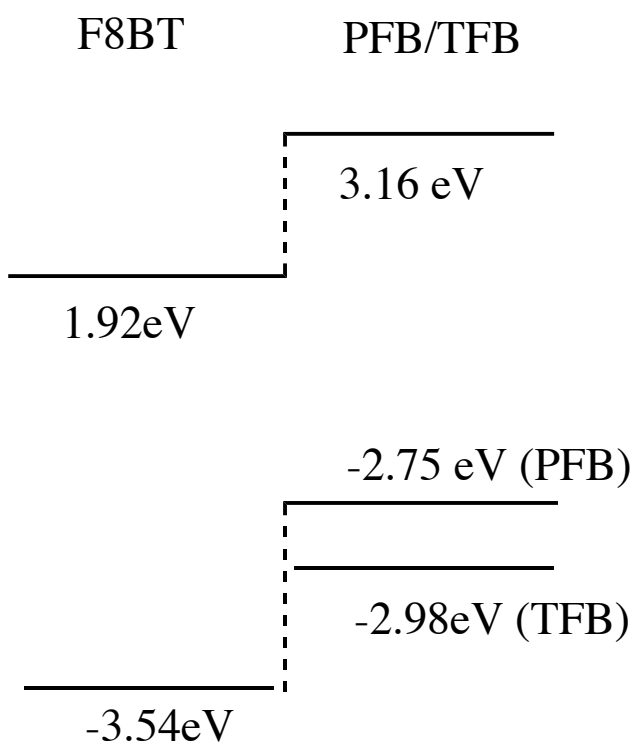
[4] e.g., Caldeira-Leggett: $\hat{\hat{L}}^{(B')}_{\mathrm{diss}} \hat{\rho}_{SE} = -i\frac{\gamma}{\hbar}[\hat{X}_E, [\hat{P}_E, \hat{\rho}_{SE}]_+] - \frac{2\gamma MkT}{\hbar^2}[\hat{X}_E, [\hat{X}_E, \hat{\rho}_{SE}]]$

Topics

Zeroth-Order Picture of a Heterojunction



polymer/polymer interface:



- HOMO/LUMO ↔ valence/conduction band
- 1st bound excited state: singlet exciton ($^1B_u^-$ in PPV); Frenkel type exciton
- @junction: compare band offset vs. exciton binding energy ($\varepsilon_B \sim 0.5$ eV)

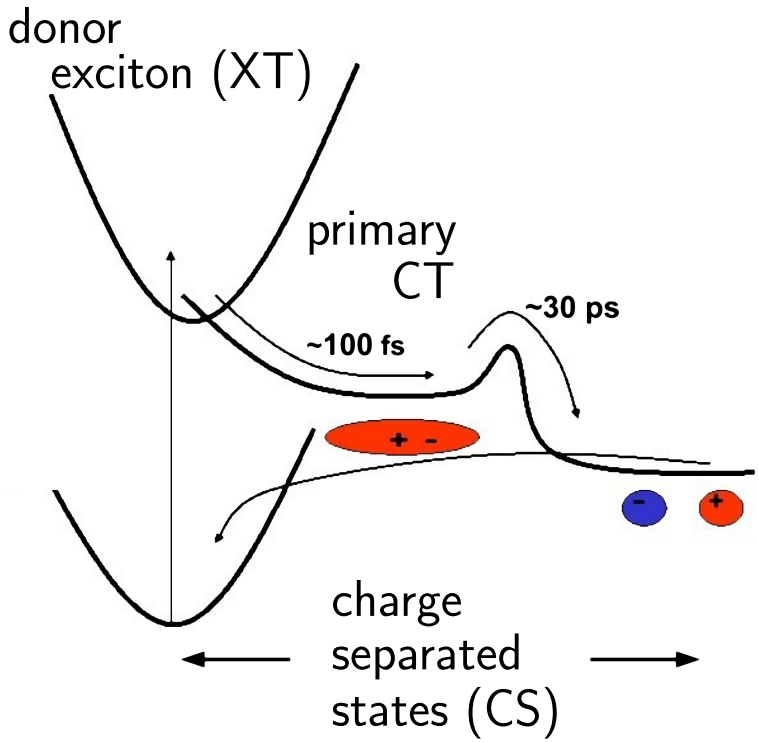
Characteristic Time Scales

– Sundström & co: time-resolved spectroscopy of poly-fluorene-fullerene blends

J. Phys. Chem. C, 112, 6558 (2008)

– Asbury & co: ultrafast infrared spectroscopy: charge separation as fast as 1-10 ps

Phys. Chem. Chem. Phys. 11, 2575 (2009)



adapted from:
http://www.chemphys.lu.se/research/projects/escdos/

- XT-CT transfer preceded by excitation energy transfer (EET)
- ultrafast ($\sim$ 100 fs) photoinduced formation of primary CT complex
- bound charges yield free charges on a $\sim$ 1–100 ps time scale
- free charges geminately recombine within $\sim$ ns scale

What is the Best Nano-Morphology?

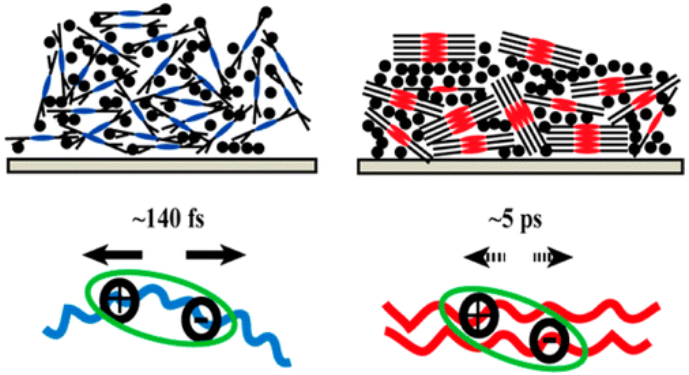
Highly ordered nanostructured domains (typically sub-10 nm) are thought to

- facilitate exciton diffusion
- favor exciton dissociation
- facilitate free carrier transport

Nanostructured domains can be achieved by

- self-assembly properties of D/A oligomers
- thin film processing methods (e.g., nanoimprint lithography)

However, the role of nanoscale ordering is controversial:



Guo et al., JACS 136, 10024 (2014)

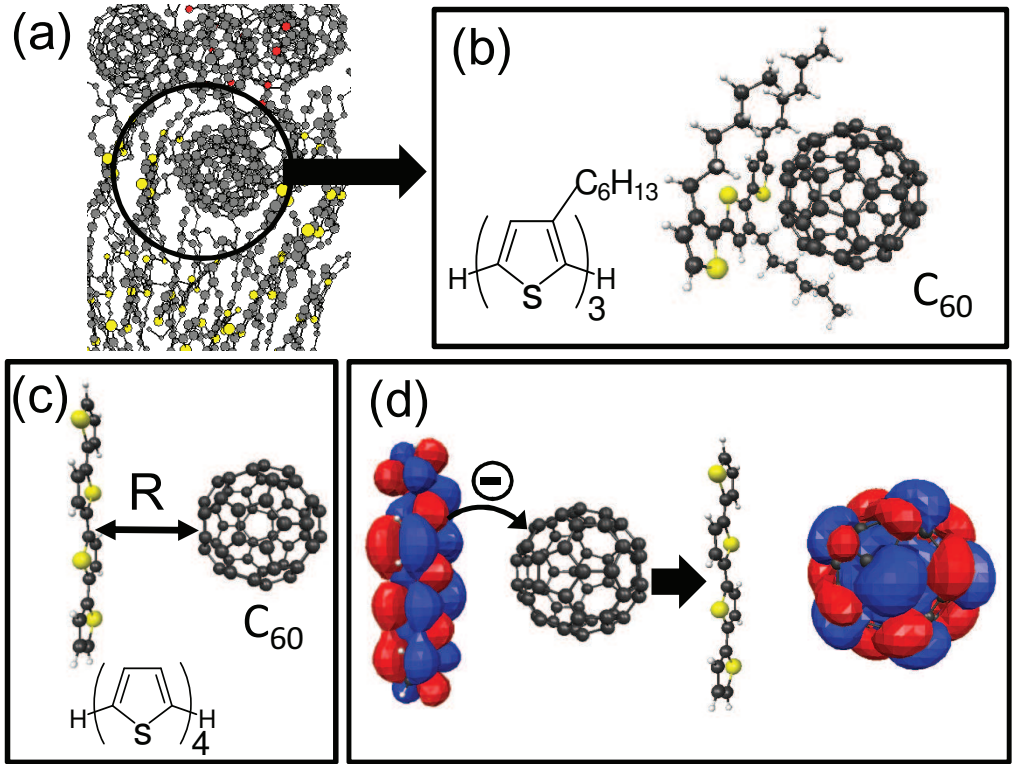
- e.g., in a recent study of DA copolymer:fullerene systems, it is shown that the charge separation energetics changes unfavorably upon formation of crystalline domains

Strategy: Model Hamiltonians & Quantum Dynamics

1. electron-hole (e-h) lattice models including vibronic interactions
2. *ab initio* (typically CC2, ADC(2)), TD-DFT or semi-empirical parametrization; diabatization procedures to generate electronic couplings
3. compute spectral densities and effective-mode decomposition
4. efficient quantum dynamics using multi-configurational methods (MCTDH)

Oligothiophene-Fullerene Junctions

(collaboration with Hiroyuki Tamura (Sendai), Keith Hughes (Bangor), Rocco Martinazzo (Milano))

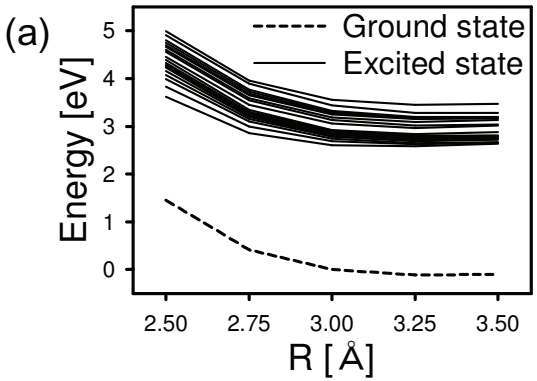


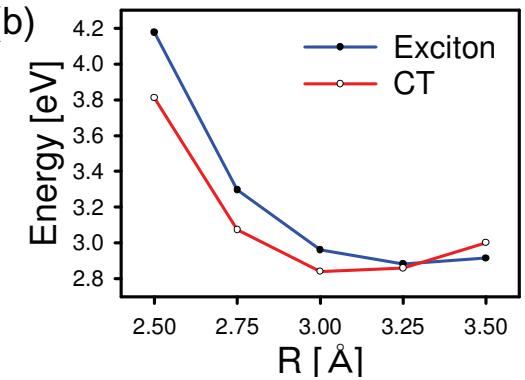
Tamura, Burghardt, Tsukada, JPCC, **115**, 10205 (2011)

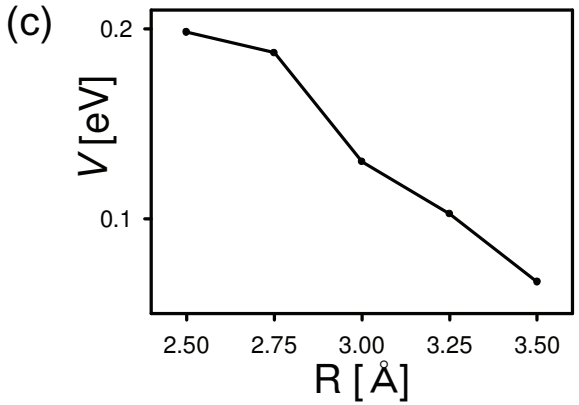
- model for polymer-fullerene heterojunctions, e.g., P3HT-PCBM [1]
- ultrafast initial charge transfer ($\sim$ 50 fs [Brabec et al., CPL (2001)])
- but subsequent generation of free charge carriers not necessarily ultrafast

[1] PCBM = phenyl-C_{61}-butyric acid methyl ester, P3HT = poly(3-hexylthiophene)

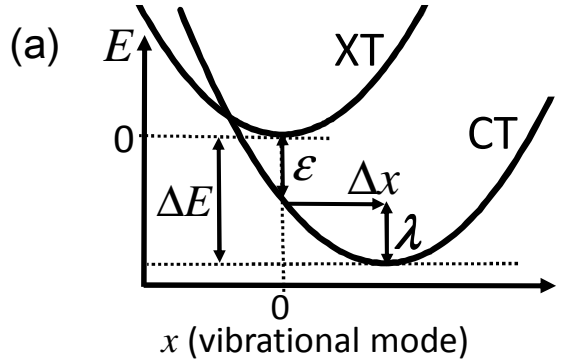
Oligothiophene-Fullerene Junction, cont'd

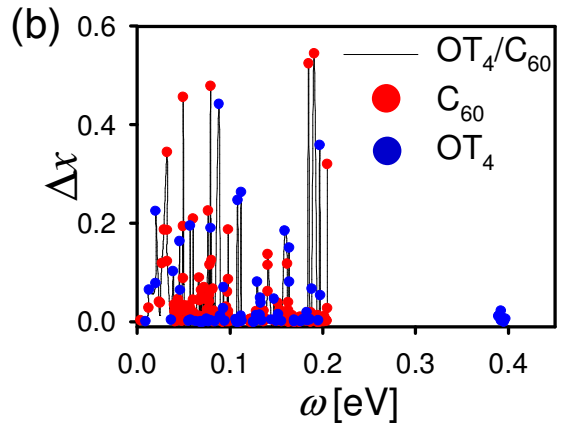






diabatic coupling:
distance dependence

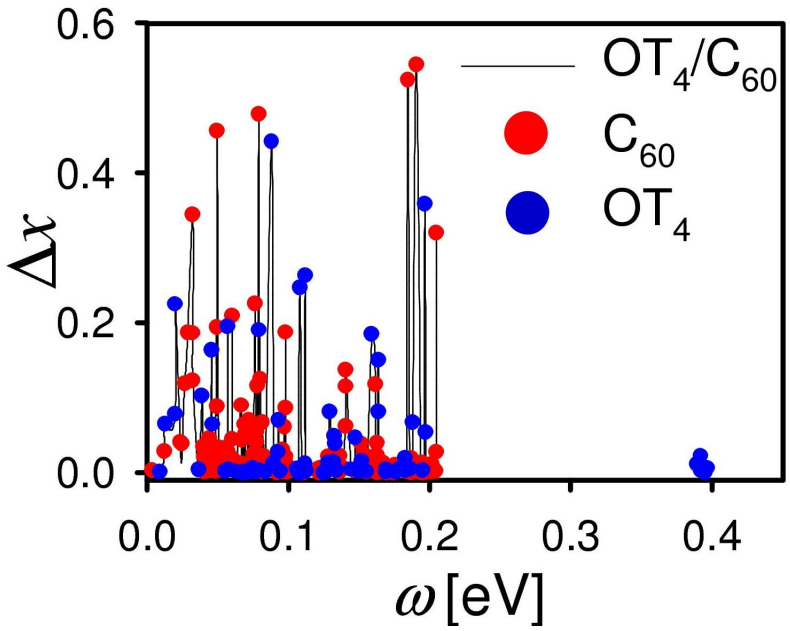


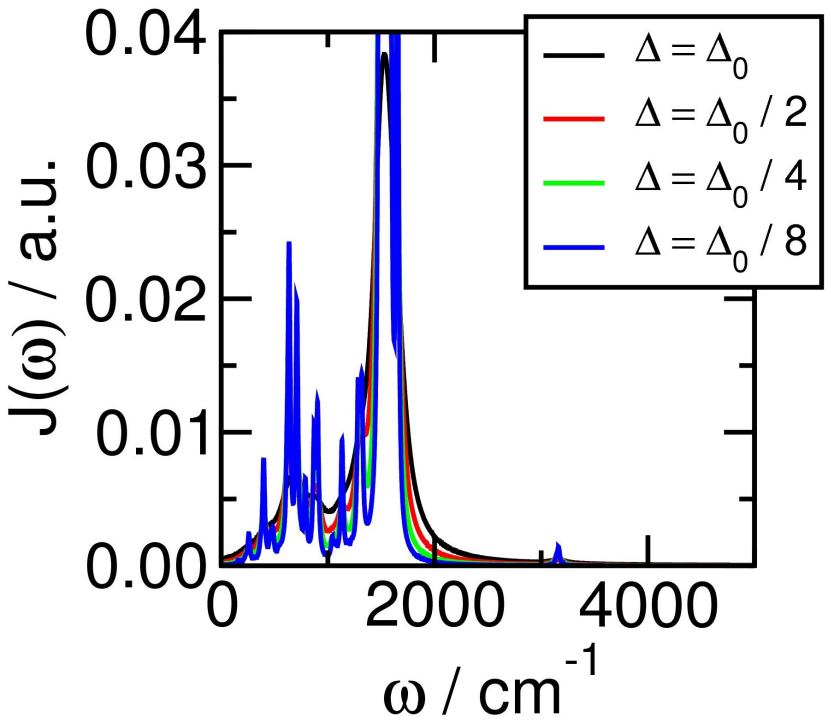


- LC-TDDFT calculations (LC = long-range corrected)
- diabatization scheme using reference functions of pure XT vs. CT character
- normal mode analysis for separate C_{60}^{-} and OT_4^{+} fragments (264 modes)

