Coherence & Decoherence in Ultrafast Molecular Processes

Non-Markovian Approaches based upon a Hierarchical Effective-Mode Decomposition

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Topics

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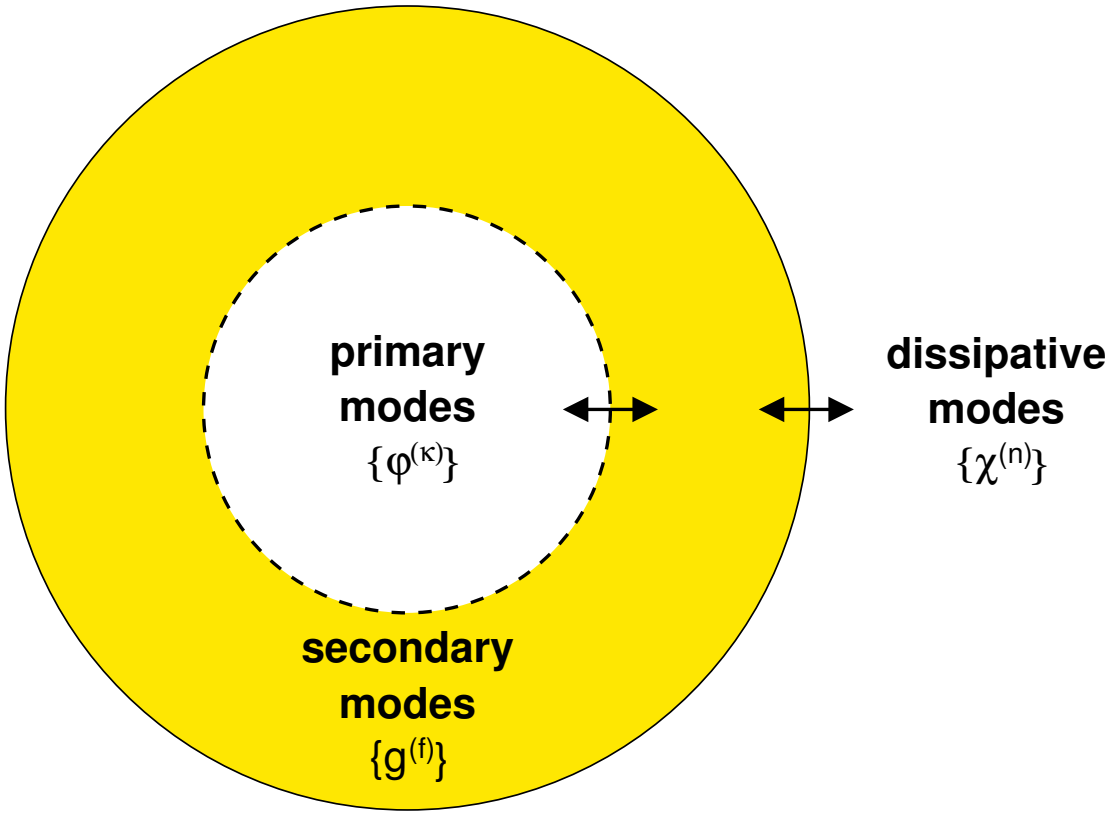
Dynamics & Reactivity in Molecular Systems

- often markedly non-Markovian: subsystem and bath (solvent, cluster, protein environment) evolve on similar time scales

- primary zone: solute or chromophore carrying initial excitation

- secondary zone: "first solvent shell", i.e., zone where system-bath correlations are dominant

- dissipative zone: external bath which can often be described by Markovian models



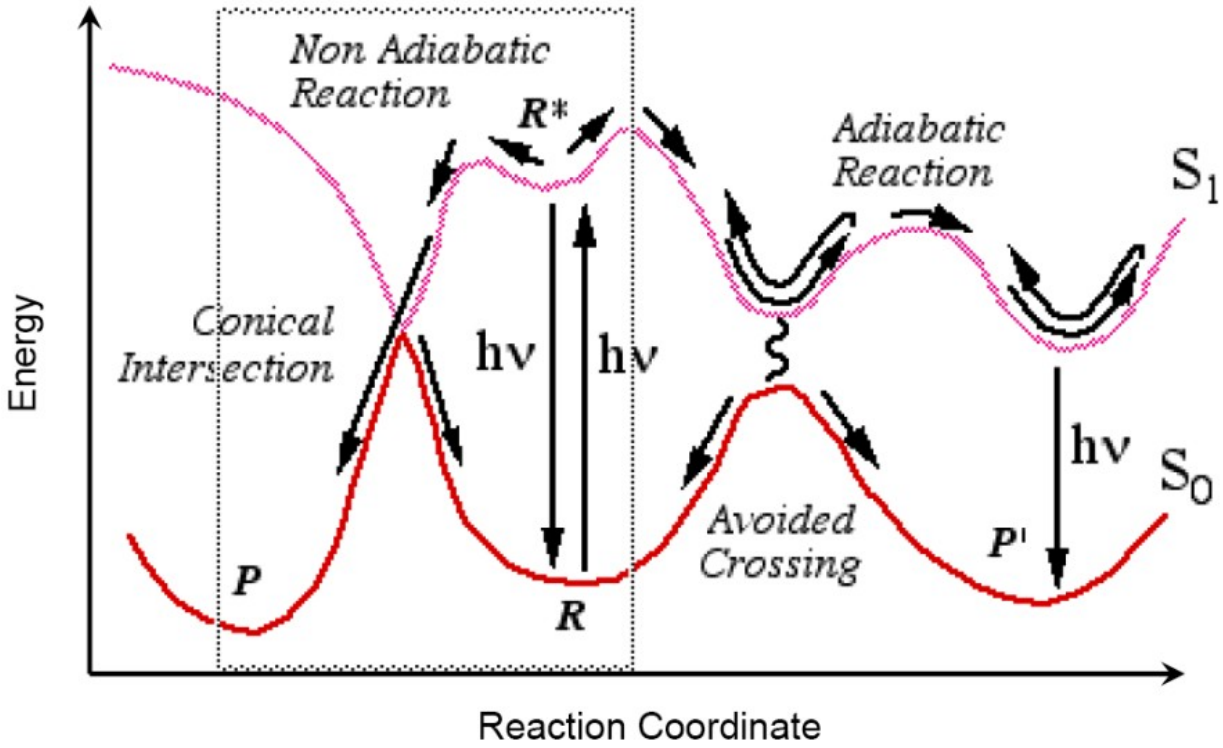
Effective-Mode Picture, in a Nutshell

- construct effective, Brownian oscillator type modes for secondary zone:

$$\hat{H}_{SB} = \hat{h}_S \sum_i c_n \hat{x}_n \longrightarrow c_{\text{eff}} \hat{h}_S \hat{X}_{\text{eff}} + \text{eff–residual bath coupling}$$

- carry out explicit dynamics in the augmented space of primary + effective/secondary modes
- approximate dissipative effects exerted by residual modes – in the simplest case, by Ohmic friction, or else by truncated Mori chains
- by-product of the analysis: hierarchy of reduced spectral densities
- non-Markovian equations for the primary subspace can be formulated – but are not the most practical way to proceed
- This approach is most useful for processes where short-time dynamical effects dominate, e.g., in photochemistry

Photochemistry: Femtosecond Events in Excited States

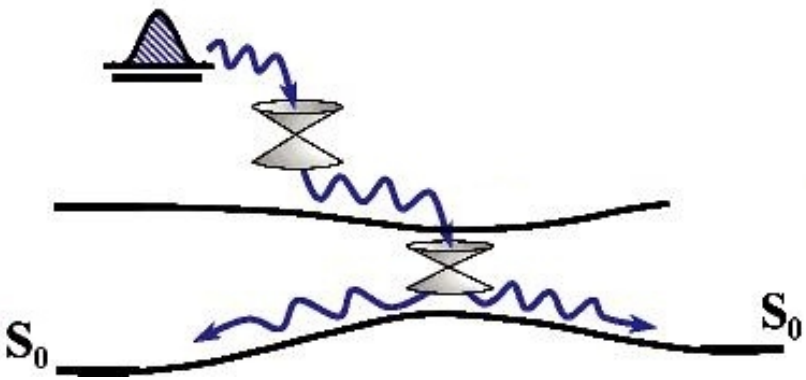


A. Piryatinski, http://cnls.lanl.gov/External/people/AndreiPiryatinski.php

- ultrafast processes, non-exponential decays, interfering dynamical pathways
- many processes require (non-adiabatic) quantum dynamics
- direct quantum propagation is often the method of choice

Landmark Topology: Conical Intersections (CoIn's)

CoIn = photochemical funnel



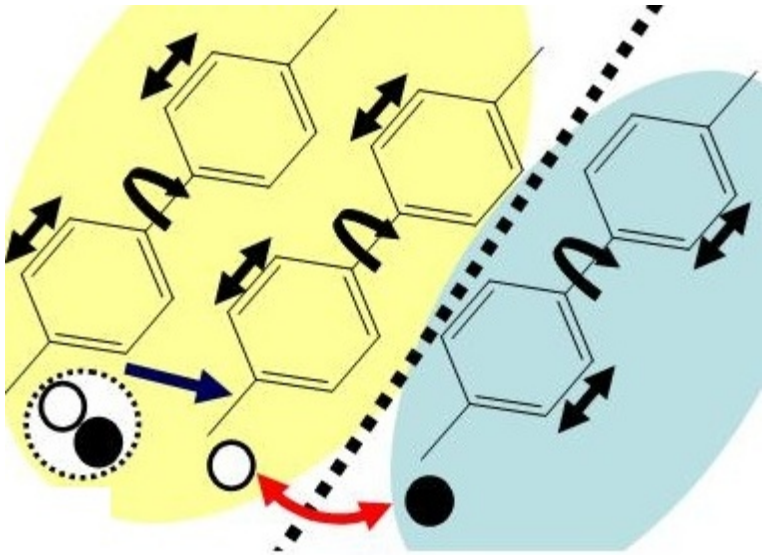
Schultz et al., J. Am. Chem. Soc. 125, 8098 (2003)

- Double cone topology at degeneracy
- CoIn topology highly anharmonic
- Extreme breakdown of the Born-Oppenheimer approximation
- Ultrafast decay (fs to ps scale)
- CoIn's are ubiquitous (Truhlar/Mead: "Principle of non-rareness of CoIn's")
- Polyatomic molecules; Jahn-Teller effect in solids

Köppel, Domcke, Cederbaum, Adv. Chem. Phys. 57, 59 (1984)
Conical Intersections, Eds. Yarkony, Köppel, Domcke (2004)

Photochemistry of "Complex" Systems

- polyatomic molecules
- solute-solvent systems
- biological chromophores & photoswitches
- extended, multi-chromophoric systems
- molecular nano-scale assemblies



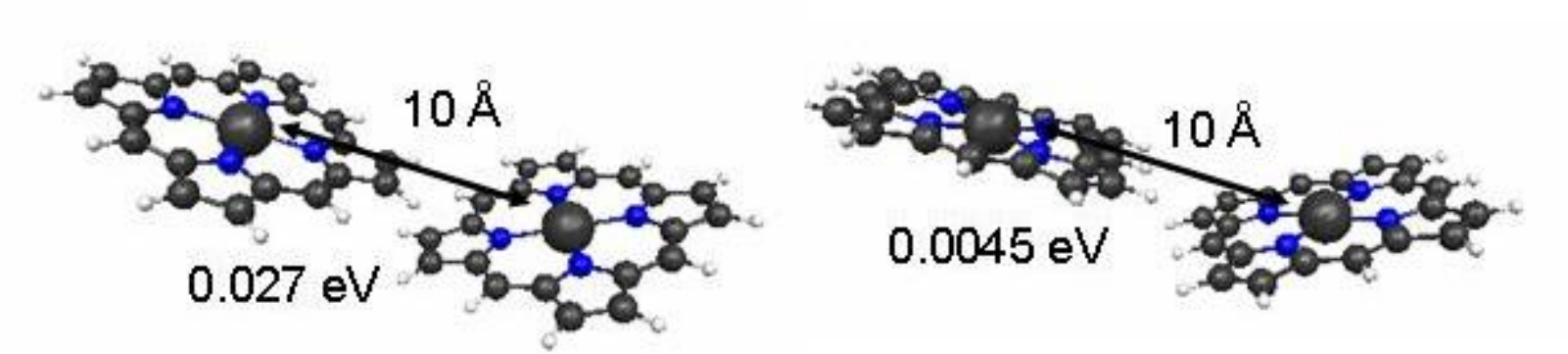
- delocalized excitations
- ultrafast processes (fs–ps)
- quantum coherence & decoherence (vibrational and electronic)
- special topologies, e.g., conical intersections

Excitons, EET, Charge Transfer

- exciton formation, delocalization & trapping
  - Frenkel excitons: $|\Psi_{\text{exciton}}\rangle = \sum_n^{n_{\text{exc}}} c_n |\Phi_n\rangle$ with $n_{\text{exc}} \sim$ 5-10, where $|\Phi_n\rangle$ = configuration with the nth monomer excited
  - trapping due to exciton-phonon interactions
- excitation energy transfer (EET, exciton migration)[1]
  - coherent vs. non-coherent (Förster limit) transfer
  - examples: EET in semiconducting polymers, light-harvesting systems, DNA, carbon nanotube (CNT) and quantum dot (QD) assemblies
- charge separation/transfer (exciton dissociation)[1]
  - examples: photovoltaic materials, e.g., semiconducting polymers, CNT-porphyrin assemblies, photosynthetic reaction center