Tamura, Burghardt, Tsukada, J. Phys. Chem. C, 115, 10205 (2011)

Oligothiophene-Fullerene Junction: Spectral Density



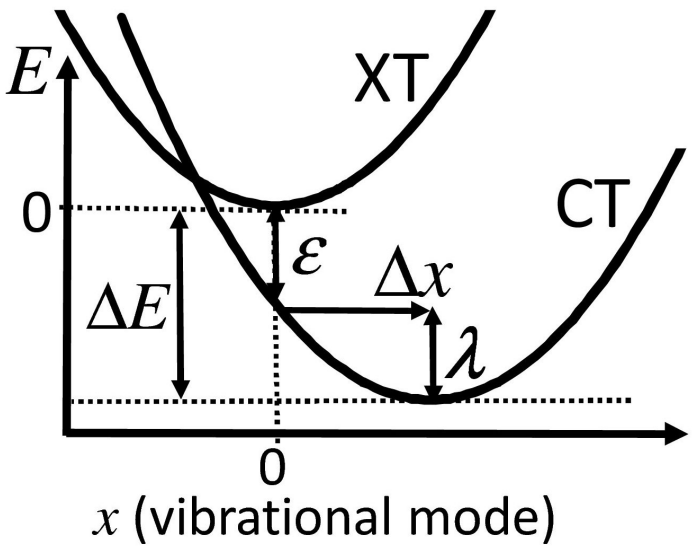


$$J(\omega) = \frac{\pi}{2} \sum_n^N \frac{c_n^2}{\omega_n} \delta(\omega - \omega_n)$$

$$J(\omega) \simeq \frac{\pi}{2} \sum_n^N \frac{c_n^2}{\pi} \frac{\Delta}{(\omega - \omega_n)^2 + \Delta^2}$$

Tamura, Martinazzo, Ruckenbauer, Burghardt, J. Chem. Phys., 137, 22A540 (2012)

Linear Vibronic Coupling (LVC) model



$$\hat{H} = \hat{H}_0 + \hat{H}_R + \hat{H}_B$$

$\hat{H}_0$: electronic part
$\hat{H}_R$: inter-fragment coordinate part
$\hat{H}_B$: phonon bath part

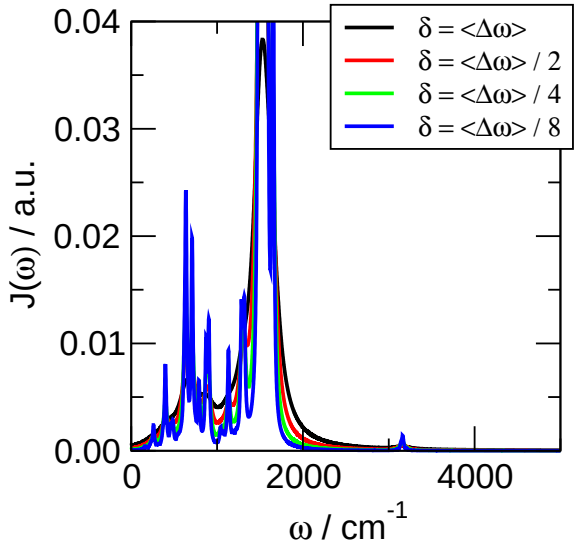
$$\hat{H}_0 = \Delta_{\mathrm{XT-CT}} |\mathrm{CT}\rangle\langle\mathrm{CT}| + \gamma\left(|\mathrm{XT}\rangle\langle\mathrm{CT}| + |\mathrm{CT}\rangle\langle\mathrm{XT}|\right)$$

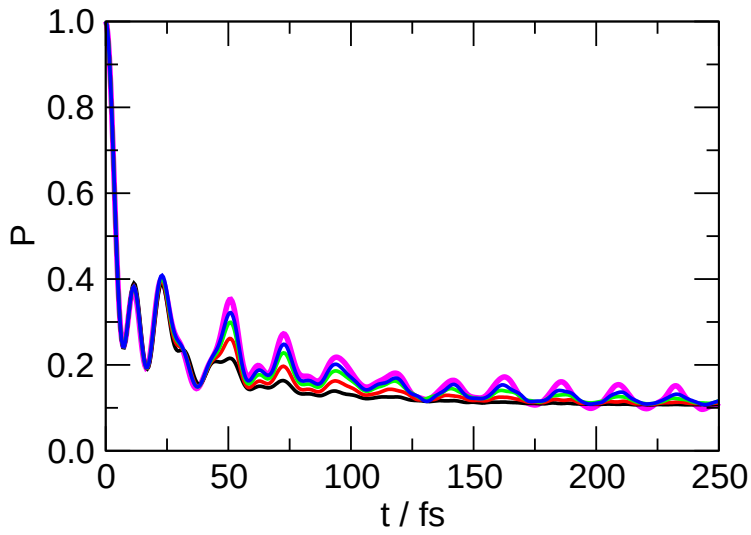
$$\begin{aligned}\hat{H}_R \quad = \quad & \frac{\omega_R}{2}(\hat{R}^2 + \hat{P}^2) + \kappa_R \hat{R}\,|\mathrm{CT}\rangle\langle\mathrm{CT}| \\ & + \gamma_R \hat{R}\left(|\mathrm{XT}\rangle\langle\mathrm{CT}| + |\mathrm{CT}\rangle\langle\mathrm{XT}|\right)\end{aligned}$$

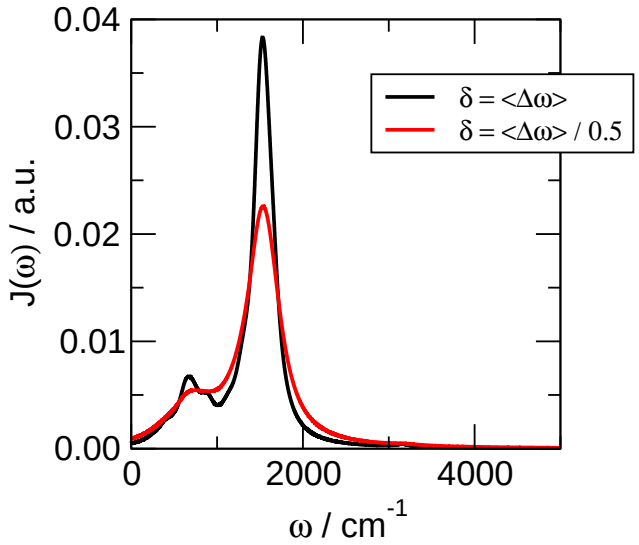
$$\hat{H}_B = \sum_{i=1}^{N} \frac{\omega_i}{2}(\hat{x}_i^2 + \hat{p}_i^2) + \sum_{i=1}^{N} \kappa_i x_i\,|\mathrm{CT}\rangle\langle\mathrm{CT}| + \sum_{i=1}^{N} \frac{\kappa_i^2}{2\omega_i}$$

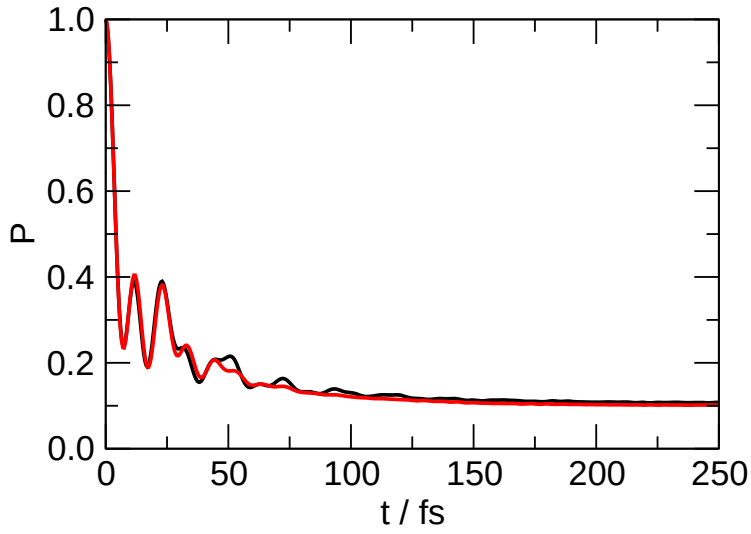
Oligothiophene-Fullerene Junction: Quantum Dynamics

spectral density





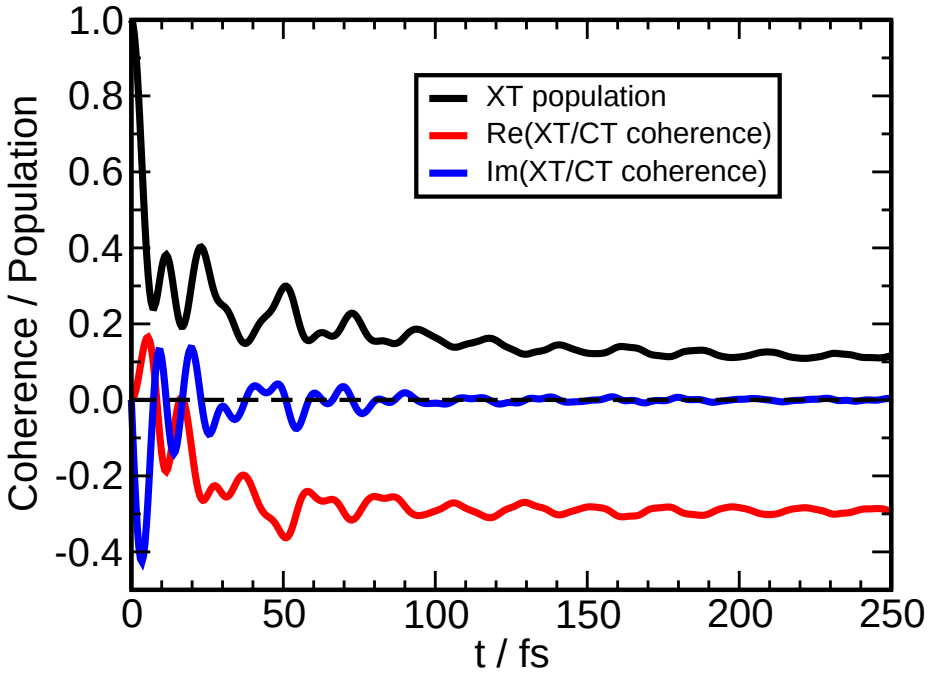


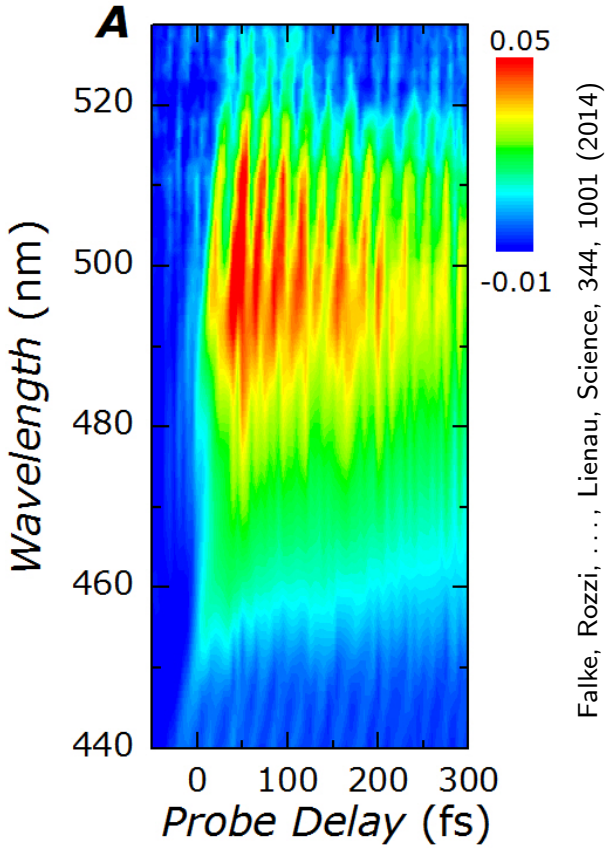


XT population

- MCTDH calculations (2 states, 61 modes); coherent features over initial 50 fs

Vibrational/Electronic/Vibronic Coherence?