[1] often involve non-adiabatic dynamics

Example 1: Excitation Energy Transfer (EET)



Tamura, Mallet, Oheim, Burghardt, J. Phys. Chem. C, 113, 7548 (2009)

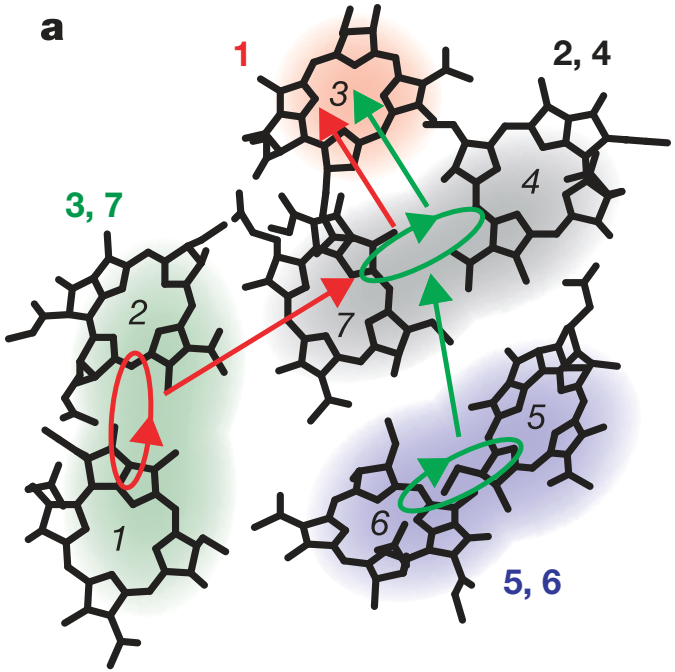
$$H = \sum_i \frac{\omega_i}{2}\left(p_i^2 + x_i^2\right) + \begin{pmatrix} \kappa_i^{(1)} x_i^{(1)} & V_{12}^{\text{Coulomb}} \\ V_{12}^{\text{Coulomb}} & \kappa_i^{(2)} x_i^{(2)} \end{pmatrix}$$

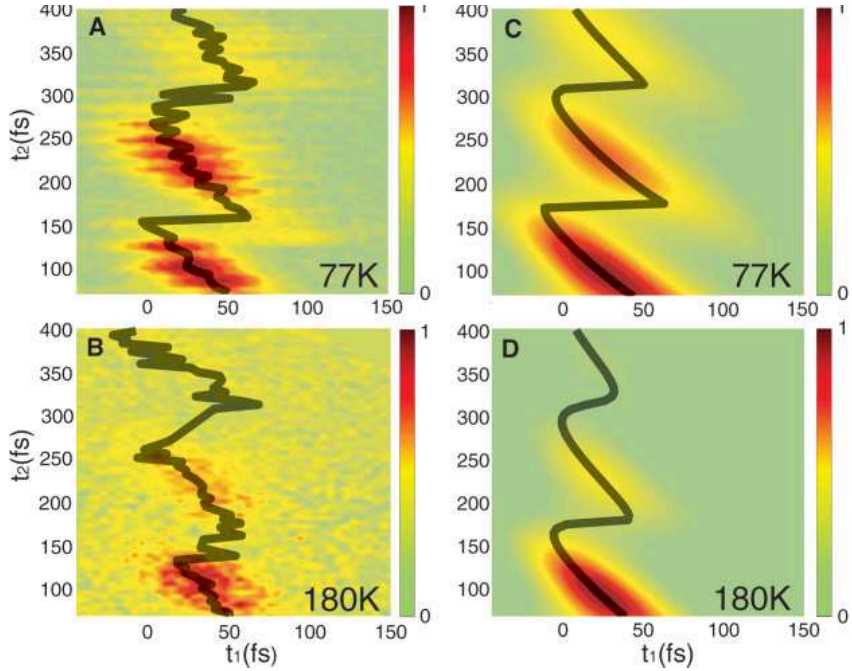
$$V_{12}^{\text{Coulomb}} = \int d\boldsymbol{r}_D \, d\boldsymbol{r}_A \, \frac{\rho_D^{(eg)}(\boldsymbol{r}_D)\, \rho_A^{(ge)}(\boldsymbol{r}_A)}{|\boldsymbol{r}_D - \boldsymbol{r}_A|}$$

- inter-monomer couplings via transition densities
- generalization of Förster rate theory & transition dipole approximation
- coherent regime: photosynthesis, artificial light-harvesting systems

"Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence"

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



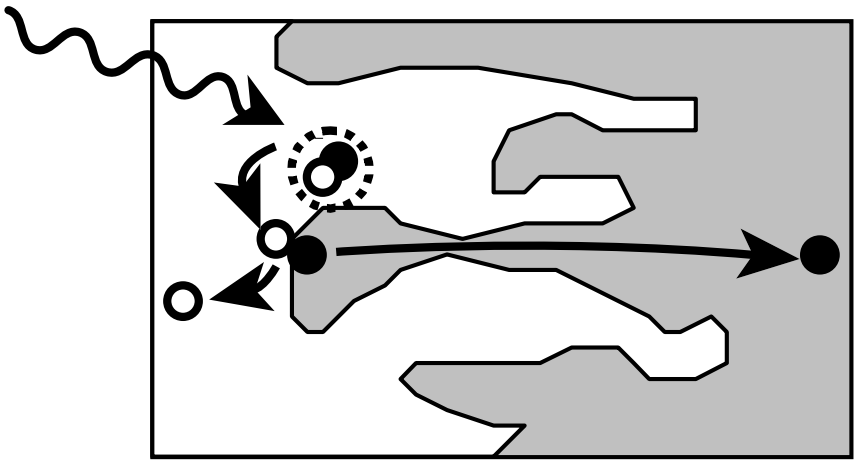


- one would expect an extremely rapid dephasing (decoherence): $\tau_{\mathrm{dec}} < 50$ fs
- but observed coherence lifetimes are $\sim$ 600 fs to 1 ps

Example 2: Exciton Dissociation at a Polymer Interface (Heterojunction)

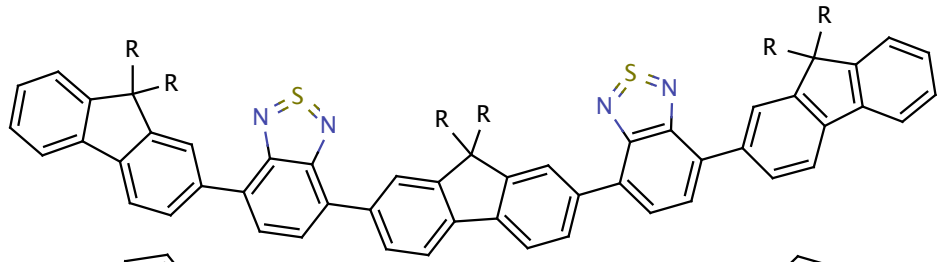
$$\text{exciton} = \text{electron} + \text{hole}$$

$\longrightarrow$ photovoltaic devices, organic light-emitting diodes (OLED's), ...

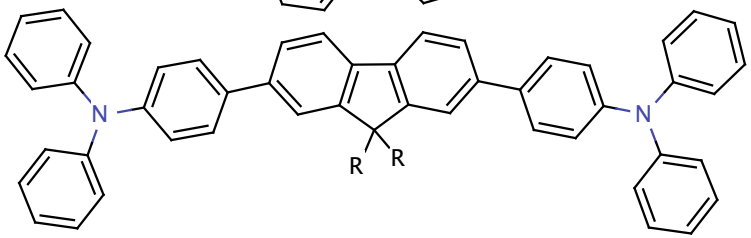


Peumans, Uchida, Forrest, Nature **125**, 8098 (2003)

F8BT:

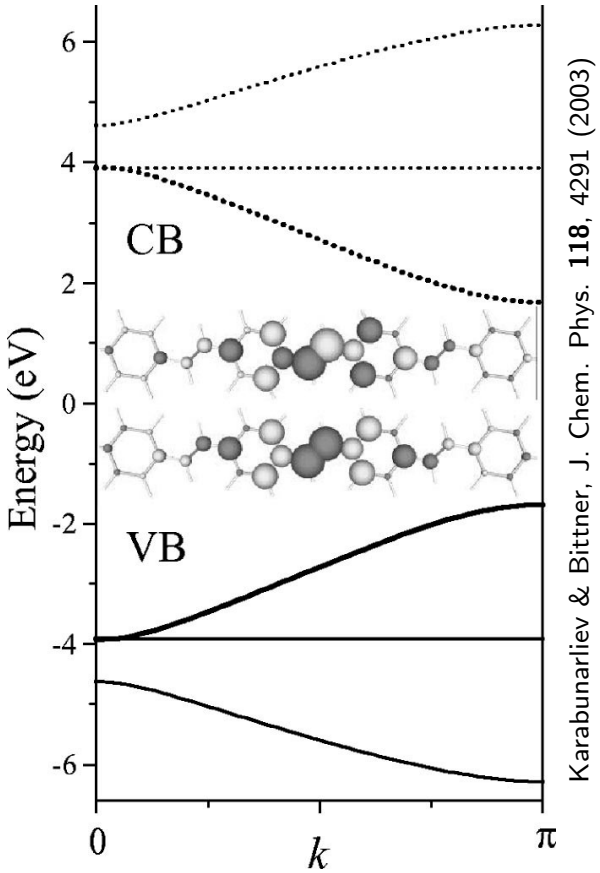


TFB:

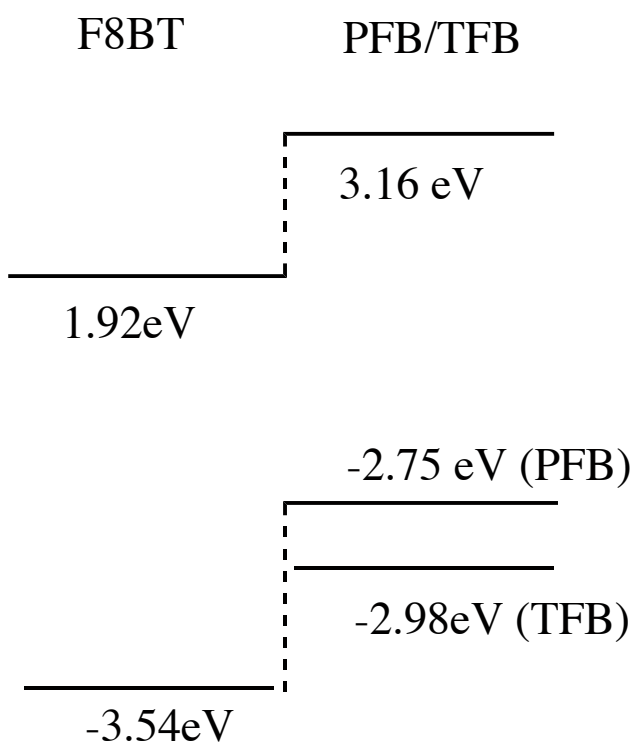


molecular-level understanding of interactions & dynamics at the polymer interface is required

Zeroth-Order Picture of a Heterojunction



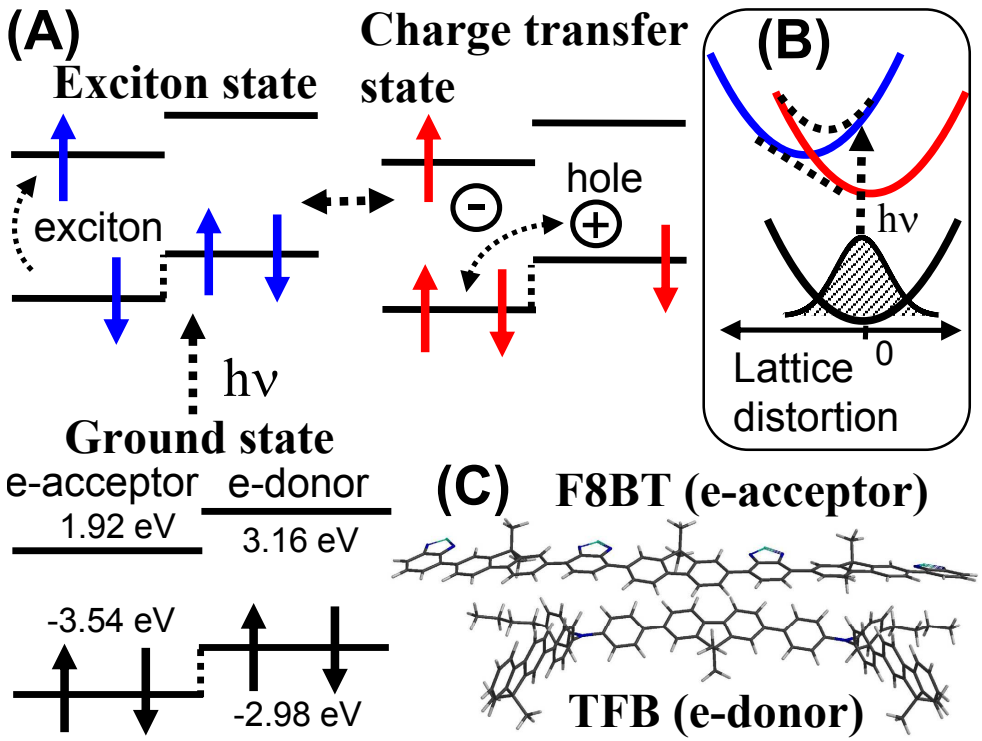
polymer/polymer interface:



- 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)

Objective: More Detailed Perspective of Ultrafast Events

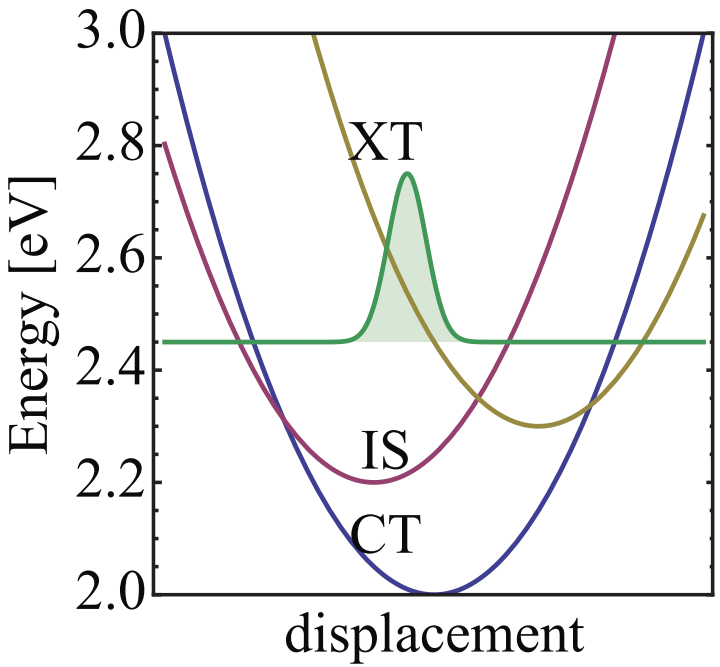
TFB:F8BT heterojunction



Tamura, Bittner, Burghardt, JCP **126**, 021103 (2007)

- initial photogeneration of an exciton state (XT, bright state)
- exciton decay to an interfacial charge transfer state (CT, exciplex)
- the XT ⟶ CT transition is mediated by electron-phonon coupling

3-State Electron-Phonon Coupling Model



$$H = \sum_i^{N\sim 30} H_i = \sum_i \frac{\omega_i}{2}\left(p_i^2 + x_i^2\right) + V_i^{\text{lin}}$$

$$V_i^{\text{lin}} = \begin{pmatrix} \kappa_i^{(1)} x_i & \lambda_i^{(12)} x_i & \lambda_i^{(13)} x_i \\ \lambda_i^{(12)} x_i & \kappa_i^{(2)} x_i & \lambda_i^{(23)} x_i \\ \lambda_i^{(13)} x_i & \lambda_i^{(23)} x_i & \kappa_i^{(3)} x_i \end{pmatrix}$$

state 1 = exciton (XT) state
state 2 = charge transfer (CT) state
state 3 = intermediate (IS) state

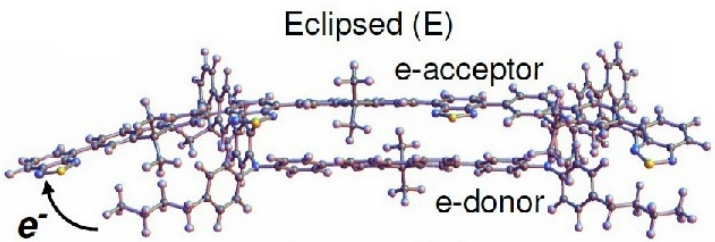
parameterization for TFB:F8BT:
polymer lattice model based on dimer;
TDDFT and semi-empirical (PM3) calculations
+ Wannier-function representation

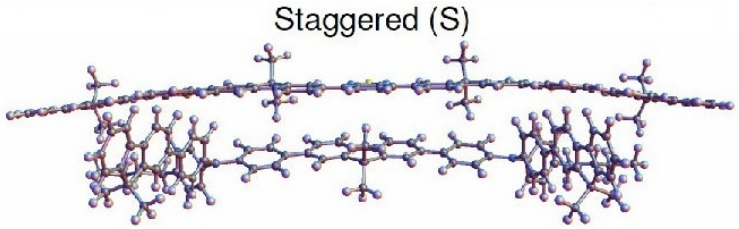
Bittner et al., JCP **122**, 214719 (2005)

phonons = C=C stretch + ring torsions

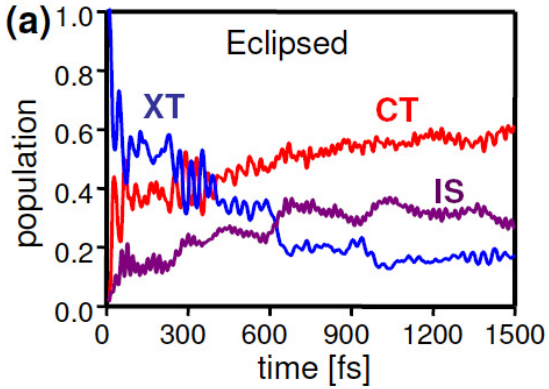
Tamura, Ramon, Bittner, Burghardt, J. Phys. Chem. B 112, 10269 (2008)

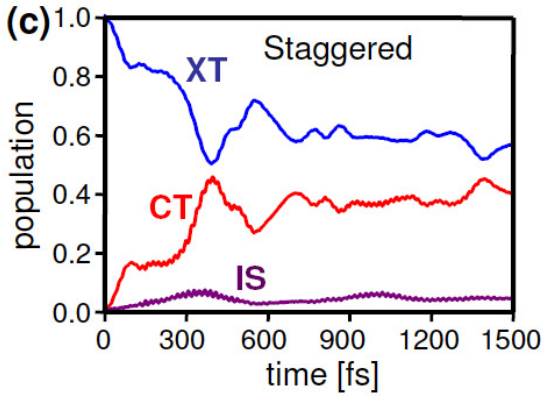
Quantum Dynamics of Exciton Dissociation



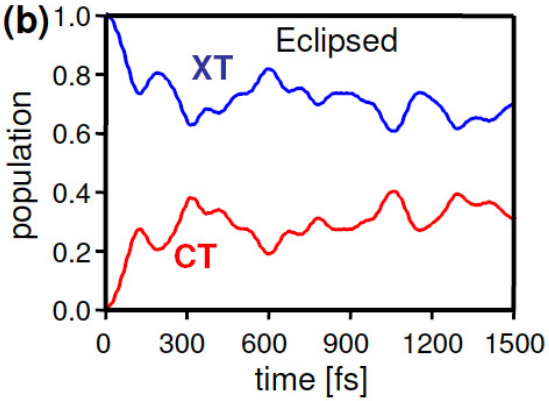


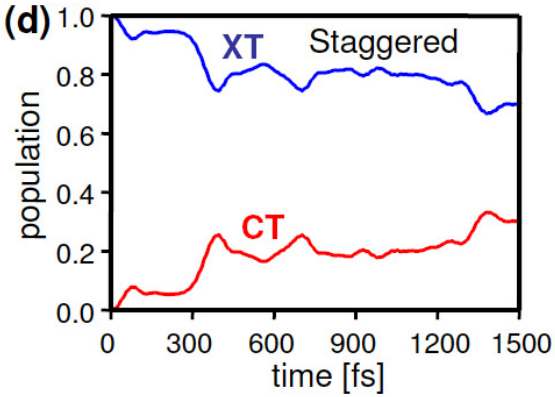
3-state





2-state



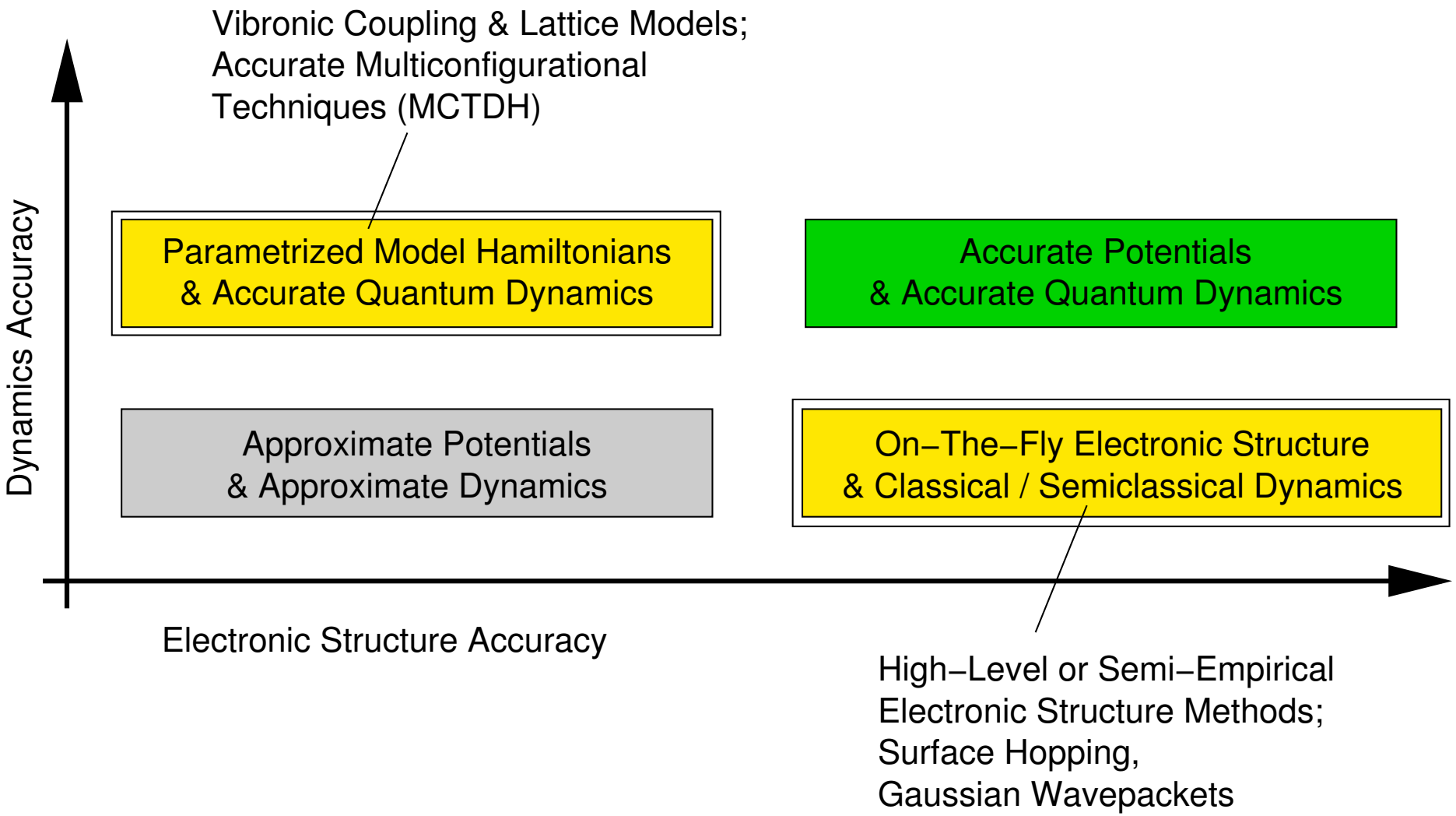


- 3-state 28-mode model
- MCTDH calculations
- sample over relevant interface configurations
- intermediate states play a key role
- qualitative agreement with time-resolved photoluminescence

Tamura, Ramon, Bittner, Burghardt, Phys. Rev. Lett. **100**, 107402 (2008)

Topics

Methods for "Large" Systems



Model Hamiltonians

- multi-mode vibronic coupling models (quasi-diabatic)
  Taylor expansion around reference geometry (CoIn; FC point)

  $$\boldsymbol{H} = (T_N + V_0)\mathbf{1} + \boldsymbol{V}$$

  $$V_{nn'} = \varepsilon_{nn'} + \sum_i \xi_i^{nn'} x_i + \sum_{i,j} \gamma_{ij}^{nn'} x_i x_j + \ldots$$

  Köppel, Domcke, Cederbaum, Adv. Chem. Phys. (1984)

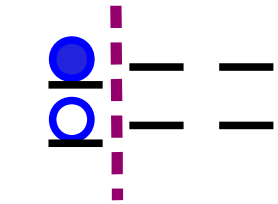
- lattice models
  site-site interactions + electron(exciton)-phonon coupling, e.g.,

  $$H = \sum_n E_0 a_n^\dagger a_n - J(a_n^\dagger a_{n+1} + a_{n+1}^\dagger a_n) + \frac{p_n^2}{2M} + \frac{W}{2}(q_{n+1} - q_n)^2 + \chi a_n^\dagger a_n (q_{n+1} - q_n)$$

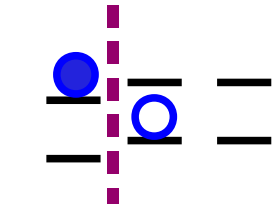
  A. S. Davydov, Phys. Scr. 20, 387 (1979), Groves & Silbey, J. Chem. Phys. **52**, 2099 (1970)

- in both cases: *ab initio* or semiempirical parametrization

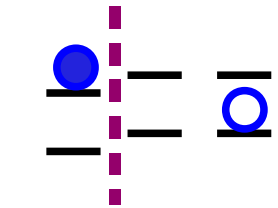
Electronic Structure – Lattice Model



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



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



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

- singly-excited electron-hole (e-h) config's: $|\mathbf{n}\rangle = |n_e \bar{n}'_h\rangle = |n_e\rangle_C \otimes |\bar{n}'_h\rangle_V$ (Wannier function basis)
- set up Hamiltonian in this basis:

$$H_{\mathrm{el}} = \sum_{\mathbf{mn}} \left(F_{\mathbf{mn}} + V_{\mathbf{mn}} \right) a^\dagger_{\mathbf{m}} a_{\mathbf{n}}$$