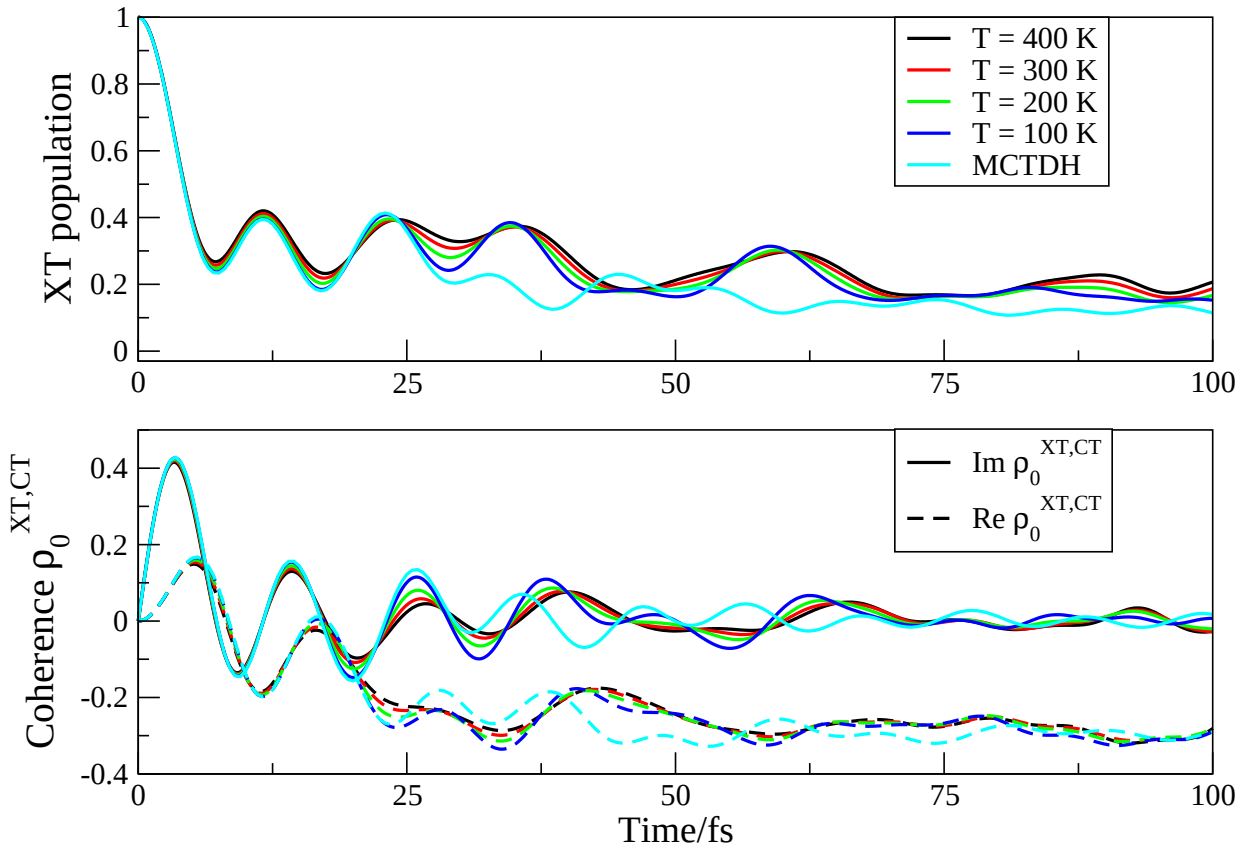




el. coherence: $\rho_{XT,CT}(t) = \mathrm{Tr}\{|\mathrm{CT}\rangle\langle\mathrm{XT}|\hat{\rho}(t)\}$

- imaginary part $(-2\gamma/\hbar)\mathrm{Im}\rho_{XT,CT}$ ⟷ population flux
- real part ⟷ stationary coherent superposition ($P_{\mathrm{XT}} \sim 0.1$, $P_{\mathrm{CT}} \sim 0.9$)
- experiment: ultrafast ET (~ 50 fs), oscillatory features [Brabec et al., CPL (2001)]) confirmed by recent pump-probe experiments by Lienau group [Science (2014)])

Temperature Dependence Not a Key Factor

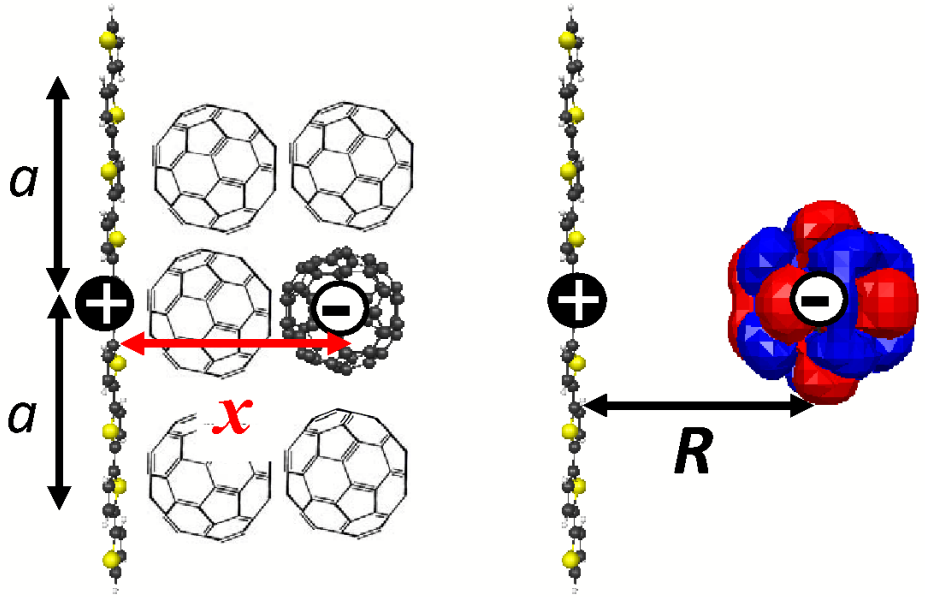


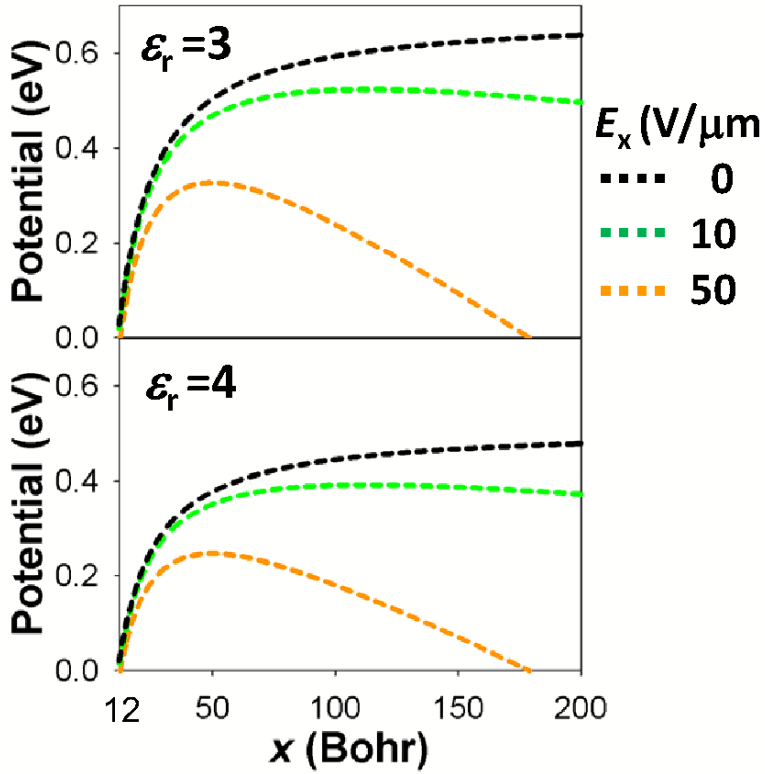
- Hierarchical Equations of Motion (HEOM) approach Tanimura, J. Phys. Soc. Jpn. **75**, 082001 (2006)
- reduced dynamics + effective mode decomposition Burghardt et al., JCP 137, 144107 (2012)
- experiments show negligible temperature dependence Pensack, Asbury, JACS 131, 15986 (2009)

Hughes, Cahier, Martinazzo, Burghardt, Chem. Phys., Femto 2013 issue, http://dx.doi.org/10.1016/j.chemphys.2014.06.015

Free Carrier Generation

(collaboration with Hiroyuki Tamura (WPI-AIMR Tohoku University))

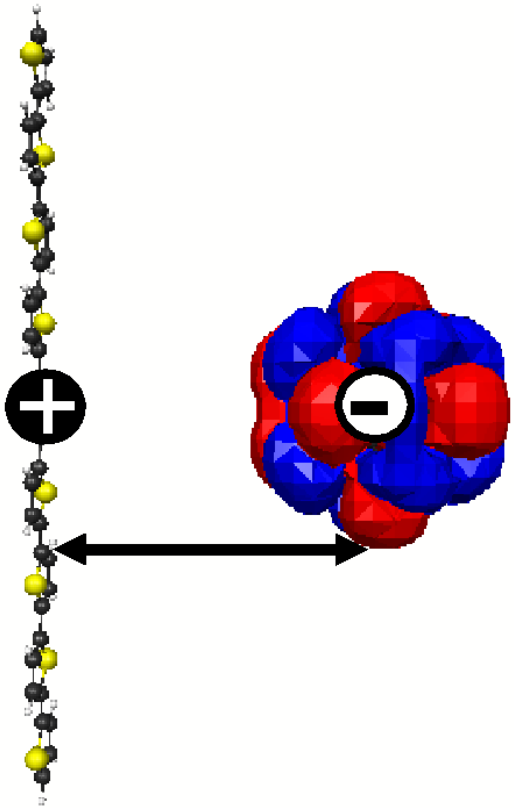




Tamura, Burghardt, JPCC, 117, 15020 (2013)

- Coulomb barrier to free carrier generation
- validity of Onsager-Braun rate model for CT break-up to be questioned
- "hot CT" hypothesis: efficient charge separation due to excess energy
- time scale of free carrier generation controversial & system-dependent (fs-μs)

Free Carrier Generation, Cont'd



- analytical e-h potential (interaction point charge/charged rod):

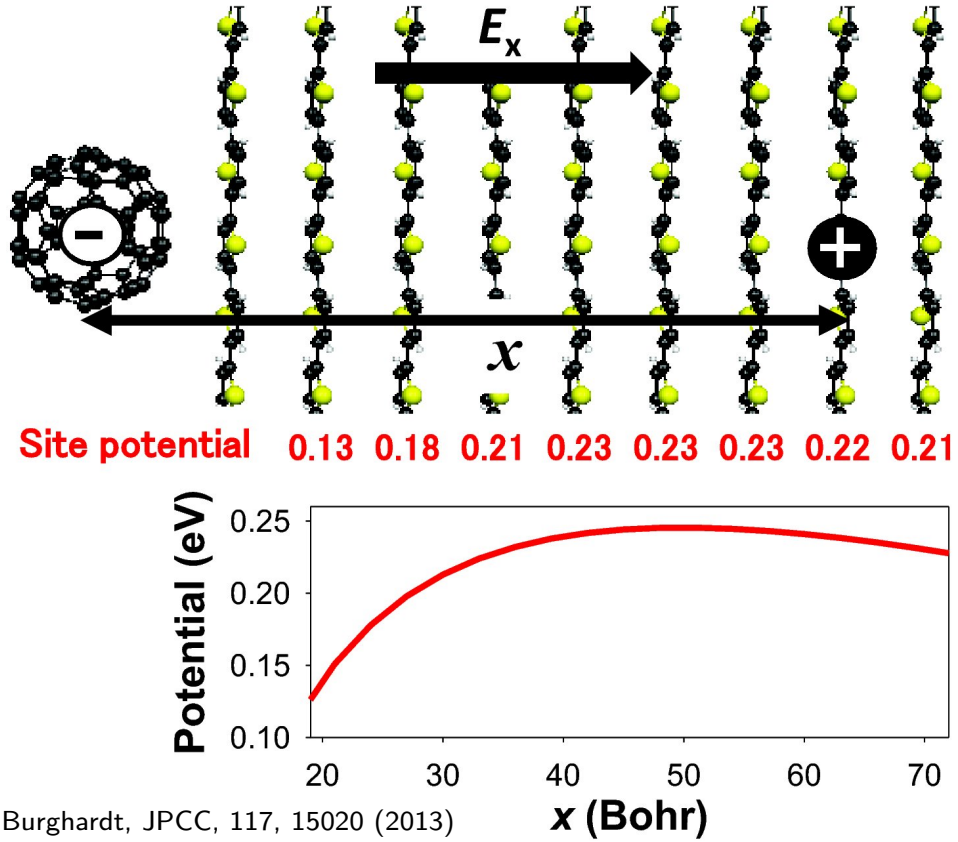
$$\phi(x) = -(1/(\varepsilon_r a))[\ln(a + \sqrt{a^2 + x^2}) - \ln x] - E_x x$$

Tamura, Burghardt, J. Phys. Chem. C, 117, 15020 (2013)

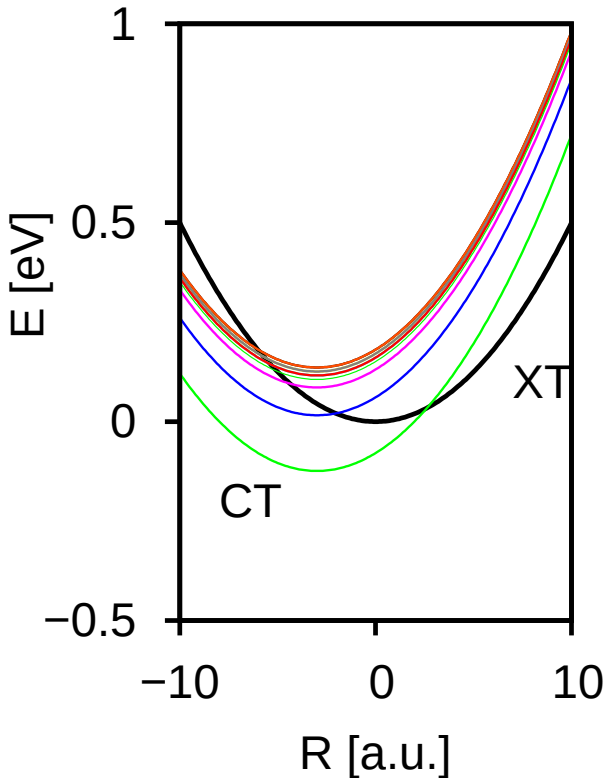
- Coulomb potential becomes shallower as the conjugation length (a) increases
- connection to analysis by Deibel/Dyakonov:[2] conjugated chain segments favor charge separation
- barrier height $\sim$ 0.5 eV ($E_x = 10$ V/μm), $\sim$ 0.3 eV ($E_x = 50$ V/μm)
- additional effect: barrier height also decreases as a function of fullerene aggregation

[2] Deibel et al., PRL 103, 036402 (2009) *"Origin of the Efficient Polaron-Pair Dissociation in Polymer-Fullerene Blends"*

Free Carrier Generation, cont'd



Tamura, Burghardt, JPCC, 117, 15020 (2013)



- lamellar stacking (regio-regular structure)
- Coulomb barrier determines on-site energy of charge separated (CS) states
- excess energy favors e-h separation; depends on initial state