- creation and annihilation op's for e-h pairs: $a^\dagger_{\mathbf{n}}|0\rangle = |\mathbf{n}\rangle = |n_e \bar{n}'_h\rangle$
- $F_{\mathbf{mn}}/V_{\mathbf{mn}}$ = single/two-particle matrix elements

Lattice Model Including Electron-Phonon Coupling

$$H = H_{\text{el}} + H_{\text{el-ph}} + H_{\text{ph}}$$

$$= \sum_{\mathbf{nm}} (F_{\mathbf{mn}} + V_{\mathbf{mn}}) a^{\dagger}_{\mathbf{m}} a_{\mathbf{n}} + \sum_{\mathbf{nm}} \sum_{k\alpha} \left(\frac{\partial F_{\mathbf{mn}}}{\partial q_{k\alpha}} \right) a^{\dagger}_{\mathbf{m}} a_{\mathbf{n}} q_{k\alpha} + \sum_{\ell\alpha} \frac{1}{2} \left(\omega^2_{\ell\alpha} q^2_{\ell\alpha} + p^2_{\ell\alpha} \right)$$

↓ diagonalize $H_0 = H_{\text{el}} + H_{\text{ph}}$ & select typically 2-3 lowest states

$$\boxed{H = \sum_i 1/2 \left(\omega_i{}^2 x_i^2 + p_i^2 \right) + V_i^{\text{lin}}} \quad \text{where} \quad V_i^{\text{lin}} = \begin{pmatrix} \kappa_i^{(1)} x_i & \lambda_i^{(12)} x_i & \lambda_i^{(13)} x_i \\ \lambda_i^{(12)} x_i & \kappa_i^{(2)} x_i & \lambda_i^{(23)} x_i \\ \lambda_i^{(13)} x_i & \lambda_i^{(23)} x_i & \kappa_i^{(3)} x_i \end{pmatrix}$$

Karabunarliev & Bittner, J. Chem. Phys. **118**, 4291 (2003), Groves & Silbey, J. Chem. Phys. **52**, 2099 (1970)

Linearized Models & CoIn Topology*

* quasi-diabatic linear vibronic coupling (LVC) form
* can be embedded in a correct representation of the overall potential via regularized diabatic states

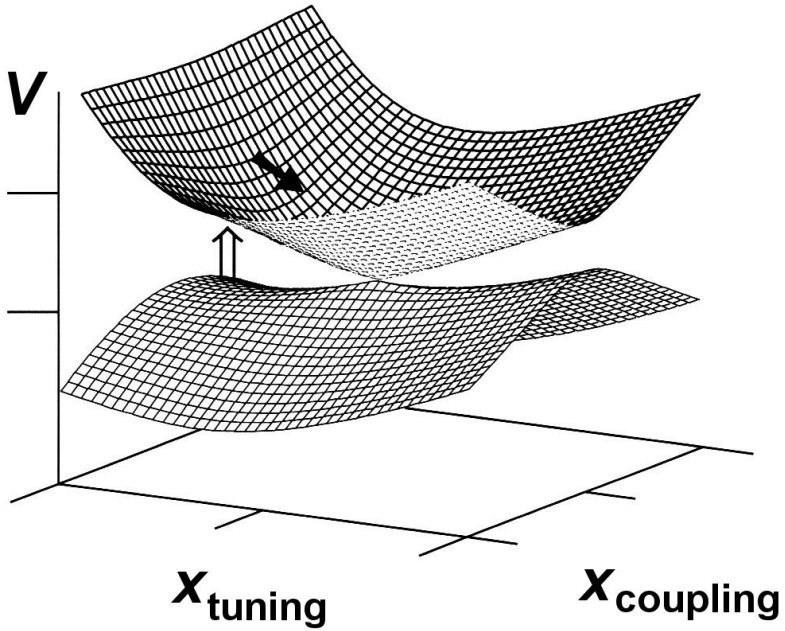
Köppel et al., J. Chem. Phys. **110**, 9371 (1999); **115**, 2377 (2001)

$$V_{\mathrm{CoIn}}(x_t, x_c) = V_0(x_t^0, x_c^0)$$

$$+ \begin{pmatrix} \kappa^{(1)}\Delta x_t & \lambda \Delta x_c \\ \lambda \Delta x_c & \kappa^{(2)}\Delta x_t \end{pmatrix}$$

$\Delta x_t = x_t - x_t^0$ tuning mode
$\Delta x_c = x_c - x_c^0$ coupling mode

2 dimensions: CoIn point
3 dimensions: CoIn seam
N dimensions: (N-2) dimensional intersection space



Quantum Dynamics Approaches

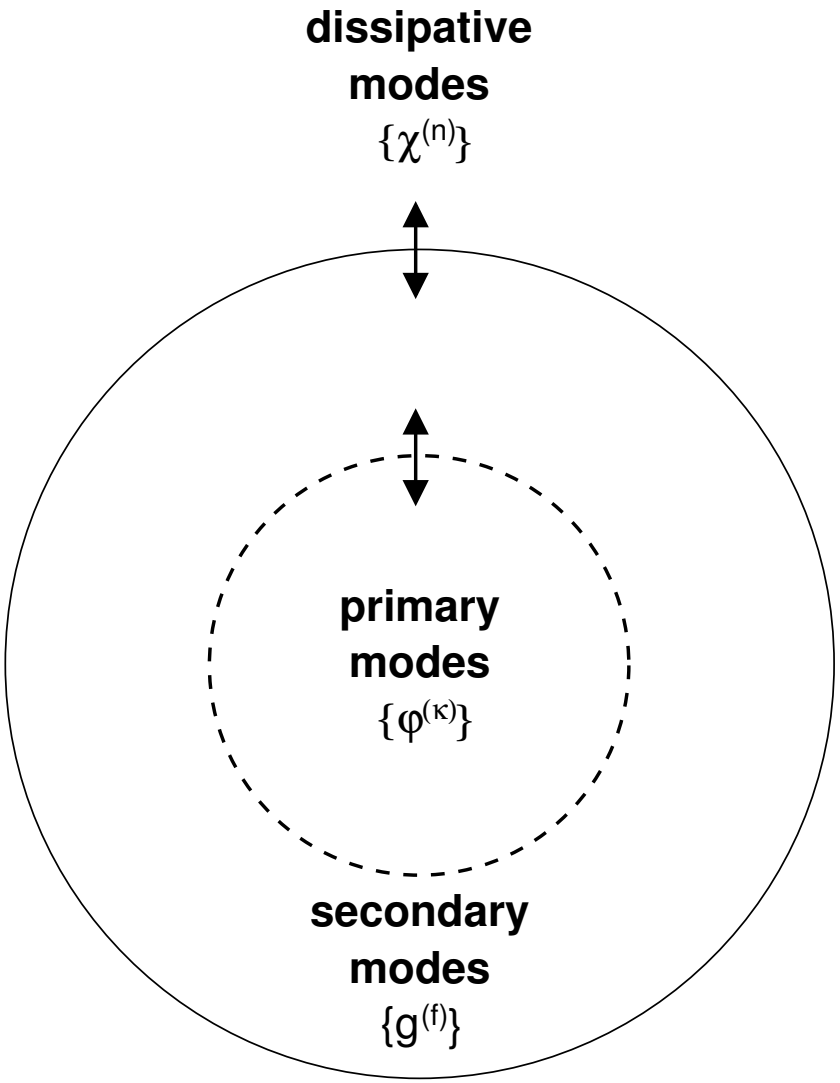
1. explicit, multidimensional dynamics for the full system + bath space: wavefunction $\psi_{SB}(t)$ or density operator $\hat{\rho}_{SB}(t) = \sum_n p_n |\psi_{n,SB}(t)\rangle\langle\psi_{n,SB}(t)|$
2. reduced dynamics (master equation) methods: $\hat{\rho}_S(t) = \mathrm{Tr}_B \hat{\rho}_{SB}(t)$
3. intermediate methods: explicit treatment of subsystem + effective-mode (E) part of the bath + master equation for residual (R) bath:

$$\frac{\partial \hat{\rho}_{SE}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{SE}, \hat{\rho}_{SE}(t)] + \hat{\hat{L}}^{(R)}_{\mathrm{diss}} \hat{\rho}_{SE}(t) \quad ; \quad \hat{\rho}_{SE}(t) = \mathrm{Tr}_R \hat{\rho}_{SER}(t)$$

$$\hat{\hat{L}}^{(R)}_{\mathrm{diss}} \hat{\rho}_{SE} = -i\frac{\gamma}{\hbar}[\hat{X}_E, [\,\hat{P}_E, \hat{\rho}_{SE}]_+] - \frac{2\gamma MkT}{\hbar^2}[\hat{X}_E, [\hat{X}_E, \hat{\rho}_{SE}]]$$

- efficient multiconfigurational methods for $S+E$, suitable for 10-100 modes
- Caldeira-Leggett type master equations for residual (R) modes

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

Gaussian-based hybrid method: G-MCTDH

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

Burghardt, Meyer, Cederbaum, JCP **111**, 2927 (1999)
Burghardt, Giri, Worth JCP **129**, 174104 (2008)

Variationally Optimized Dynamics

$$\Psi(r_1,\ldots,r_P,t) = \sum_{j_1}\cdots\sum_{j_P} A_{j_1\ldots j_P}(t) \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t) \prod_{\kappa=M+1}^{P} g_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

$$g_j^{(\kappa)}(r_\kappa,t) = \exp\left[r_\kappa \cdot a_j^{(\kappa)}(t)\cdot r_\kappa + \xi_j^{(\kappa)}(t)\cdot r_\kappa + \eta_j^{(\kappa)}(t)\right]$$

multidimensional Gaussian functions:

- quasi-classical motion
- on-the-fly dynamics
- analytical integrals

Dirac-Frenkel variational principle:

$\langle\delta\Psi|H - i\frac{\partial}{\partial t}|\Psi\rangle = 0$ ⟶ dynamical equations (symplectic structure)

- up to 50-100 modes – exponential scaling problem ($\sim fN^{f+1}$) is alleviated

Dynamical Equations

Burghardt, Meyer, Cederbaum, JCP 111, 2927 (1999)

coefficients: $$i\dot{A} = S^{-1}\Big[H - i\tau\Big]A$$

spf's (primary modes): $$i\dot{\varphi}^{(\kappa)} = \left(\hat{1} - \hat{P}^{(\kappa)}\right)\Big[\rho^{(\kappa)}\Big]^{-1}\hat{H}^{(\kappa)}\varphi^{(\kappa)}$$

gwp's (secondary modes): $$i\dot{\Lambda}^{(\kappa)} = \Big[C^{(\kappa)}\Big]^{-1}\ Y^{(\kappa)}$$

$$C^{(\kappa)}_{j\alpha,l\beta} = \rho^{(\kappa)}_{jl}\langle\frac{\partial g^{(\kappa)}_j}{\partial\lambda^{(\kappa)}_{j\alpha}}\Big|(\hat{1}-\hat{P}^{(\kappa)})\Big|\frac{\partial g^{(\kappa)}_l}{\partial\lambda^{(\kappa)}_{l\beta}}\rangle \quad ; \quad Y^{(\kappa)}_{j\alpha} = \sum_l\langle\frac{\partial g^{(\kappa)}_j}{\partial\lambda^{(\kappa)}_{j\alpha}}\Big|(\hat{1}-\hat{P}^{(\kappa)})\hat{H}^{(\kappa)}_{jl}\Big|g^{(\kappa)}_l\rangle$$

- evolution under multiconfigurational mean-field Hamiltonian
- coupled, variational equations for Gaussian parameters
- correlations between primary vs. secondary subspace

Topics

Reduced-Dimensional Models for Large Systems

e.g. N secondary-zone modes coupled to electronic subsystem (primary zone)

$$H = \sum_{i=1}^{N} H_0^{(i)} + \begin{pmatrix} \kappa_i^{(1)} x_i & \lambda_i x_i \\ \lambda_i x_i & \kappa_i^{(2)} x_i \end{pmatrix} \xrightarrow{?} H_{\text{eff}} = \sum_{i=1}^{n_{\text{eff}}} \tilde{H}_0^{(i)} + \begin{pmatrix} K_i^{(1)} X_i & \Lambda_i X_i \\ \Lambda_i X_i & K_i^{(2)} X_i \end{pmatrix}$$

N potentially very large!

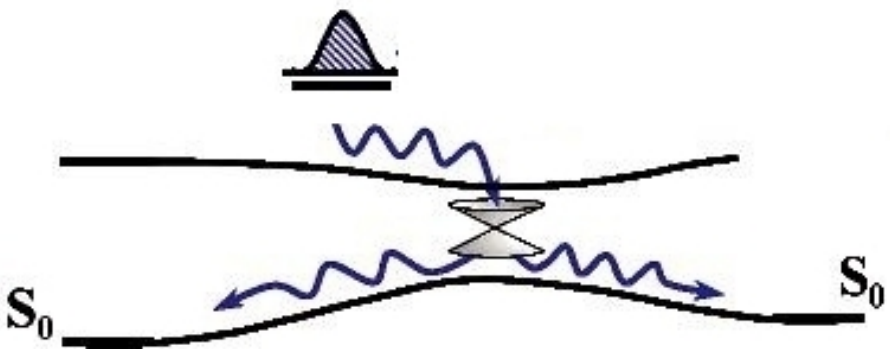
n_{eff} small

- approximation should be valid on short time scales
- X_i's are collective modes – "generalized reaction coordinates"

Conical Intersection (CoIn): Three Effective Modes

Precursors in solid state physics:
"cluster modes"
"interaction modes"

(O'Brien 1971, Toyozawa, Inoue 1966)



electronic subsystem

effective modes $\{X_1, X_2, X_3\}$

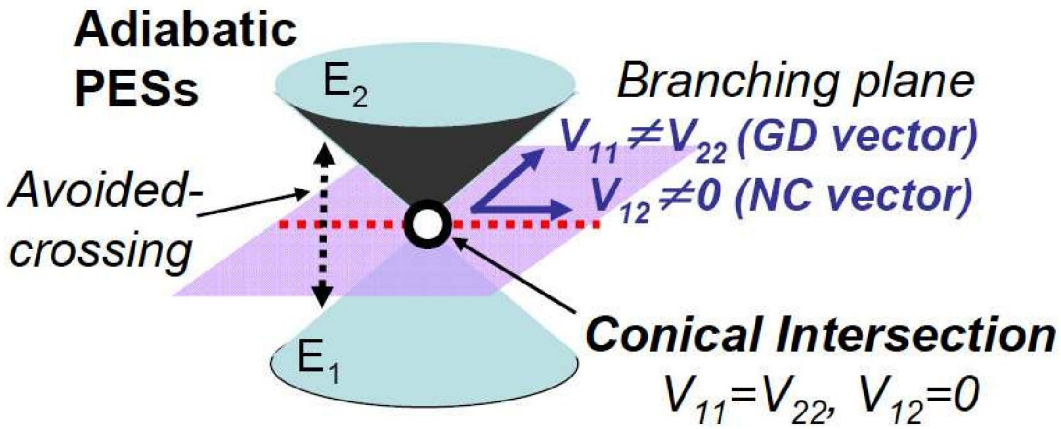
residual modes $\{X_4, \ldots, X_N\}$

- effective modes describe short-time dynamics exactly
- for n electronic states: $n(n+1)/2$ effective modes

Cederbaum, Gindensperger, Burghardt, Phys. Rev. Lett., **94**, 113003 (2005)
Burghardt, Gindensperger, Cederbaum, Mol. Phys. **104**, 1081 (2006)
Gindensperger, Burghardt, Cederbaum, J. Chem. Phys. **124**, 144104, 144105 (2006)

Why Three Effective Modes?

$$H = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N} \frac{\omega_i}{2}\left(p_i^2 + x_i^2\right) + V_i^{\text{lin}} \qquad V_i^{\text{lin}} = \frac{1}{2}\kappa_i^{(+)} x_i + \begin{pmatrix} \frac{1}{2}\kappa_i^{(-)} x_i & \lambda_i x_i \\ \lambda_i x_i & -\frac{1}{2}\kappa_i^{(-)} x_i \end{pmatrix}$$



$X_+ = \sum_i \kappa_i^{(+)} x_i$ shift

$X_- = \sum_i \kappa_i^{(-)} x_i$ energy gap

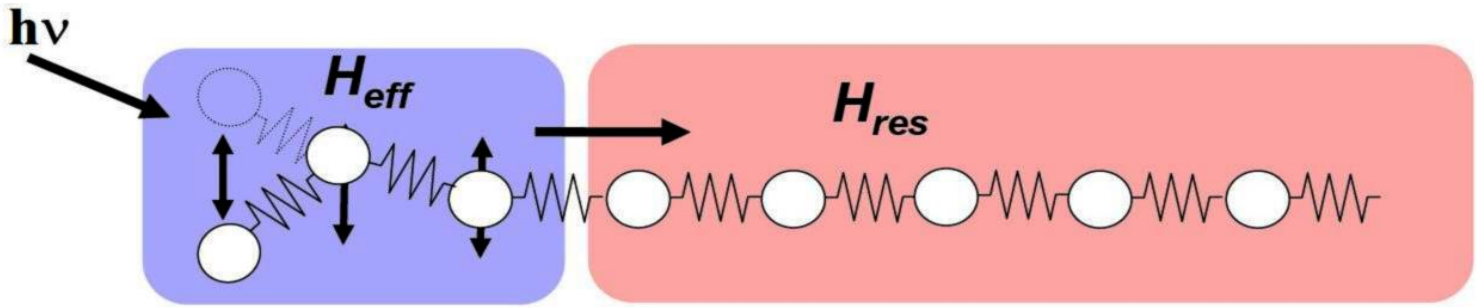
$X_\Lambda = \sum_i \lambda_i x_i$ coupling

- X_-, X_Λ span the branching plane (cf. Atchity & Xantheas & Ruedenberg (1999))
- X_+ lies in the $(N-2)$-dimensional intersection space

Additional Transformations in Residual Space

⟶ Hierarchical Electron-Phonon (HEP) Model:

effective modes + chain(s) of residual modes



- the chain "unravels" the dynamics as a function of time
- more precisely: truncation at the order n (i.e., $3n+3$ modes) conserves the Hamiltonian moments (cumulants) up to the $(2n+3)$rd order

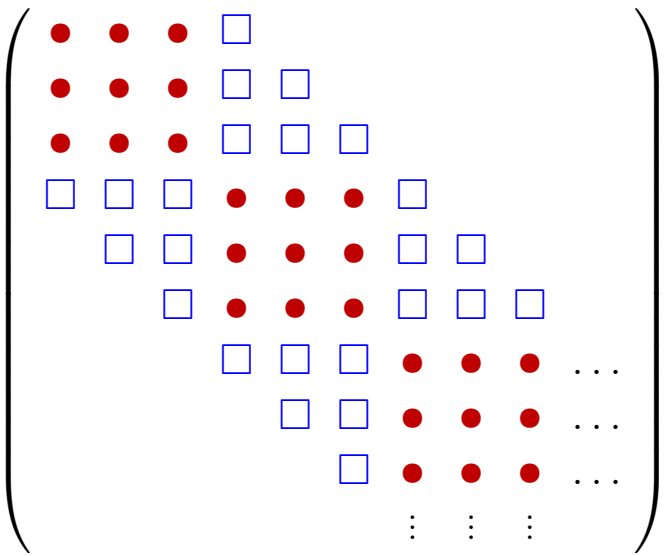
Tamura, Bittner, Burghardt, JCP **127**, 021103 (2007), Gindensperger, Cederbaum, JCP 127, 024107 (2007)

Hierarchical electron-phonon (HEP) model

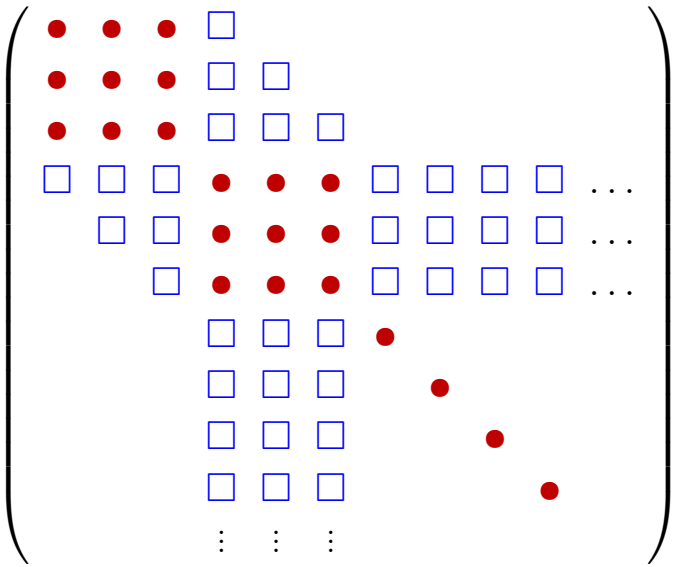
$$\hat{H}^{(n)} = \hat{H}_{\text{eff}} + \sum_{l=1}^{n} \hat{H}_{\text{res}}^{(l)}$$

$$\hat{H}_{\text{res}}^{(l)} = \sum_{i=3l+1}^{3l+3} \frac{\Omega_i}{2}(\hat{P}_i^2 + \hat{X}_i^2)\hat{1} + \sum_{i=3l+1}^{3l+3} \sum_{j=i-3}^{i-1} d_{ij}\left(\hat{P}_i\hat{P}_j + \hat{X}_i\hat{X}_j\right)\hat{1}$$

$\mathbf{d} =$



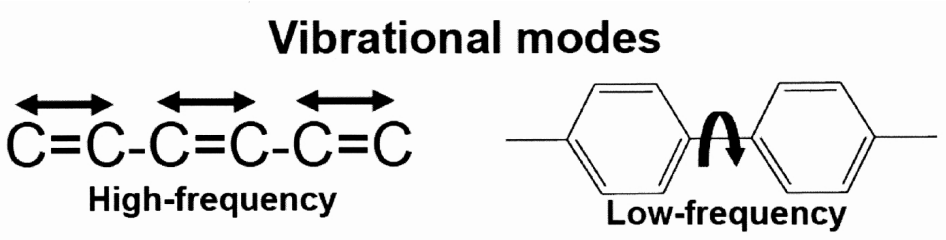
$\mathbf{d} =$



chain + Markovian closure

Tamura, Bittner, Burghardt, JCP 126, 021103 (2007); Gindensperger, Köppel, Cederbaum, JCP 126, 034106 (2007)

Effective Modes for TFB:F8BT Heterojunction



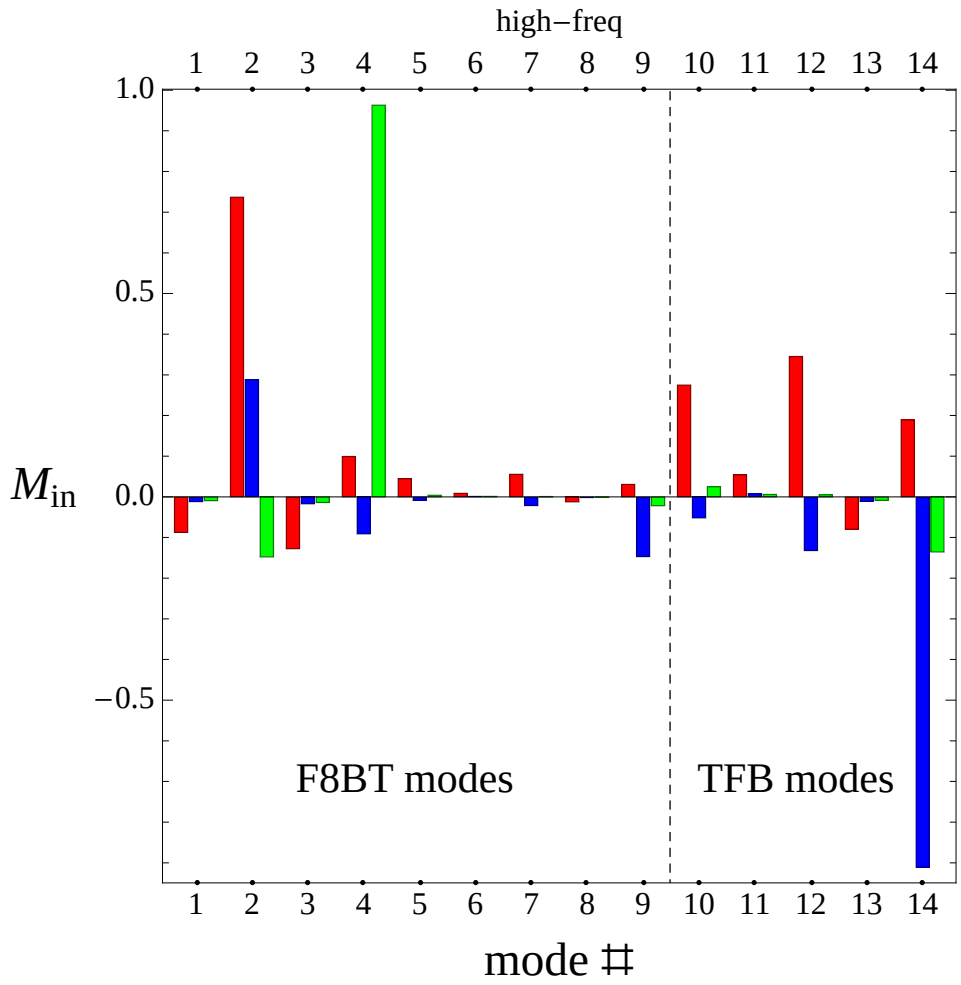
HEP hierarchy / 2-state model:

(X_1, X_2, X_3): high-frequency

(X_4, X_5, X_6): low-frequency

(X_7, X_8, X_9): high-frequency

- phonon branches appear in alternation!