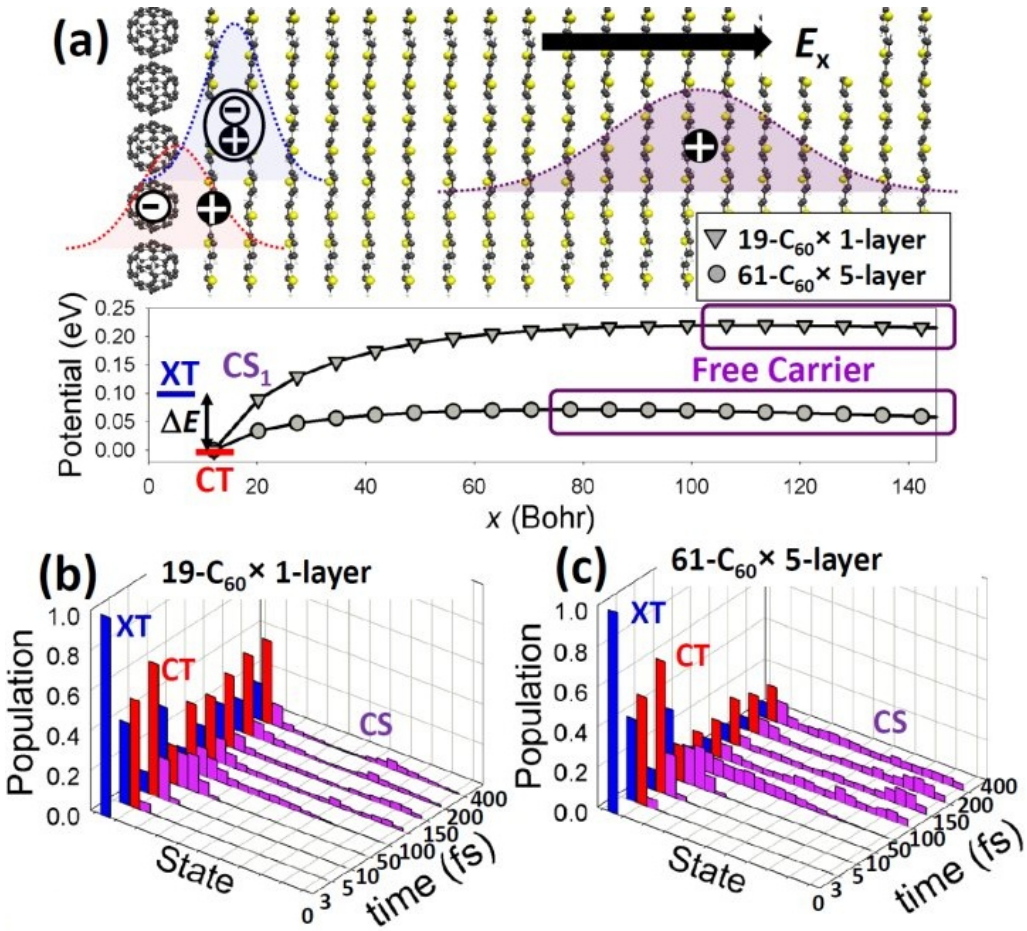
Dynamics of Free Carrier Generation

$$\hat{H} = \hat{H}_{\text{XT-CT}}(\mathbf{x}) + \sum_n \hat{H}^{(n)}_{\text{CS}}(\mathbf{x})|\text{CS}_n\rangle\langle\text{CS}_n| + t(\mathbf{x})(|\text{CS}_1\rangle\langle\text{CT}| + \sum_{nn'}|\text{CS}_n\rangle\langle\text{CS}_{n'}| + h.c.)$$

- extended XT/CT/CS Hamiltonian
- MCTDH calculations
  (20 states, 110 modes)
- transfer integrals: $t \sim 0.1$ eV

factors favoring ultrafast e-h separation:

- exciton (XT) excess energy:
  "Hot CT" mechanism
- XT delocalization in H-aggregate donor
- hole delocalization due to oligomer
  (thiophene) conjugation
- electron delocalization over fullerene
  aggregates: strong decrease of barrier



Tamura, Burghardt, JACS (Communication) 135, 16364 (2013)

Electron Delocalization in Ordered Fullerene Domains is Crucial

- significant reduction of barrier height as a function of fullerene aggregation
- in agreement with recent experiments:

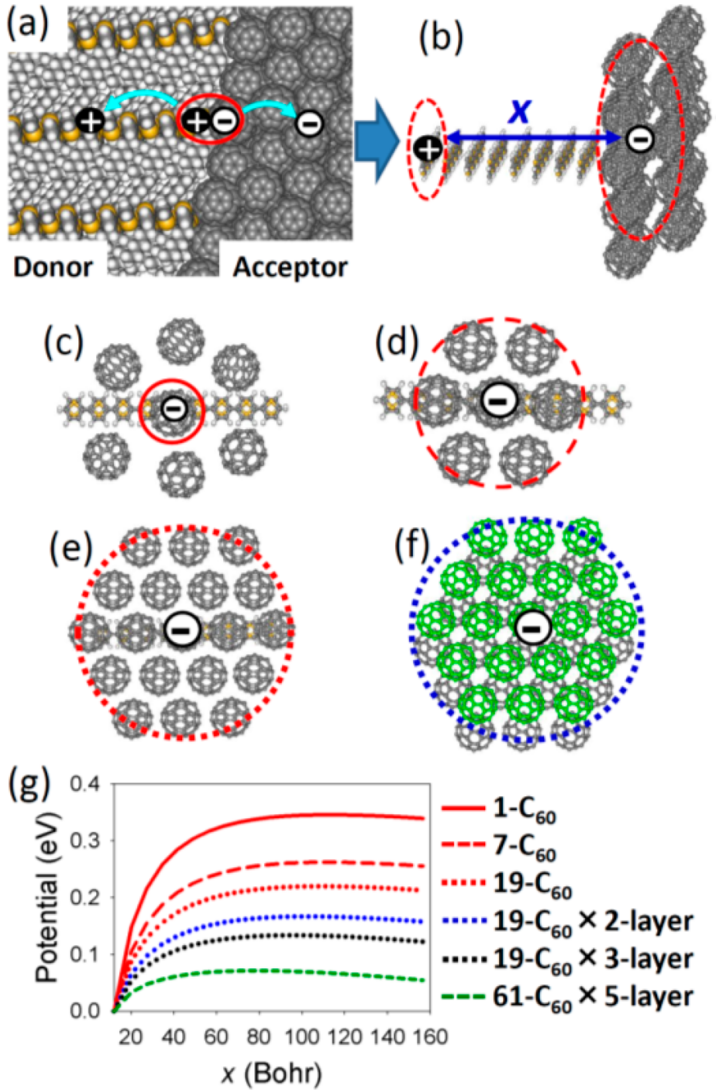
  Gélinas et al., Science*express* 10.1126/science.1246249

  Electro-Absorption (EA) experiments detect charge separated species

  EA signal only observed for high fullerene loading, e.g., 1:4 D/A mixture, not for 4:1 mixture$^{(*)}$

  ultrafast charge separation of $\sim$5 nm, impeding recombination

$^{(*)}$However, both blends exhibit $<$ 100 fs XT quenching

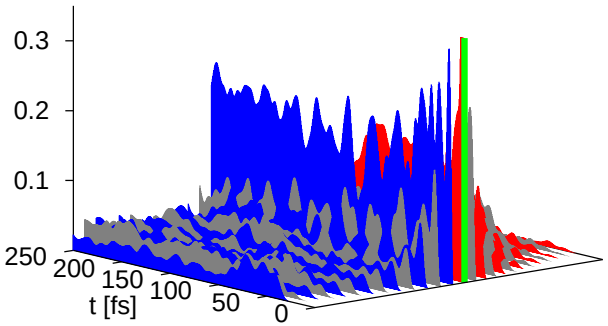


Tamura, Burghardt, JACS (Communication) 135, 16364 (2013)

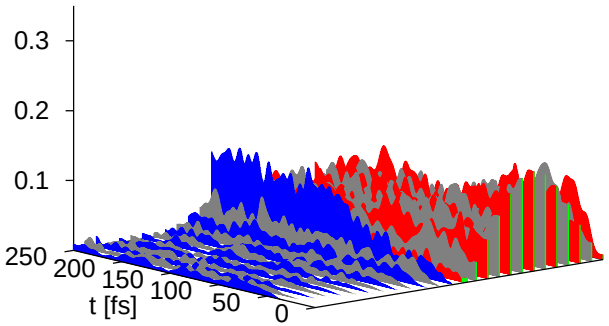
Role of Exciton Delocalization

$$\hat{H} = \hat{H}_{\mathrm{XT_1\text{-}CT}}(\mathbf{x}) + \sum_n \hat{H}^{(n)}_{\mathrm{CS}}(\mathbf{x})|\mathrm{CS}_n\rangle\langle\mathrm{CS}_n| + t(\mathbf{x})(|\mathrm{CS}_1\rangle\langle\mathrm{CT}| + \sum_{nn'}|\mathrm{CS}_n\rangle\langle\mathrm{CS}_{n'}| + h.c.)$$
$$+ \sum_n \hat{H}^{(n)}_{\mathrm{XT}}(\mathbf{x})|\mathrm{XT}_n\rangle\langle\mathrm{XT}_n| + j(\mathbf{x})\sum_{nn'}(|\mathrm{XT}_n\rangle\langle\mathrm{XT}_{n'}| + h.c.)$$

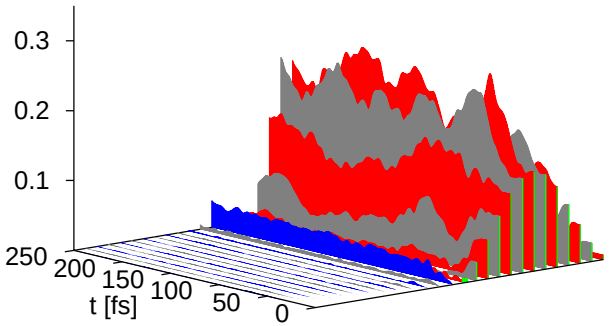
CT/CS states: blue/grey, XT: red/grey



(1) localized initial exciton



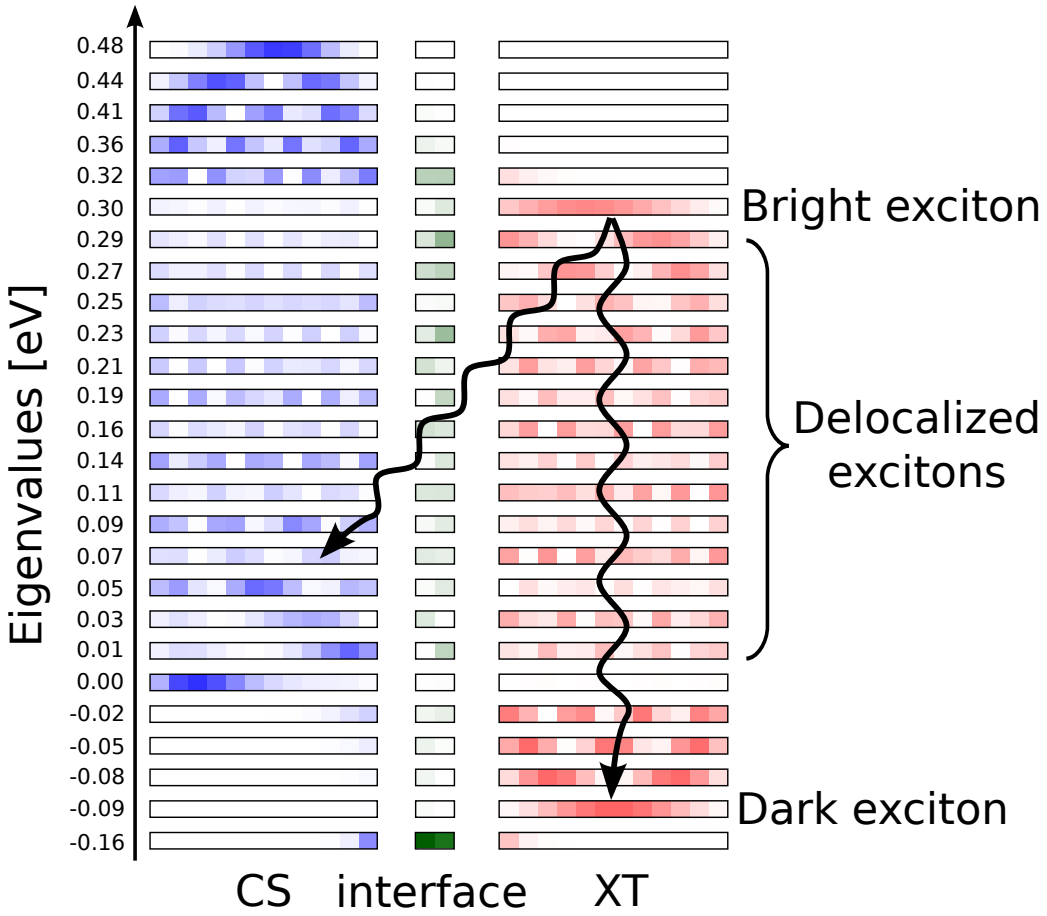
(2) bright initial exciton

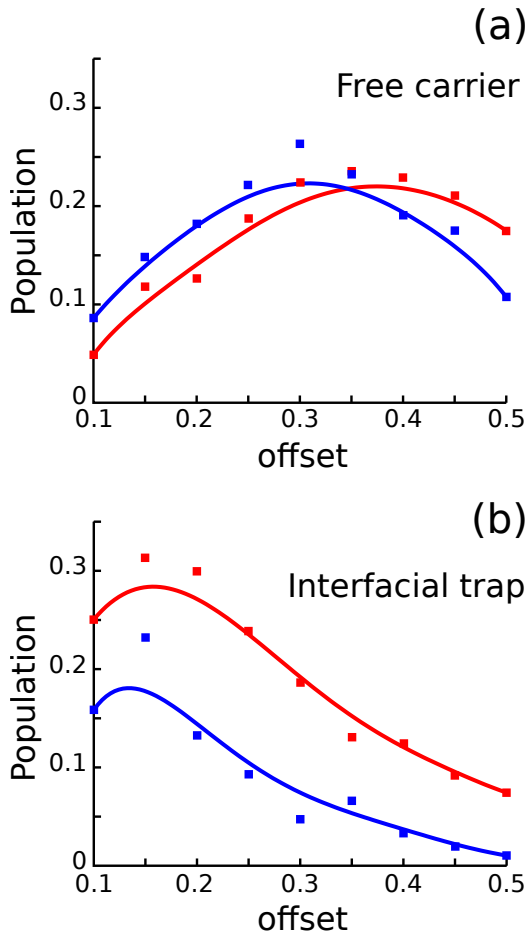


(3) dark initial exciton

- CT/CS generation depends on exciton (de)localization
- H aggregate (here, oligothiophene): upper exciton state is bright
- localized initial condition permits efficient transfer
- bright XT can decay to dark XT, which is in turn ineffective at charge transfer

Electronic Eigenstate Picture





- interplay of delocalization, internal conversion, and charge transfer
- optimal XT/CS_1 offset to maximize free carrier yield

Huix-Rotllant, Tamura, Burghardt, J. Phys. Chem. Lett., submitted.

"Quantum coherence controls the charge separation in a prototypical organic photovoltaic system"

Lienau and collaborators (Science, 2014)

- electronic and spatial coherence play an essential role:
  - dynamics of spatially delocalized vibronic wavepackets
  - delocalized superposition states (excitons and charge separated states)

  These effects determine the efficiency of the primary, ultrafast processes.

- however, various loss factors can arise on longer time scales:
  - e-h recombination
  - charge carrier trapping

  These effects can be captured by kinetic equations.

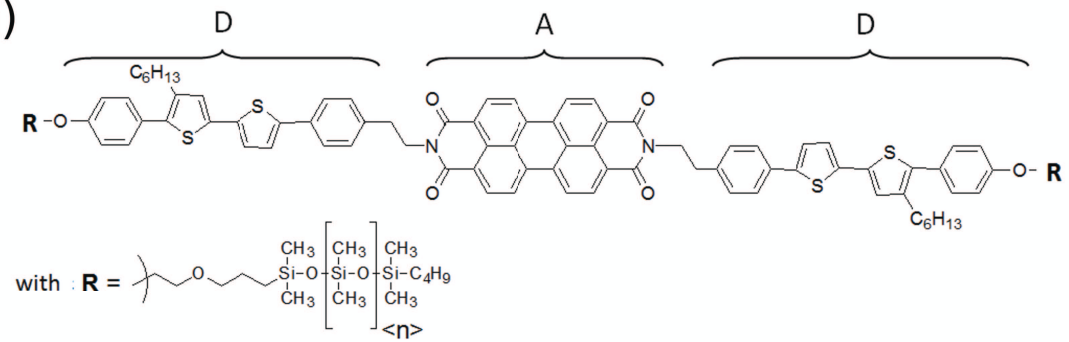
- Note:
  - nanoscale order can be decisive for energy/charge transfer events
  - ultrafast charge separation does not always entail overall efficiency!