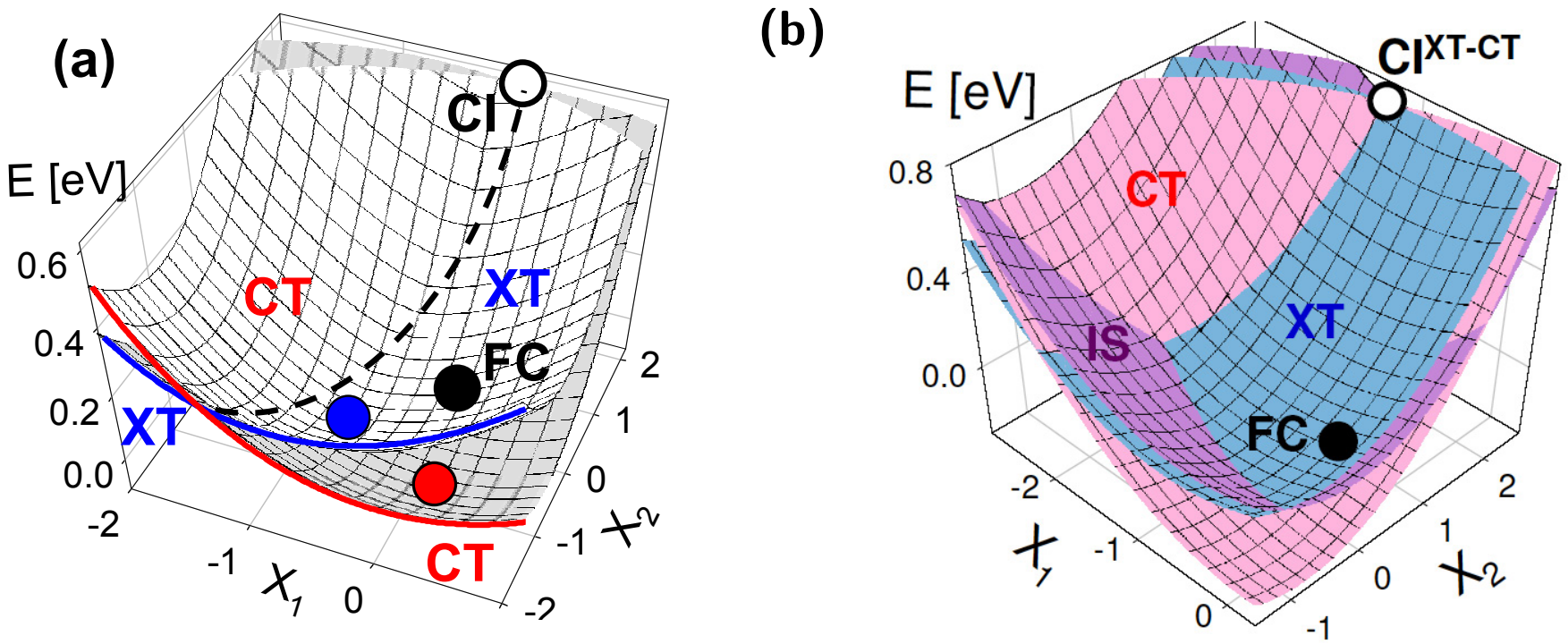
Tamura, Bittner, Burghardt, JCP **126**, 021103 (2007),
Pereverzev, Bittner, Burghardt, JCP **131**, 034104 (2009)

Nonadiabatic Coupling Region

representation in the branching space coordinates (X_1, X_2)

2-state XT/CT model

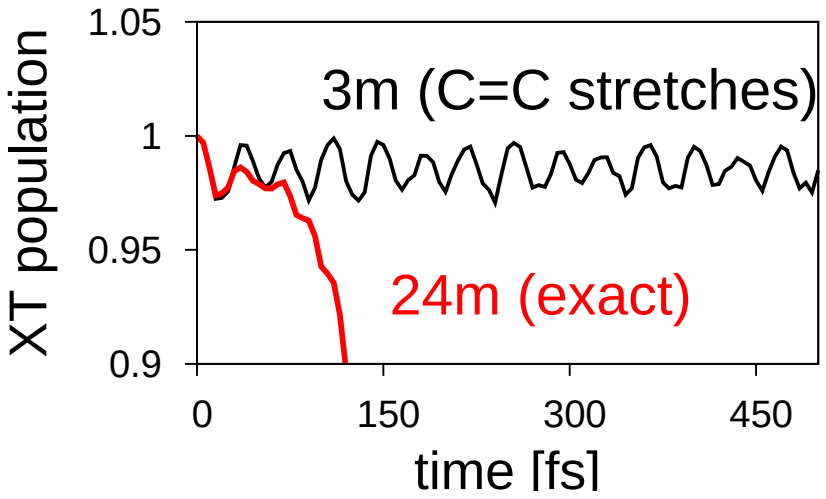
3-state XT/CT/IS model

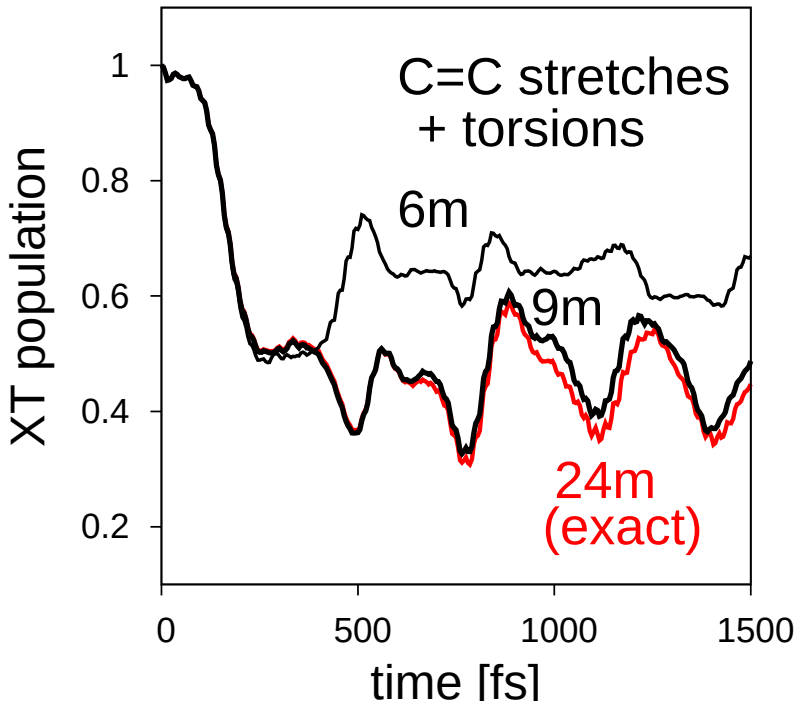


The dynamics happens "below" a conical intersection

2-State Model: Effective-Mode Dynamics (Cont'd)

Tamura, Bittner, Burghardt, JCP **126**, 021103 (2007), JCP **127**, 034706 (2007)



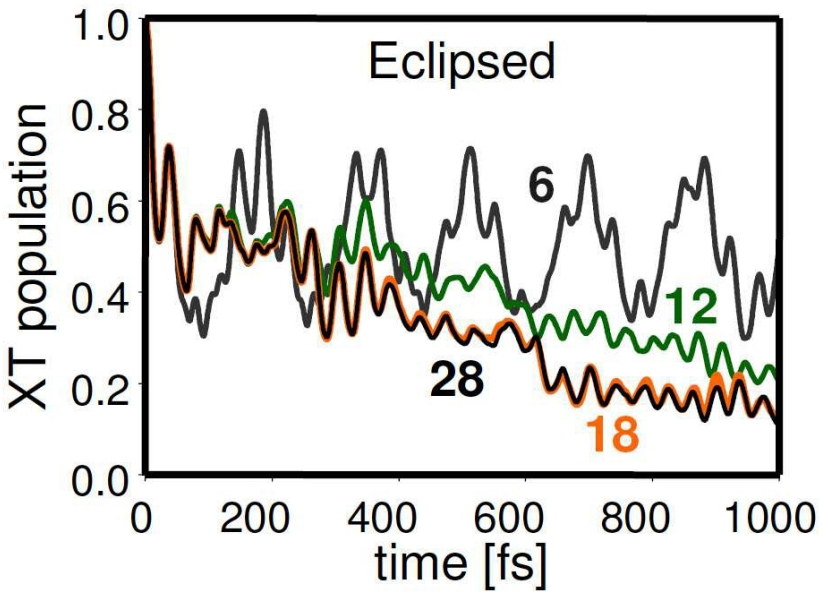


- 3 effective modes: not a good approximation on relevant time scale
- 6 effective modes: qualitatively correct ⟶ torsional modes are crucial!
- 9 effective modes: very close to exact 24-mode result

3-State Effective-Mode Model

Tamura, Ramon, Bittner, Burghardt, J. Phys. Chem. B 112, 495 (2008), Phys. Rev. Lett. 100, 107402 (2008)

$$H_{\text{eff}} = H_0 + \sum_{i=1}^{6} \begin{pmatrix} K_i^{(1)} X_i + D_i X_i & \Lambda_i^{(12)} X_i & \Lambda_i^{(13)} X_i \\ \Lambda_i^{(12)} X_i & K_i^{(2)} X_i - D_i X_i & \Lambda_i^{(23)} X_i \\ \Lambda_i^{(13)} X_i & \Lambda_i^{(23)} X_i & K_i^{(3)} X_i \end{pmatrix} + \text{bilinear couplings}$$



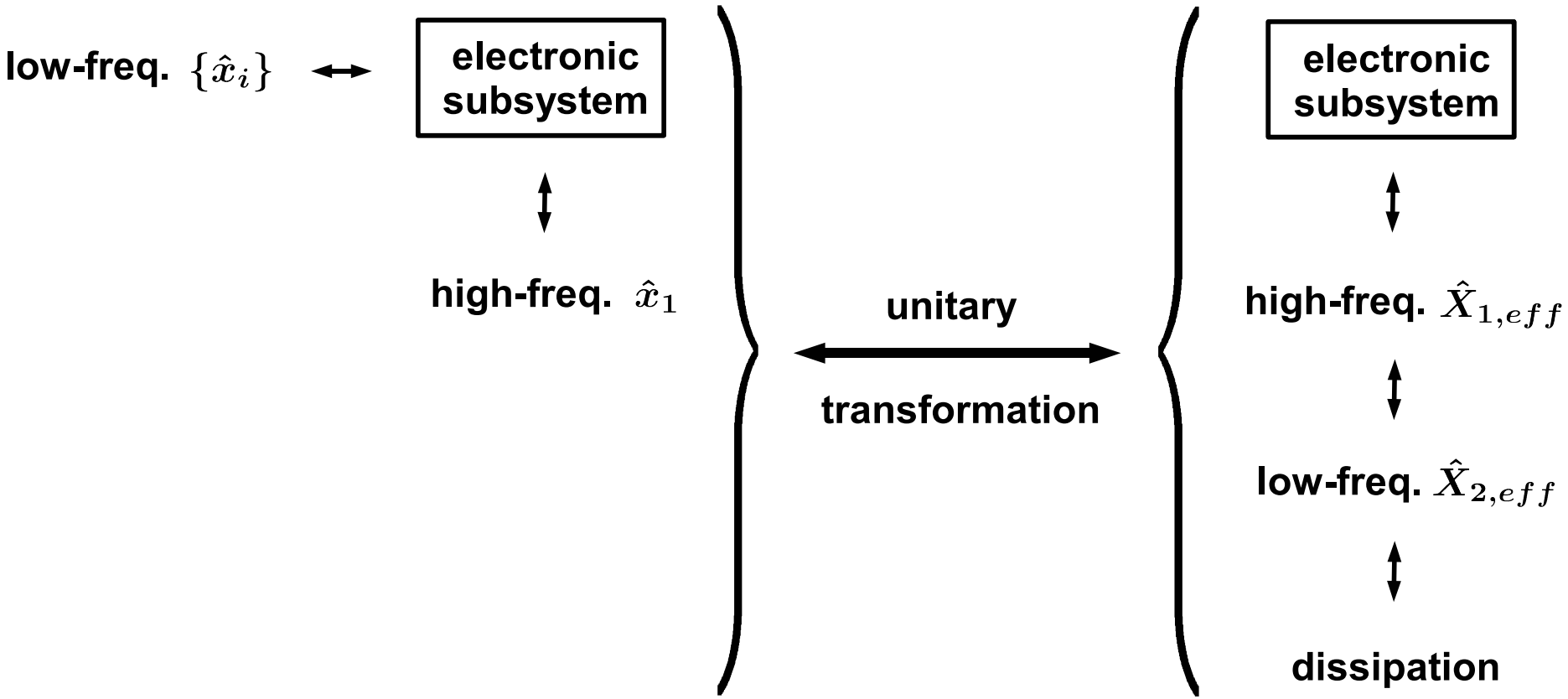
$X_1 \ldots X_6$: high-frequency

$X_7 \ldots X_{12}$: low-frequency

$X_{13} \ldots X_{18}$: high-frequency

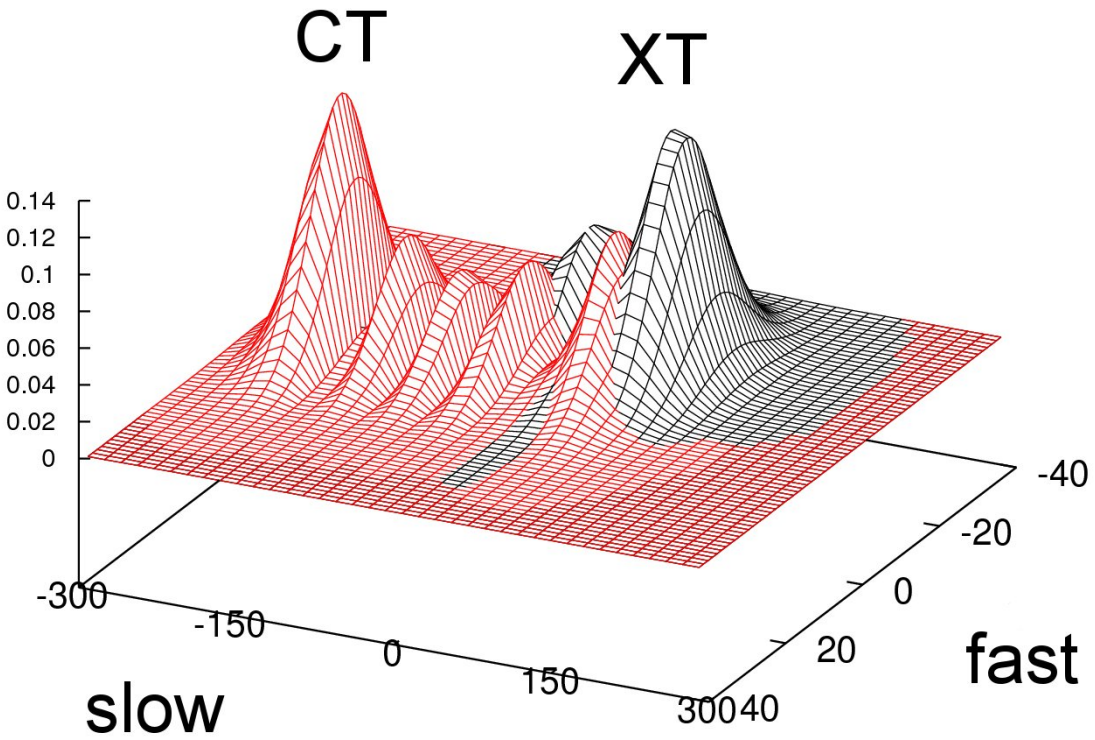
→ same pattern as 2-state!

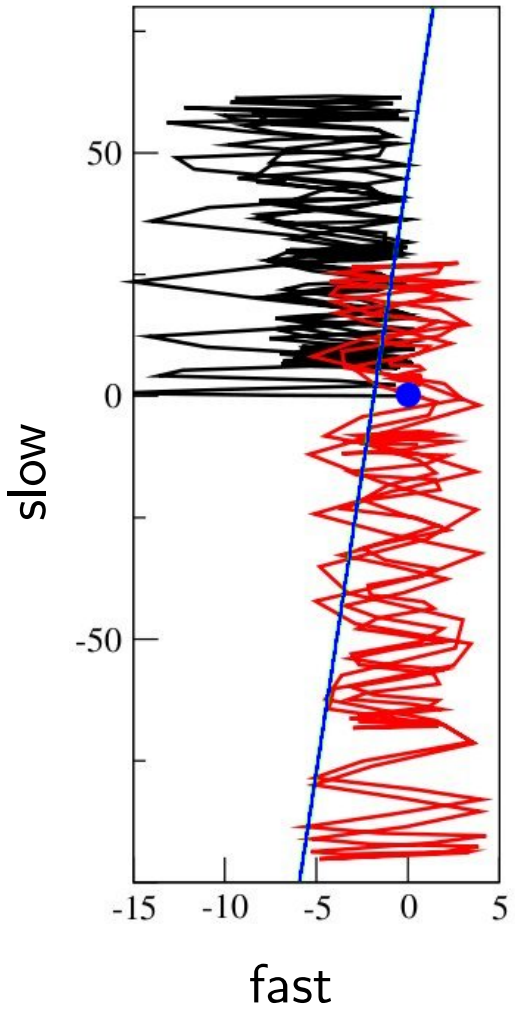
Minimal Model: High-Frequency Mode + Low-Frequency Bath



→ connections to models of electron transfer (Sumi-Marcus etc.)

Why Do the Torsional (Slow) Modes Play a Key Role?





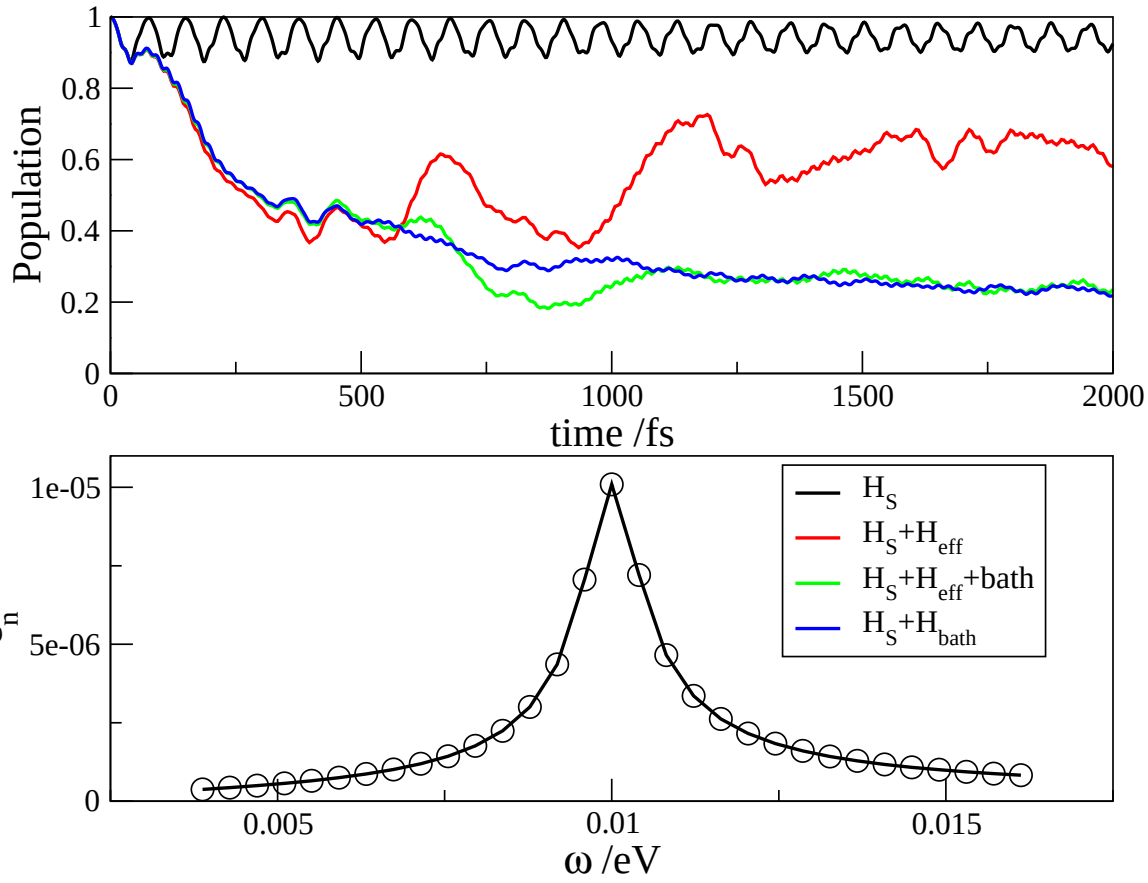
- XT-CT transition induced by low-frequency motion
- location of avoided-crossing seam decisive

Hughes, Christ, Burghardt, J. Chem. Phys., **131**, 024109 (2009)

High-Frequency Mode + Eff. Low-Frequency Mode + Dissipation

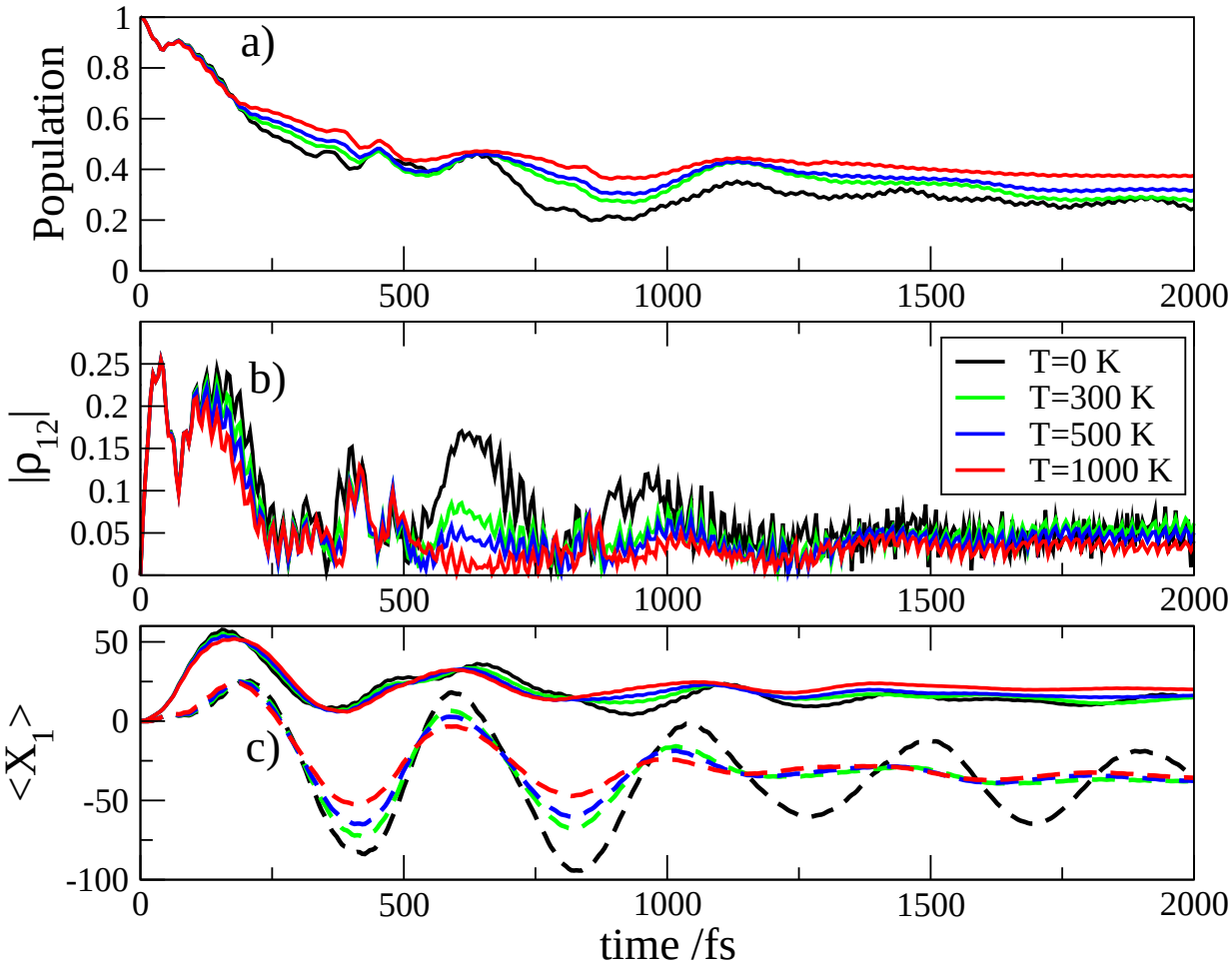
spectral density

$$J(\omega) = \frac{2\gamma\omega D^2}{(\Omega^2 - \omega^2)^2 + 4\gamma^2\omega^2}$$



- Brownian-oscillator picture: effective low-frequency mode + dissipation
- note: very strong friction can quench the transfer

Electronic Coherence Preserved on Short Time Scales



- electronic coherence evolves concerted with low-frequency motion

Bottom Line – Vibronic-Coupling Mechanism

- XT-CT transfer mechanism
  - high-frequency modes largely determine coupling to electronic subsystem but exhibit essentially diabatic dynamics
  - low-frequency modes induce XT–CT transition (cf. Bixon-Jortner theory: resonant decay via quasi-continuum of vibronic states)
- coherent nature of the transfer
  - collective modes dominate on short time scales
  - hierarchical electron-phonon model: sequential correlations
  - as a result, coherence can persist on the relevant transfer time scale
  - dissipation acts with a delay
- even though we've studied a model Hamiltonian, these conclusions should have some general validity

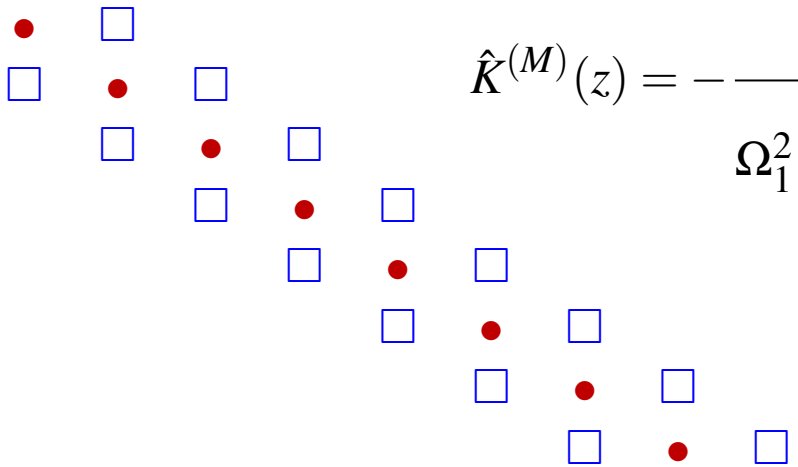
Topics

Spectral Densities

- generalized Brownian oscillator models
- construct a series of approximate spectral densities based upon HEP model
- continued fraction form (cf. Mori chain)