Highly Ordered DA Assemblies: Controlled Nano-Morphology

- novel donor-acceptor systems: triads organized in smectic films (Méry, Haacke, Strasbourg)

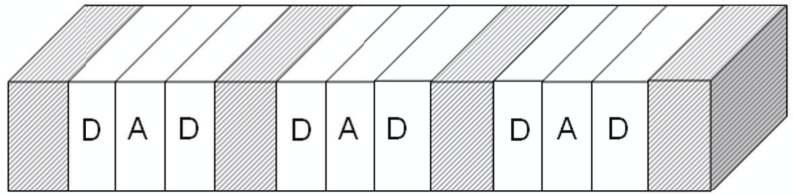
  (Collaboration Haacke (Strasbourg), Dreuw (Heidelberg))
  J. Wenzel, A. Dreuw, I. Burghardt, PCCP 15, 11704 (2013)

a)



- possibly higher efficiency than standard BHJ architectures: eliminate exciton diffusion step
- overcome recombination problem?

b)

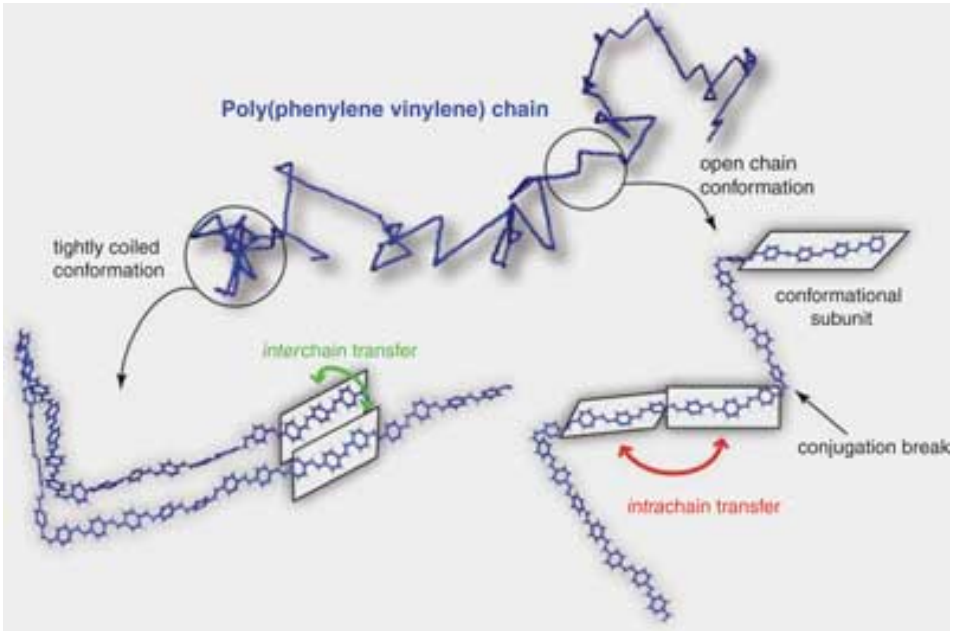


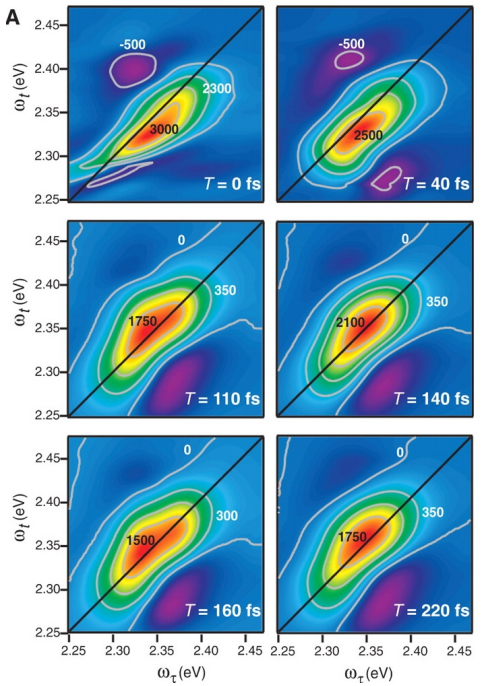
S. Haacke and collaborators, PCCP, 14, 273 (2012)

- competing ultrafast energy and charge transfer processes
- pronounced influence of stacking interactions
- environmental effects (e.g., amorphous vs. liquid crystalline phases)

Topics

EET in Organic Semiconducting Polymers

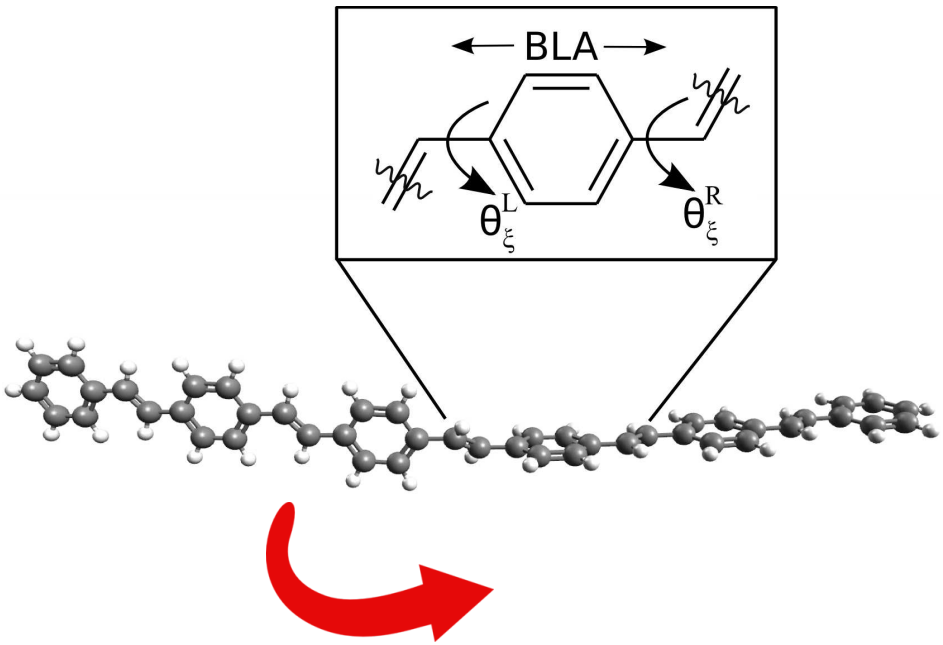




Collini, Scholes, Science 323, 369 (2009)

∼0.1-1 ps: coherent intra-chain excitation energy transfer (EET) dynamics
∼0.1-1 ps: self-trapped exciton-polaron states
∼0.1-few ps: torsional geometry relaxation interfering with EET
∼1-10 ps: inter-chain EET
∼ps-ns: thermally assisted hopping

How do Excitons Migrate across a Torsional Defect (Kink)?



- full quantum dynamical study for minimal oligomer model
- MCTDH (up to 36 states, 22 vibrational modes)
- monomer-based diabatic Hamiltonian
- *ab initio* based parametrization

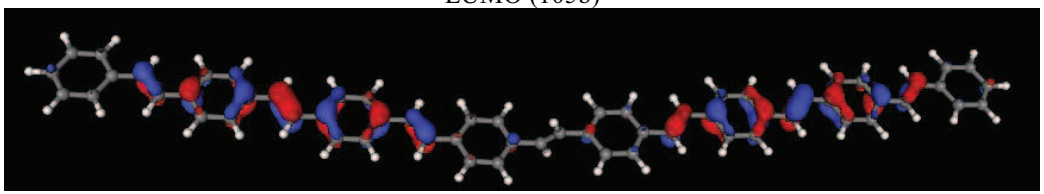
Binder, Wahl, Römer, Burghardt,
Faraday Discuss 163, 205 (2013)
Panda, Plasser, Aquino, Burghardt, Lischka
J. Phys. Chem. A, 117, 2181 (2013)

- Is a Frenkel exciton model ($|\Psi_{\text{exciton}}\rangle = \sum_n^{n_{\text{exc}}} c_n |\Phi_n\rangle$) sufficient?
- Is the transfer dynamics on ultrafast time scales coherent or of hopping type?
- What is the role of electron-phonon coupling?
- Is a trapped exciton-polaron generated and if so, on which time scale?

Electronic Structure of Oligomers (OPV's)

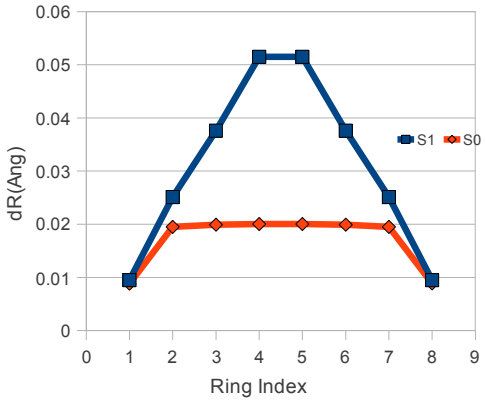
(Collaboration Lischka group (Texas Tech))

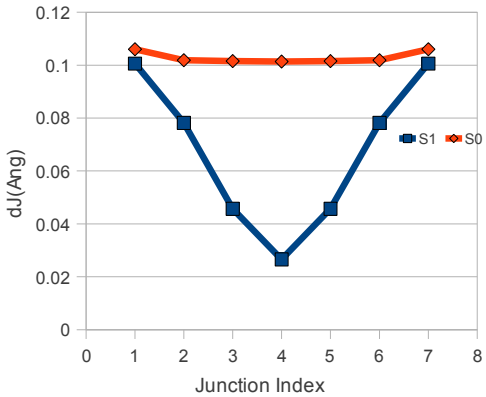
LUMO (105b)

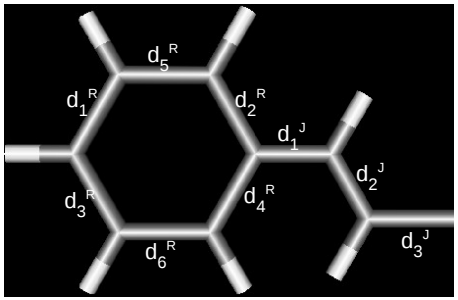


HOMO (106a)

- high-level electronic structure methods (ADC, CC2, MRCI)
- exciton trapping, due to BLA modes, described correctly





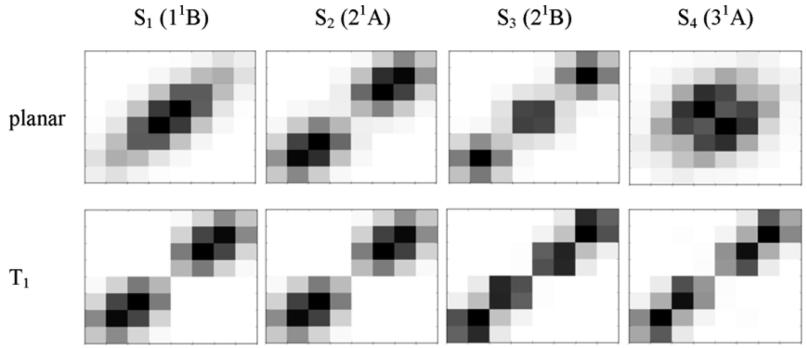


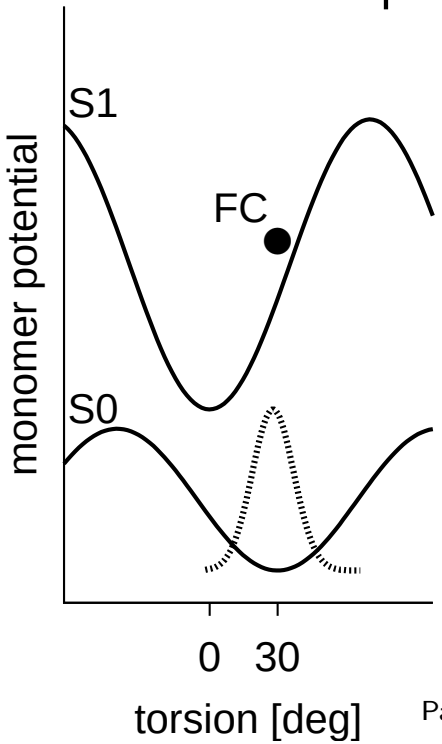
Panda, Plasser, Aquino, Burghardt, Lischka, JPCA, 117, 2181 (2013), see also: Sterpone, Rossky, JPCB 112, 4983 (2008), Nayyar et al., JPCL 2, 566 (2011)

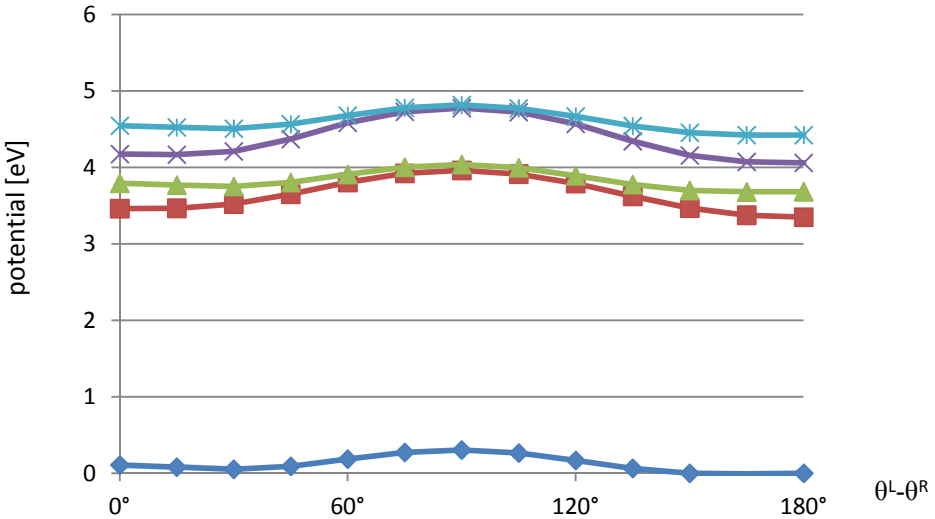
Electronic Structure of Oligomers (OPVs)

Collaboration with Lischka group (Texas Tech)

- *ab initio* ADC(2) calculations
- transition densities reveal that excitons are *not* of pure Frenkel type: full e-h picture more accurate
- torsional and BLA profiles (OPV-8)

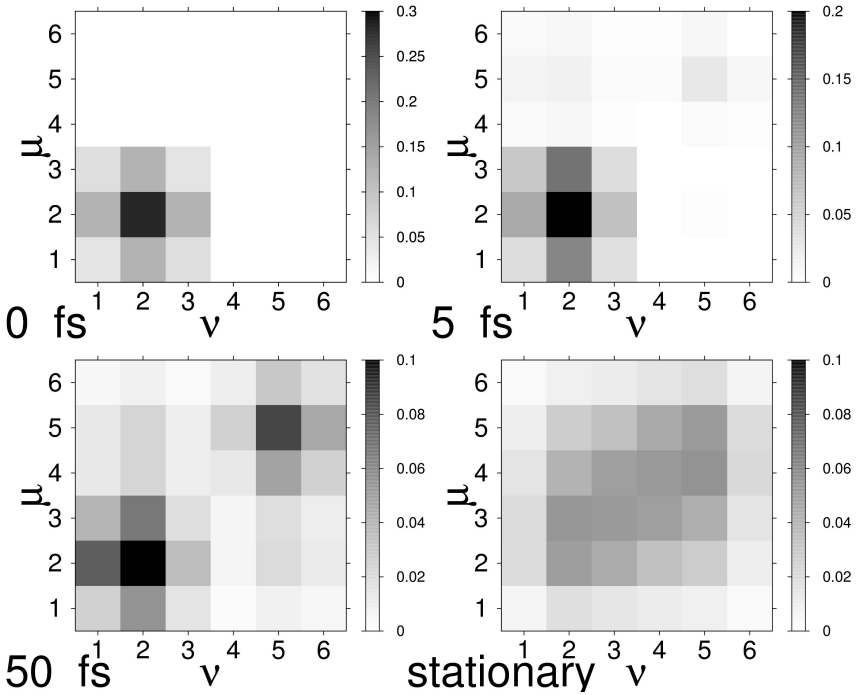


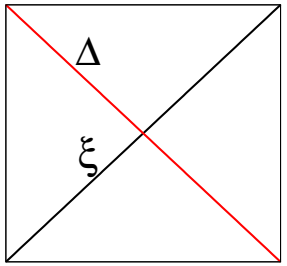




Panda, Plasser, Aquino, Burghardt, Lischka, J. Phys. Chem. A, 117, 2181 (2013)

Full *e*-*h* Dynamics (Merrifield Hamiltonian)





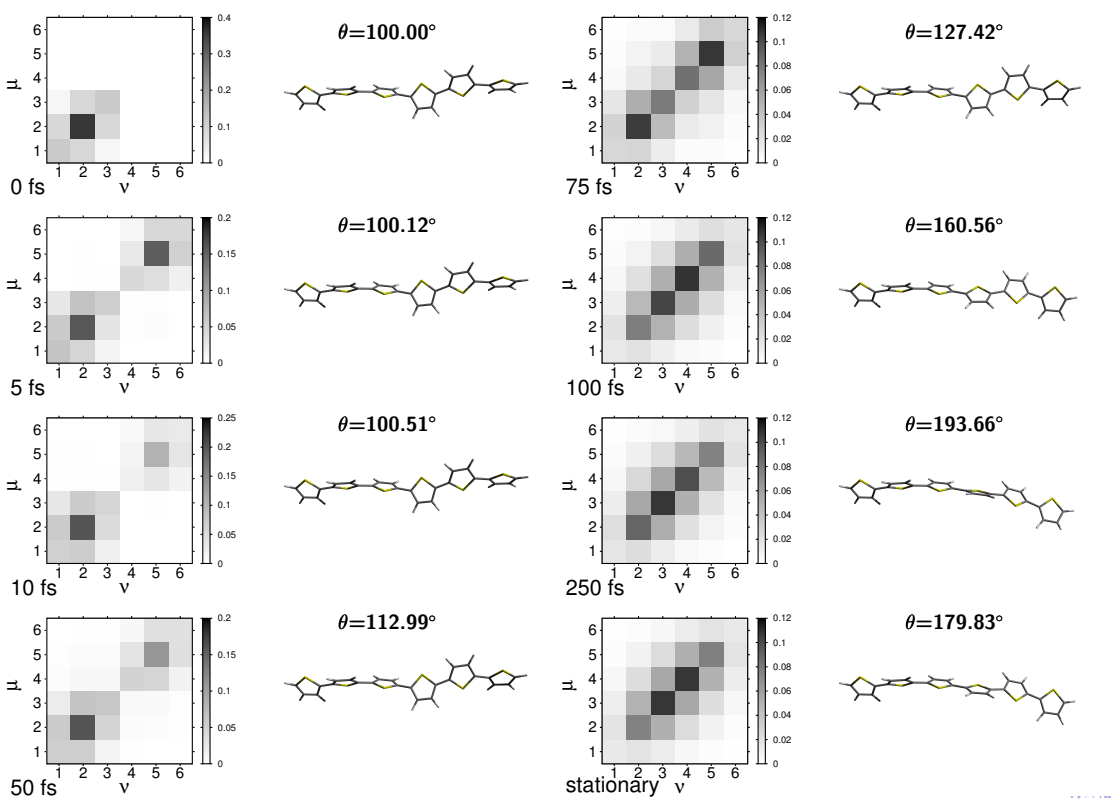
$\xi = (\nu + \mu)/2$: center-of-mass coordinate
$\Delta = (\nu - \mu)$: *e*-*h* distance coordinate

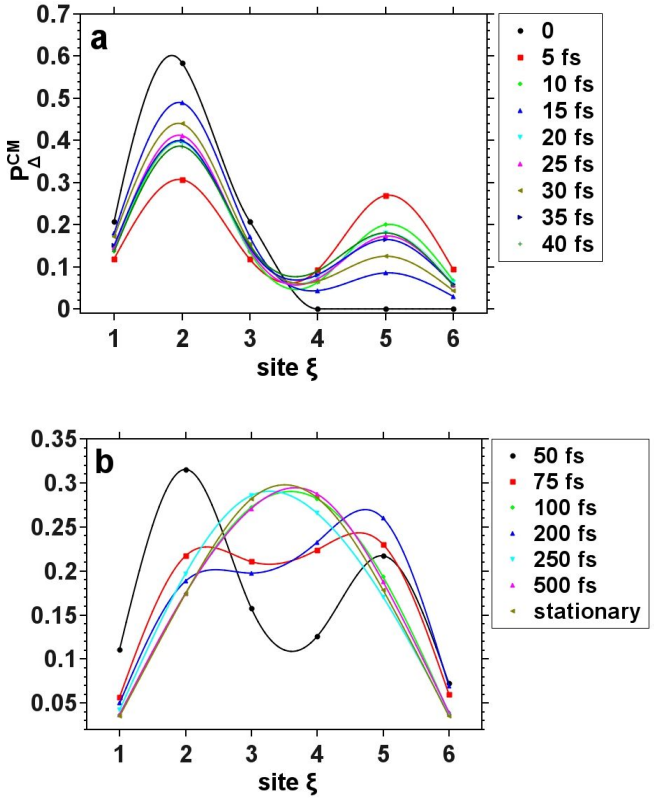
diagonal width: "delocalization length"
off-diagonal width: "coherence size"

- electron-hole dynamics: $\hat{H} = \sum_{\nu\mu} \sum_{\nu'\mu'} H_{\nu\mu,\nu'\mu'} |\nu\mu\rangle\langle\nu'\mu'|$
- MCTDH calculations for minimal lattice (6^2 states, 15 modes)
- matches electronic structure analysis in terms of transition densities
- local exciton ground state = LEGS reached (cf. Tozer, Barford, JPCA 116, 10310 (2012))
- transients involving large *e*-*h* separations

Binder, Wahl, Römer, Burghardt, Faraday Discuss. 163, 205 (2013), Wahl, Binder, Burghardt, Comp. Theor. Chem. 1040, 167 (2014)

LEGS Formation on a Minimal Lattice

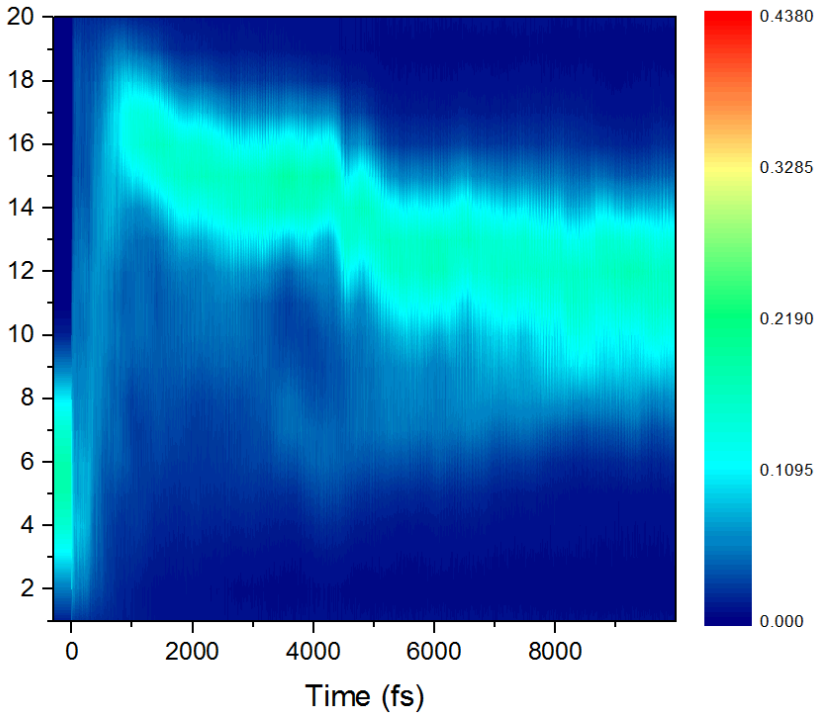




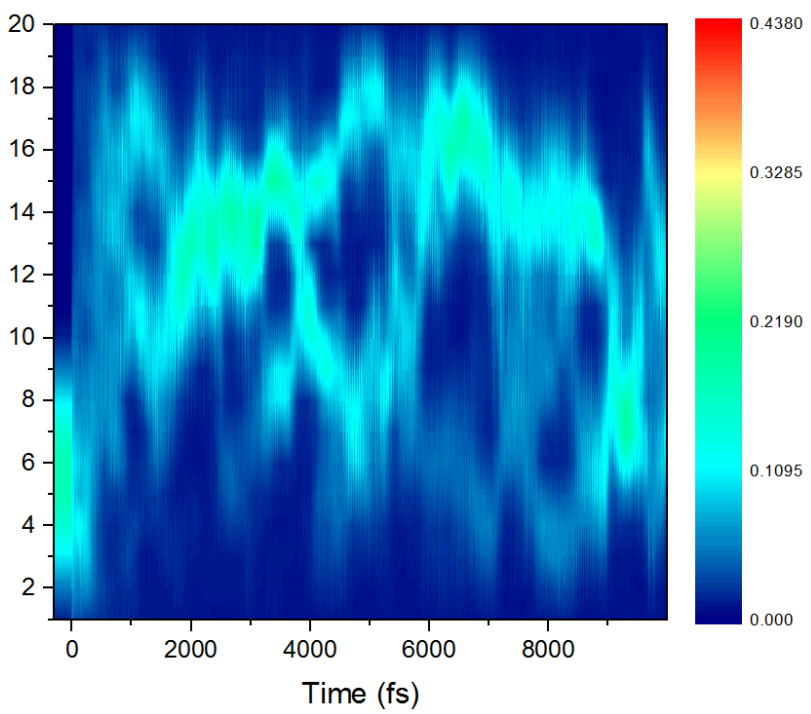
- fastest time scale: oscillatory transients
- stationary exciton-polaron $\sim$ 250 fs (same time scale as torsional relaxation)
- irreversible LEGS (exciton-polaron) formation through decoherence/relaxation *via* electron-phonon coupling on a finite lattice, cf. Pouthier, JCP 137, 114702 (2012)

Exciton Migration – Ehrenfest Dynamics

10 K



100 K



- mean-field Ehrenfest Dynamics (40 Frenkel states, 40 torsions/BLA's)
- trapped state at low temperatures
- at increasing temperatures, fluctuations start driving exciton migration
- similar observations by Barford & co Tozer, Barford, JPCA 116, 10310 (2012)

Summary

1. On the Way to Quantum Dynamics for Extended Systems
   - combine model Hamiltonians & electronic structure information
   - alternative/complementary to QM/MM + on-the-fly approaches
   - ongoing work: systematic inclusion of static disorder

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   - ultrafast ($\sim$ 50-100 fs), coherent initial charge separation
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Where Do We Stand? – Tentative Answers . . .

- *Is "quantum-driven" functionality a robust feature, or rather an accidental occurrence?*

  It's a robust feature, assuming that the molecular system is prepared (e.g., by photoexcitation) in such a way that quantum effects determine the system's nonequlibrium response, at least on short time scales.

- *To what extent does quantum entanglement "scale up" into these systems that are at the border between the microscopic and macroscopic world?*

  Entanglement is limited by decoherence effects; however, in highly ordered systems, collective excitations and entanglement can extend over many subunits.

- *Do specific environments act so as to protect low-dimensional subsystems from decoherence?*

  Yes, biological and material systems typically exhibit specific environments – these act in a non-Markovian fashion and could protect subsystems from decoherence.

- *To what extent can effective descriptions of these systems be found?*

  Effective descriptions relating to model Hamiltonians combined with realistic spectral densities are useful to some extent. Beyond these, the full complexity of the system can be explored in atomistic *on-the-fly* calculations (E. Pollak).

Acknowledgments & Collaborations

Group Frankfurt:

- M. Biswas
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- P. Eisenbrandt
- M. Polkehn
- M. Huix-Rotllant

Former members:

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- M. Ruckenbauer
- J. Ortiz-Sánchez

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- F. Plasser (Heidelberg, Germany)
- J. Wenzel, A. Dreuw (Heidelberg, Germany)
- S. Haacke, S. Méry (Strasbourg, France)
- F. Sterpone (IBPC, Paris)
- E. R. Bittner (Houston University, USA)
- L. S. Cederbaum (Heidelberg, Germany)
- A. Panda (IIT Guwahati, India)
- D. Beljonne (Université de Mons, Belgium)

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Theoretical Chemistry
of Complex Systems

AK Burghardt

How Fast is Decoherence?

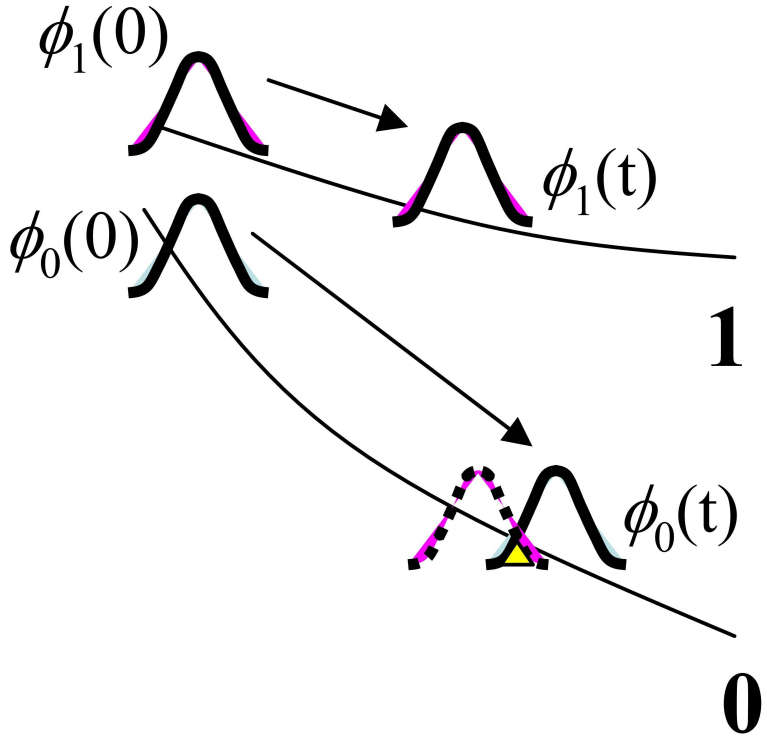
$$|\psi(t)\rangle = c_0(t)|0\rangle|\phi_0(t)\rangle + c_1(t)|1\rangle|\phi_1(t)\rangle$$

electronic coherence:

$$\rho_{01}(t) = \mathrm{Tr}[|0\rangle\langle 1|\hat{\rho}(t)]$$
$$= \langle 1|\hat{\rho}(t)|0\rangle = c_1^*(t)c_0(t)\langle\phi_1(t)|\phi_0(t)\rangle$$

- coherence $\propto$ overlap of nuclear wavefunctions
- typical decoherence times: ~ 30 fs (estimate from $\tau_{\mathrm{dec}} \sim \tau_g(6k_BT/\lambda)^{1/2}$ or $\tau_{\mathrm{dec}} \sim \gamma^{-1}(\lambda_T/\Delta x)^2$)

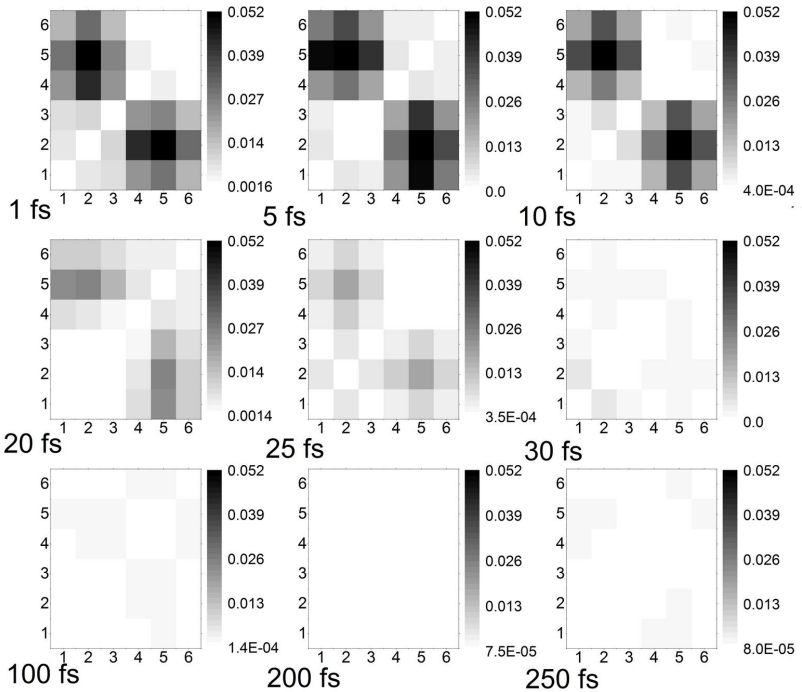
  Prezdho, Rossky, PRL 81, 5294 (1998)
- loss of coherence *not* captured by classical trajectory picture



picture: P. Rossky et al.

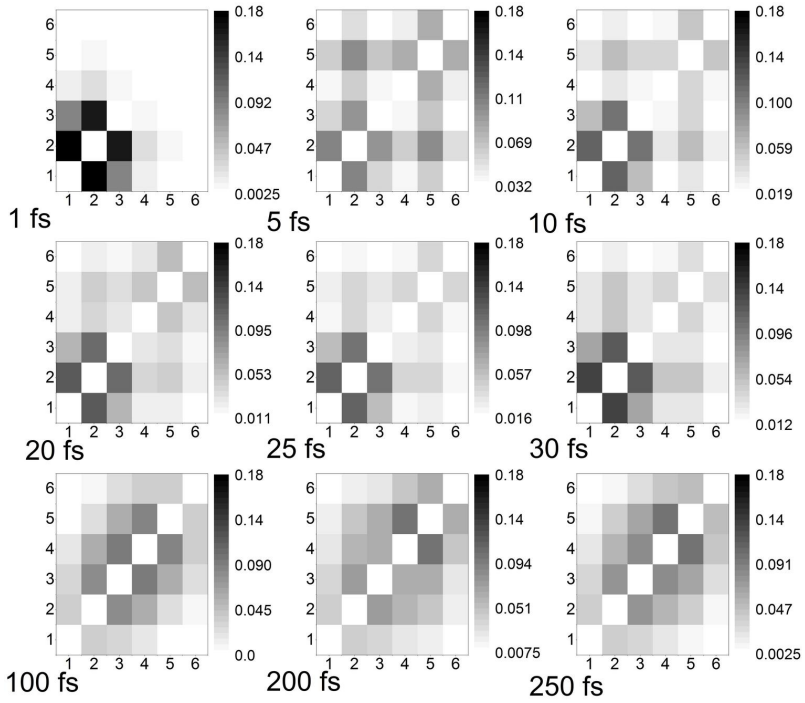
Coherence Evolution

$$\mathrm{Im}\rho_{\nu\nu,\mu\mu}(t) = \mathrm{Im}\,\mathrm{Tr}\{|\nu\nu\rangle\langle\mu\mu|\hat{\rho}(t)\}$$



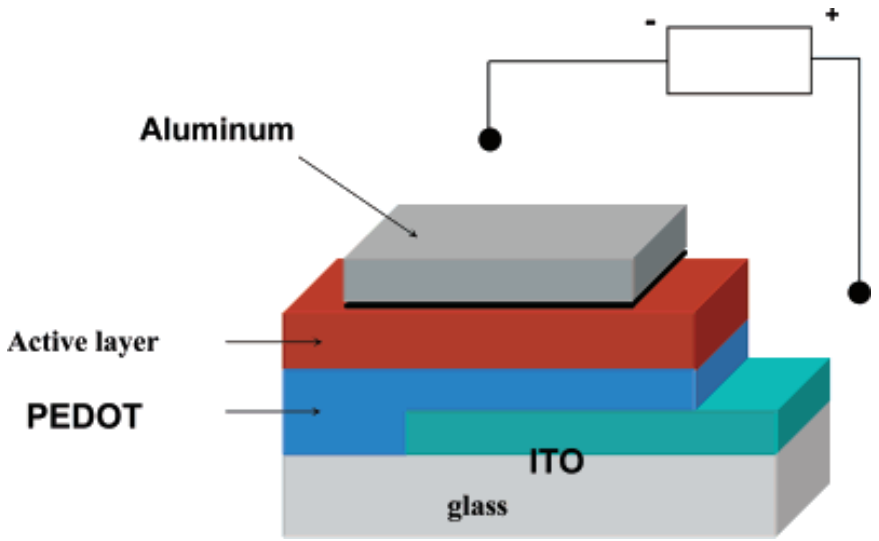
- Imaginary part ◄► population flux
- ultrafast decay time (∼50 fs)

$$\mathrm{Re}\rho_{\nu\nu,\mu\mu}(t) = \mathrm{Re}\,\mathrm{Tr}\{|\nu\nu\rangle\langle\mu\mu|\hat{\rho}(t)\}$$



- Real part ◄► stationary superposition
- reaches stationary LEGS coherence

New Materials for Optoelectronics



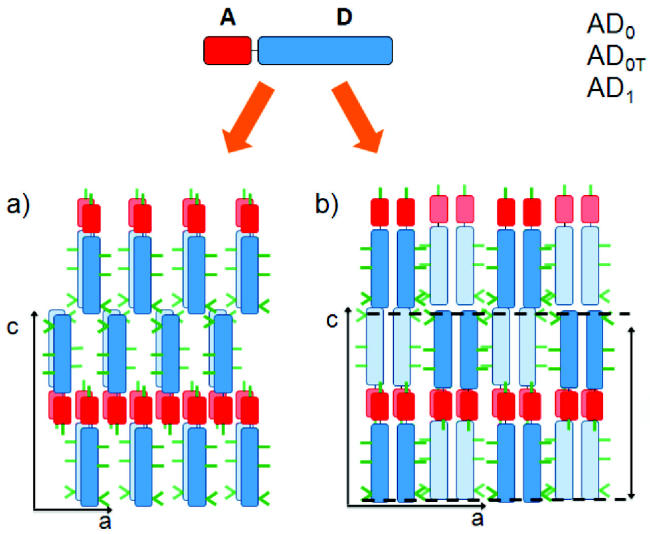
Gunes et al., Chem. Rev. **107**, 1324 (2007)

OLED ↓

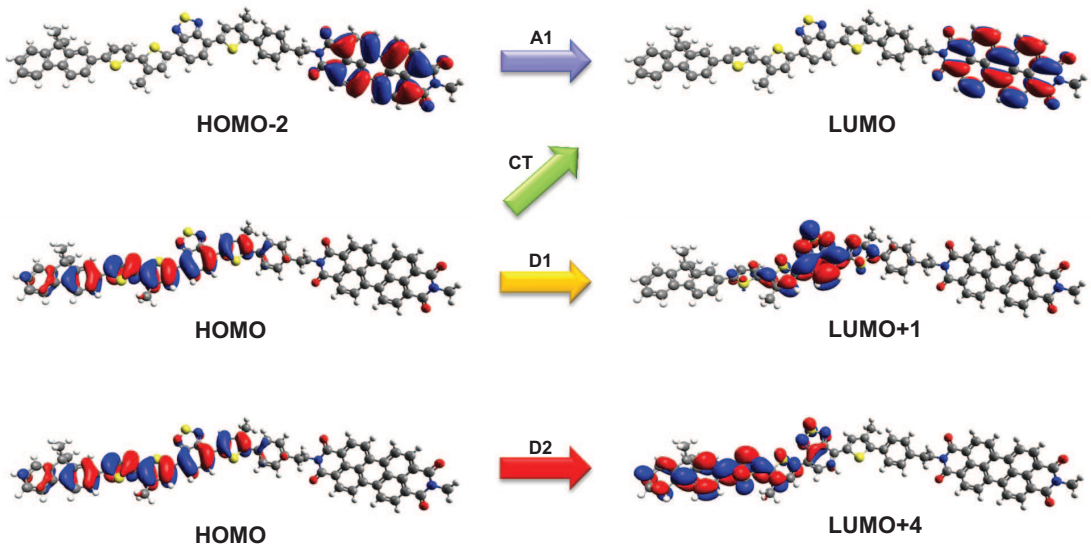
charge injection
charge transport
recombination → excitons
radiative decay of excitons

↑ photovoltaic element

New Generation of Dyads/Triads



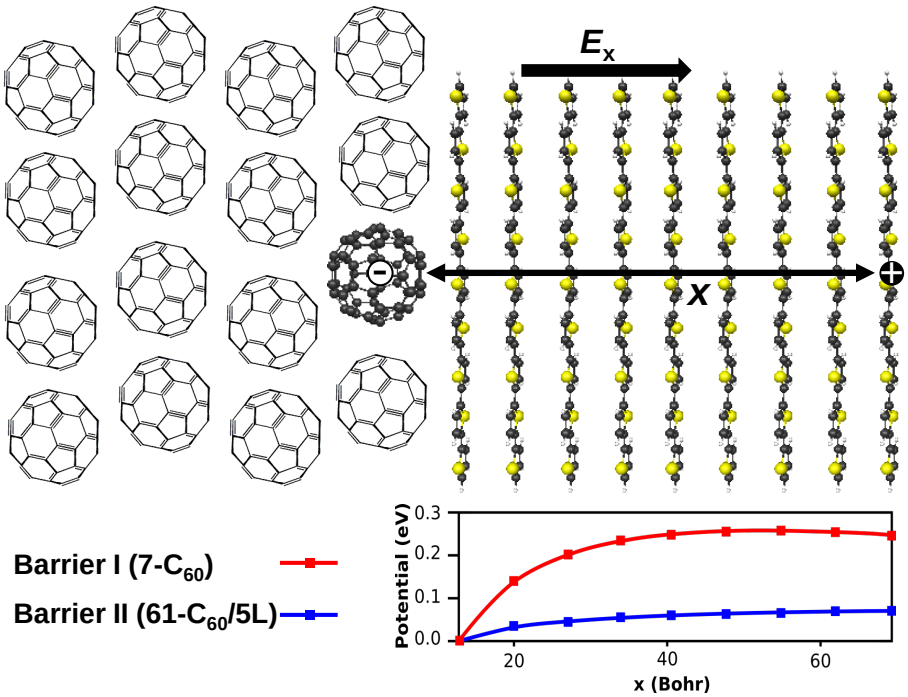
Schwartz et al., JACS 136, 5981 (2014)

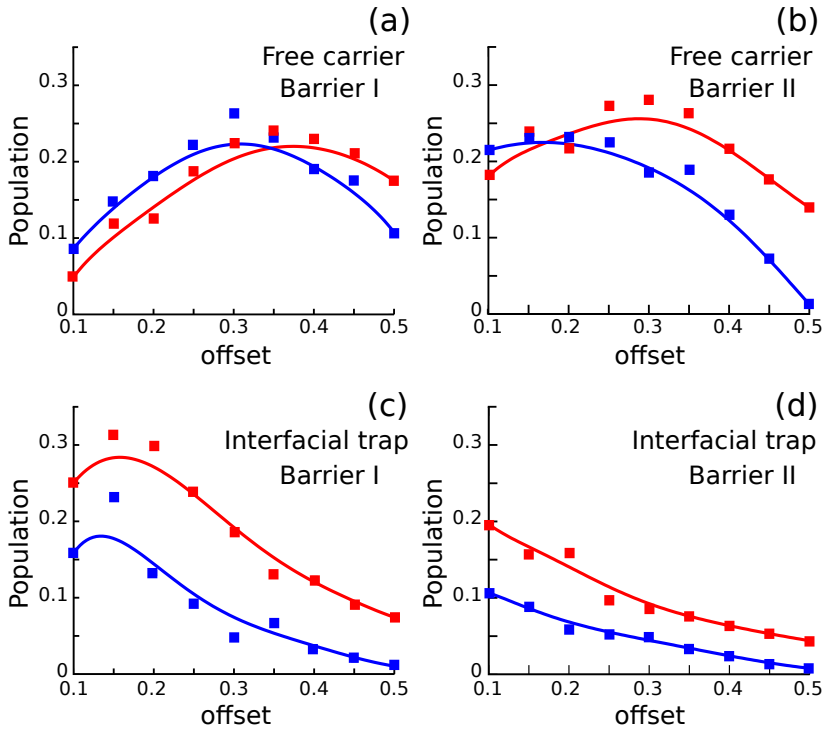


Roland, Eisenbrandt et al., in preparation

- tunable donor species: alternating thiophene/fluorene/benzothiadiazole units; electrodeficient bridge to the perylene acceptor
- organization in lamellae (both DA and ADA – but not DAD)
- comparatively slow CT formation (hundreds of ps); less recombination

How to Optimize the Free Carrier Yield





- free carrier population $\sim$ IQE (internal quantum efficiency)
- interfacial trap is less populated with increasing offset $\Delta E_{\text{offset}} = \varepsilon^{\text{XT}} - \varepsilon^{\text{CT}}$
- lower barrier (II) favors free carrier generation

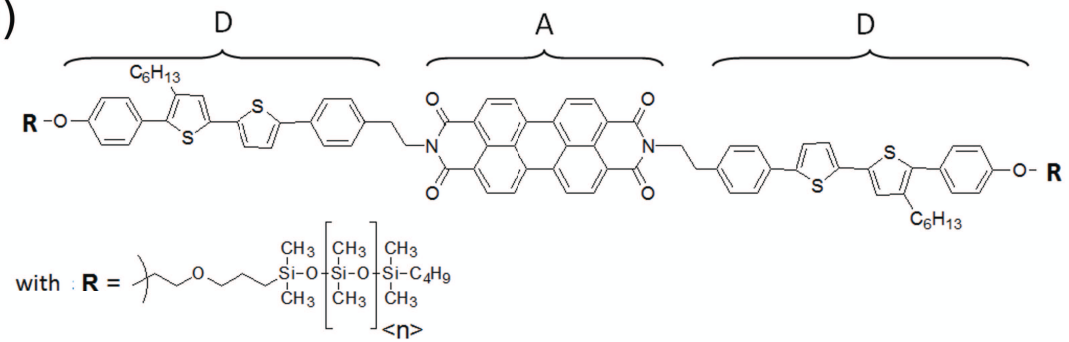
Highly Ordered DA Assemblies: Controlled Nano-Morphology

- novel donor-acceptor systems: triads organized in smectic films (Méry, Haacke, Strasbourg)

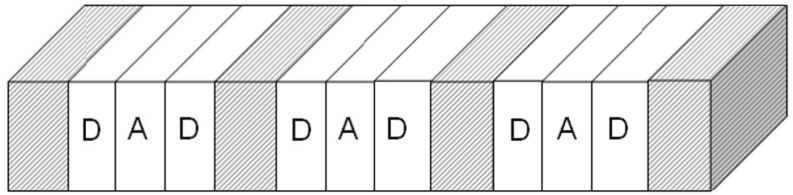
  (Collaboration Haacke (Strasbourg), Dreuw (Heidelberg))

- possibly higher efficiency than standard BHJ architectures: eliminate exciton diffusion step
- overcome recombination problem?

a)



b)

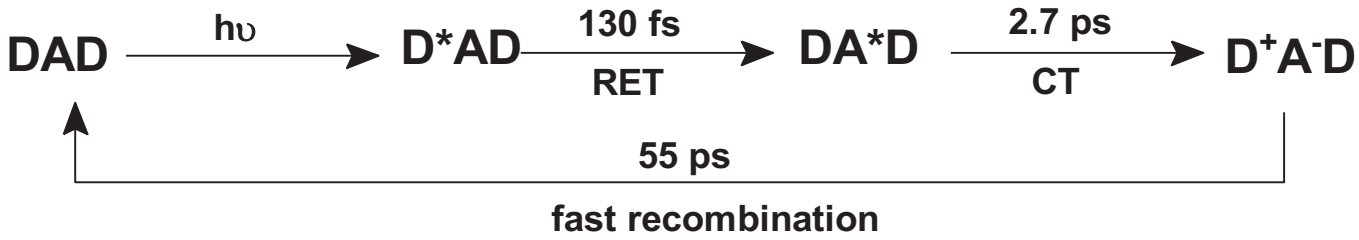


S. Haacke and collaborators, PCCP, 14, 273 (2012)

- competing ultrafast energy and charge transfer processes
- pronounced influence of stacking interactions
- environmental effects (e.g., amorphous vs. liquid crystalline phases)

Solution Phase: Sequential EET and CT Dynamics

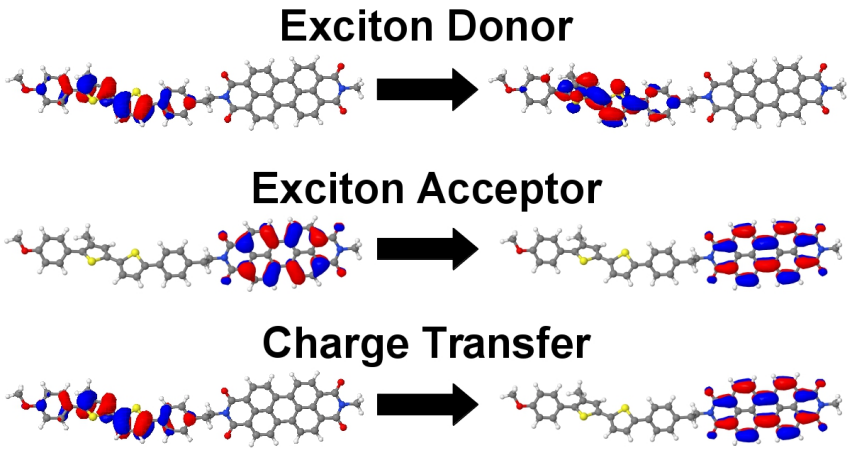
- triad in solution (chloroform): ultrafast EET (∼100 fs) followed by slower CT



- localized D^* vs. A^* excitons

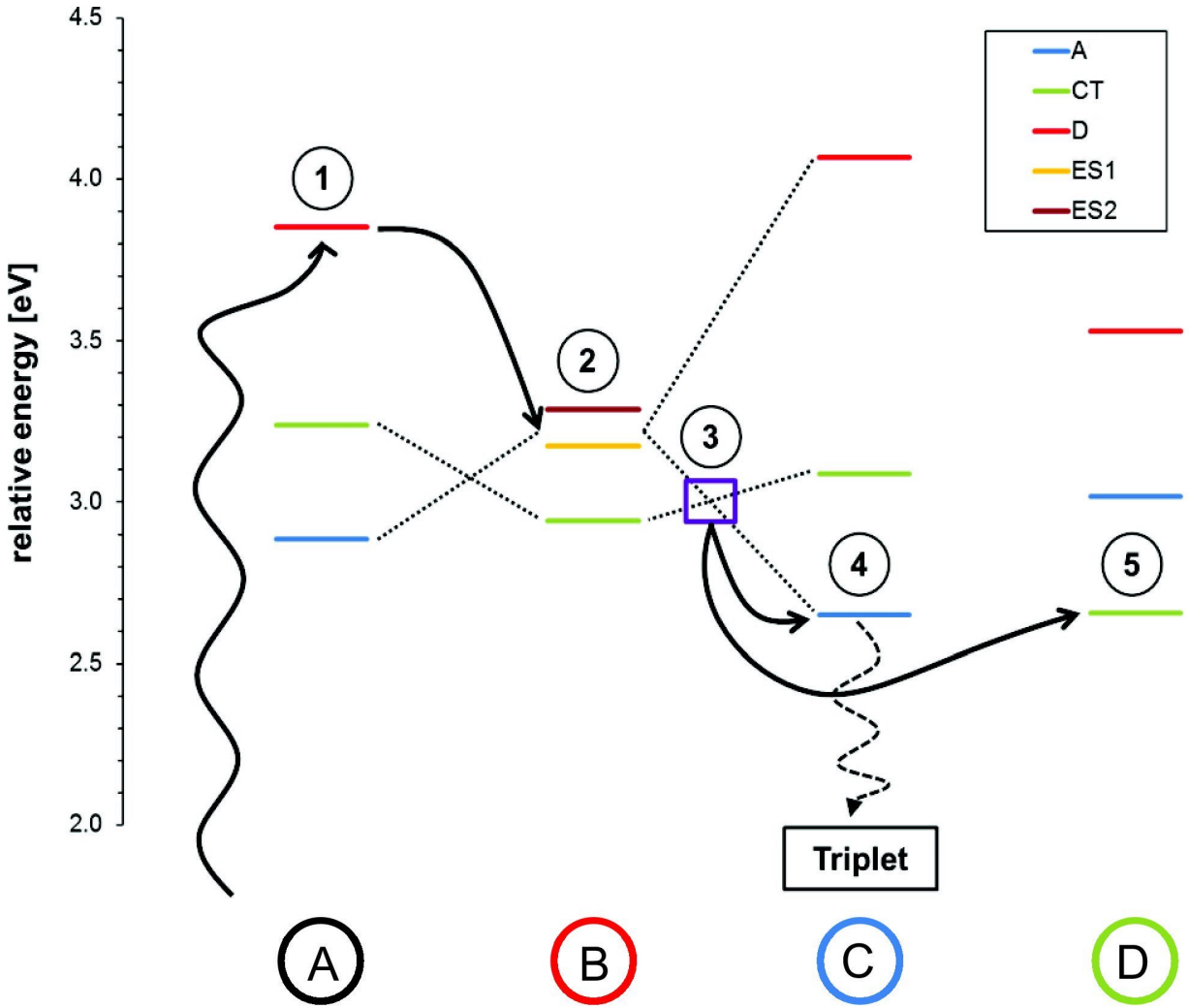
  J. Wenzel, A. Dreuw, I Burghardt, PCCP 15, 11704 (2013)

- CT state is generated from A^*
- but, in liquid crystal films: ultrafast CT becomes dominant!



Dyad Electronic Structure

- LC-TDDFT calculations
- three relevant states:
  $D \equiv (D^*A)$
  $A \equiv (DA^*)$
  $CT \equiv (D^+A^-)$
- geometries:
  (A) = FC geometry
  (B) = A/D crossing:
  excitonic $ES1/2$ states
  (C) = A minimum
  (D) = CT minimum
- CT state has 68 D (!)
  dipole moment



J. Wenzel, A. Dreuw, I Burghardt, PCCP 15, 11704 (2013)

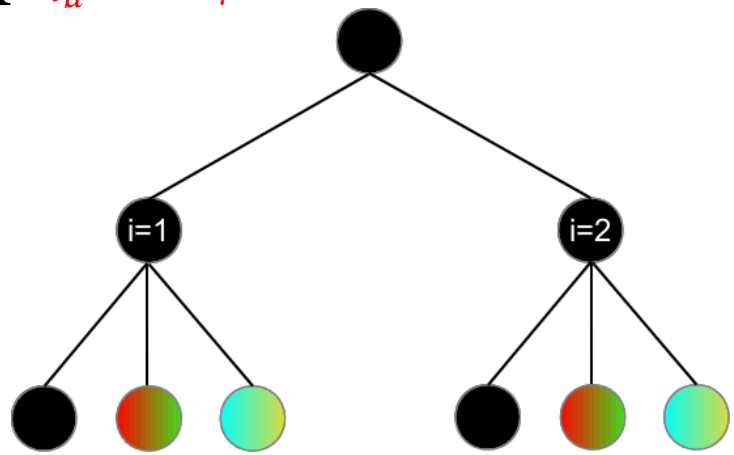
Multi-Layer(ML)-MCTDH: Wavefunction Ansatz

$$\Psi(r,t) = \sum_J A_J(t)\Phi_J(r,t) \;\; = \sum_J A_J(t) \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

where the 1st-layer SPFs $\varphi_{j_\kappa}^{(\kappa)}$ are now built as superpositions of 2nd-layer SPFs,

$$\varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa)}(t)\Phi_L^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa)}(t) \prod_\mu \varphi_{l_\mu}^{(\kappa,\mu)}(r_{\kappa_\mu},t)$$

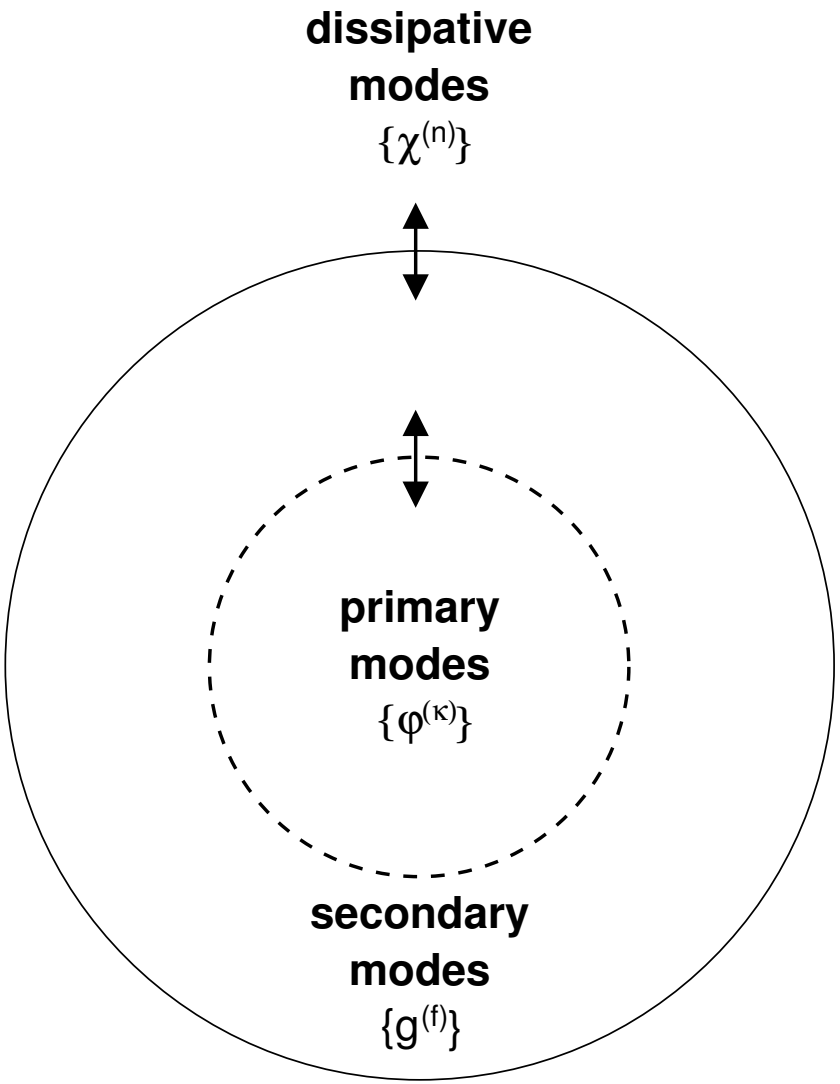
. . . and so on . . .



- intra-SPF correlations *via* MCTDH form
- continue to higher orders: ML-MCTDH
- "hierarchical Tucker format"

Wang, Thoss, J. Chem. Phys. 119, 1289 (2003), Manthe, J. Chem. Phys. 128, 164116 (2008), Vendrell, Meyer, J. Chem. Phys. 134, 044135 (2011)

Multiconfigurational Methods (MCTDH & Co)



$$\Psi(r,t) = \sum_J A_J(t)\ \Phi_J(r,t)$$

$$\text{with } \Phi_J(r,t) = \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

Multi-Configuration Time-Dependent Hartree

Meyer et al., CPL **165**, 73 (1990), Manthe et al., JCP **97**, 3199 (1992), Beck et al., Phys. Rep. **324**, 1 (2000)

Multi-layer MCTDH (ML-MCTDH)

Wang, Thoss, JCP **119**, 1289 (2003), Manthe, JCP **128**, 164116 (2008), Vendrell, Meyer, JCP **134**, 044135 (2011)

Gaussian variant: (ML-)G-MCTDH & vMCG

$$\Phi_J(r,t) = \underbrace{\prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{primary nodes}} \quad \underbrace{\prod_{\kappa=M+1}^{P} g_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{secondary modes}}$$

Burghardt, Meyer, Cederbaum, JCP **111**, 2927 (1999), Burghardt, Giri, Worth, JCP **129**, 174104 (2008), Römer, Ruckenbauer, Burghardt JCP **138**, 064106 (2013)