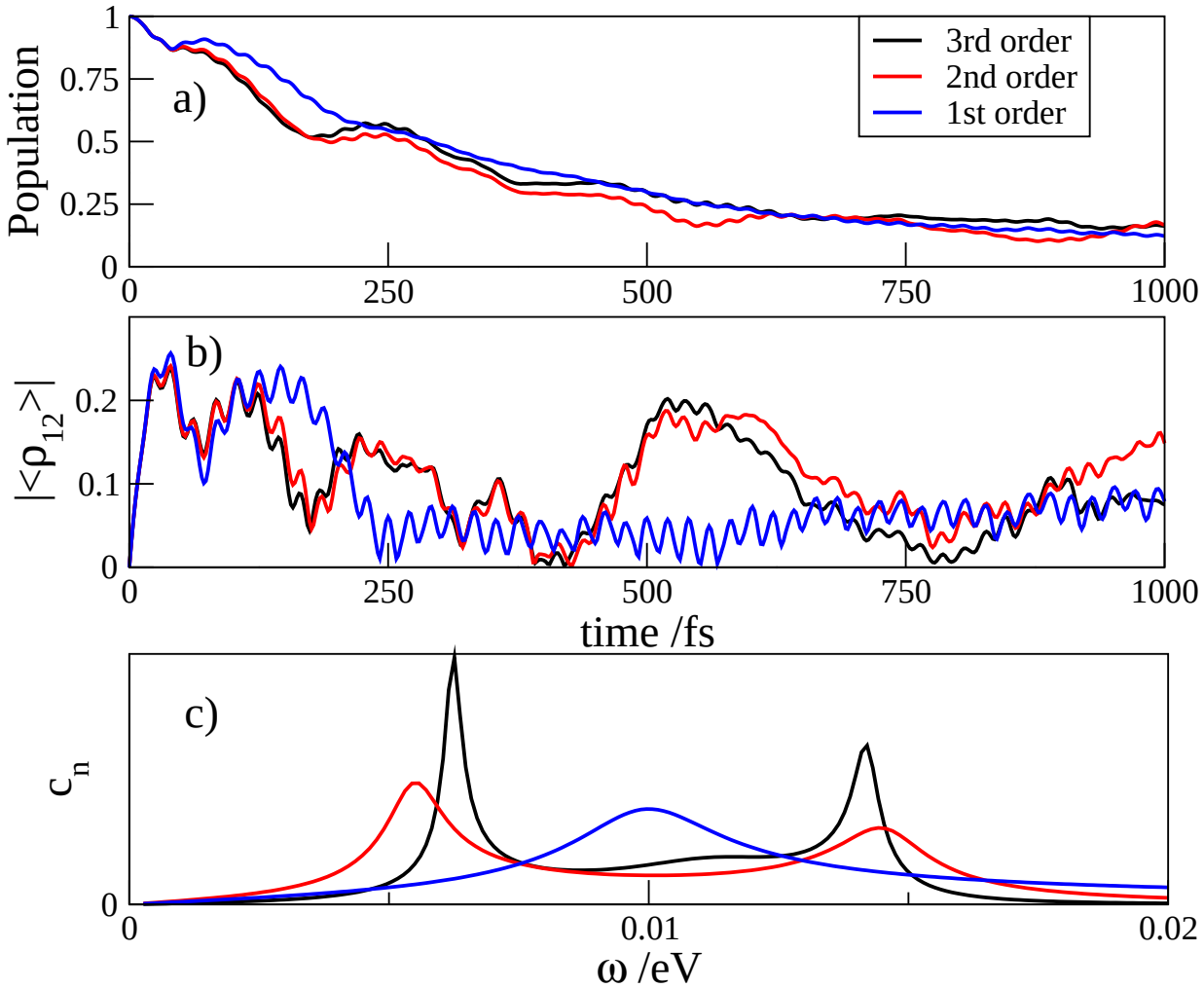
$$J^{(M)}(\omega) = \lim_{\varepsilon \to 0^+} \mathrm{Im}\, K^{(M)}(\omega - i\varepsilon)$$

Garg et al., J. Chem. Phys. 83, 4491 (1985), Hughes, Christ, Burghardt, J. Chem. Phys. 131, 024109 (2009)



$$\hat{K}^{(M)}(z) = -\cfrac{D^2}{\Omega_1^2 - z^2 - \cfrac{d_{1,2}^2}{\Omega_2^2 - z^2 - \cdots \cfrac{d_{M-2,M-1}^2}{\Omega_{M-1}^2 - z^2 - \cfrac{d_{M-1,M}^2}{\Omega_M^2 - z^2 + i2\gamma z}}}}$$

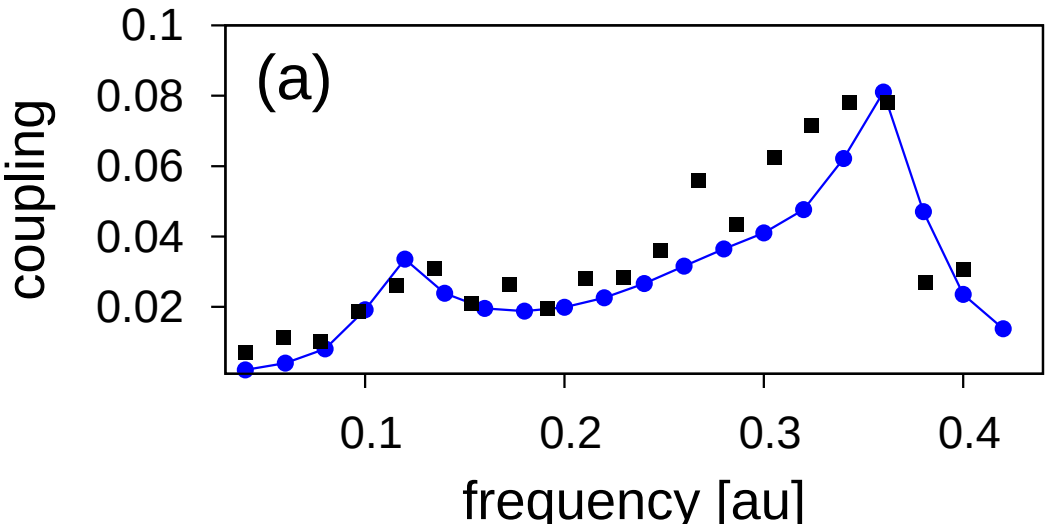
Hierarchy of Approximate Spectral Densities

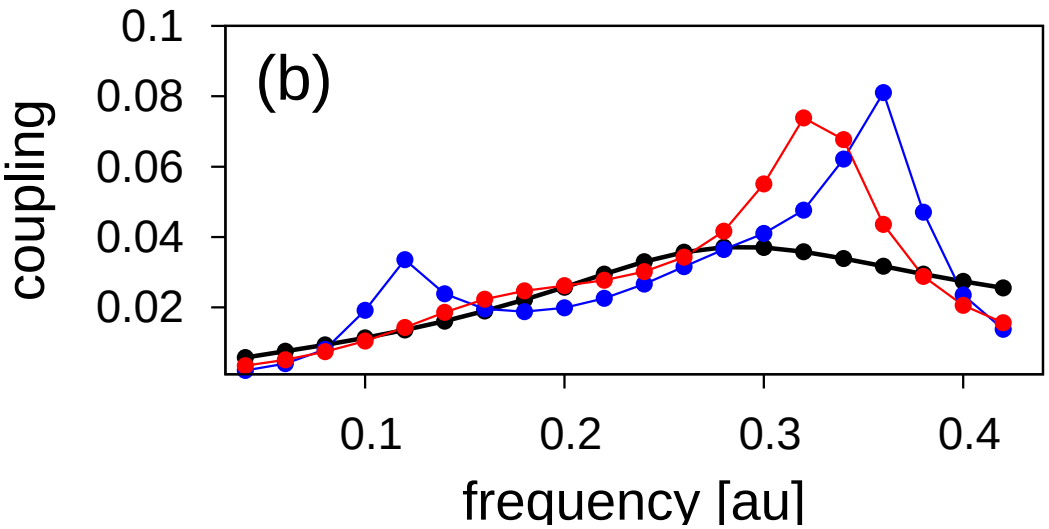


- approximation = Mth order Mori chain + Markovian closure
- this is equivalent to an Mth order spectral density
- the environment's spectral density is successively resolved as a function of time

Hughes, Christ, Burghardt, J. Chem. Phys. 131, 024109, 124108 (2009)

Spectral Densities, Cont'd

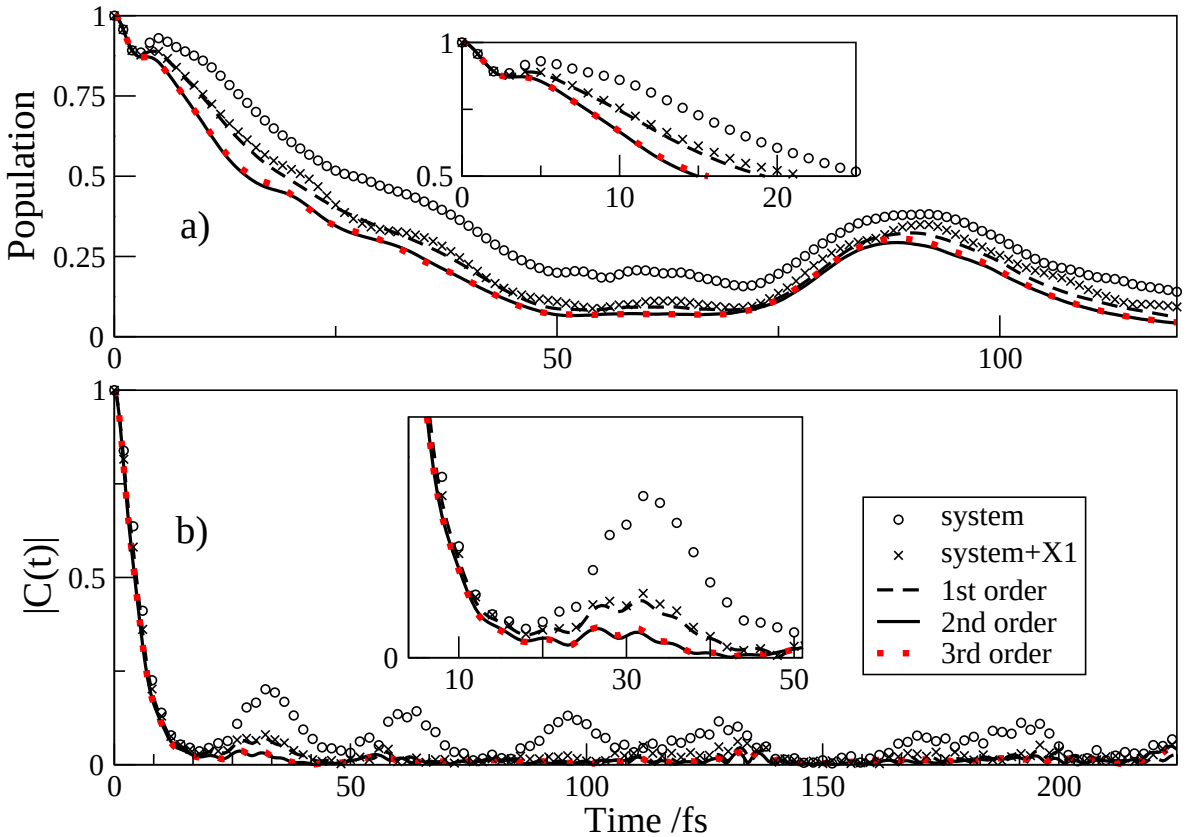




- fit an arbitrary spectral density to a Kth order Mori chain model
- construct successive Mth order, $M < K$, approximations
- here, $K = 3$, $M = 2$, $M = 1$
- dynamics according to Mth order Mori chain with Markovian closure

S_2-S_1 CoIn in Pyrazine: 4+20 Mode Model

tuning-mode bath, $H_{\rm int} = \sum_{i=1}^{N_B} \kappa_i^{(-)} x_i \sigma_z \equiv K X_1 \sigma_z$: 1 effective mode per order M



- 20-mode bath fitted to $K = 3$ Mori chain + Markovian closure
- construct successive Mth order, $M < K$, approximations
- here, $M = 2, 3$ in very good agreement

Coln's: Extension to Correlated Spectral Densities

$$\hat{H} = \hat{H}_0 + \hat{H}_{SB} = \hat{H}_0 + \sum_{i=1}^{N_B} \left[\kappa_{B,i}^{(+)} \hat{x}_{B,i} \hat{1} + \kappa_{B,i}^{(-)} \hat{x}_{B,i} \hat{\sigma}_z + \lambda_{B,i} \hat{x}_{B,i} \hat{\sigma}_x \right]$$

$$\boldsymbol{J}(\omega) = -\sum_{n=1}^{N_B} \begin{pmatrix} -\kappa_n^{(-)2} & -i\kappa_n^{(-)}\kappa_n^{(+)} & \kappa_n^{(-)}\lambda_n \\ i\kappa_n^{(-)}\kappa_n^{(+)} & -(\kappa_n^{(-)2} + \lambda_n^2) & -i\lambda_n\kappa_n^{(+)} \\ \kappa_n^{(-)}\lambda_n & i\lambda_n\kappa_n^{(+)} & -\lambda_n^2 \end{pmatrix} \delta(\omega - \omega_{B,n})$$

- $\boldsymbol{J}$ written in the basis of subsystem Heisenberg operators $\{\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\}$
- three system-bath coupling mechanisms (tuning, coupling, shift)
- diagonal vs. cross-correlated spectral densities

Connection to Reduced-Dynamics Approach

- spectral densities are related to correlation functions,

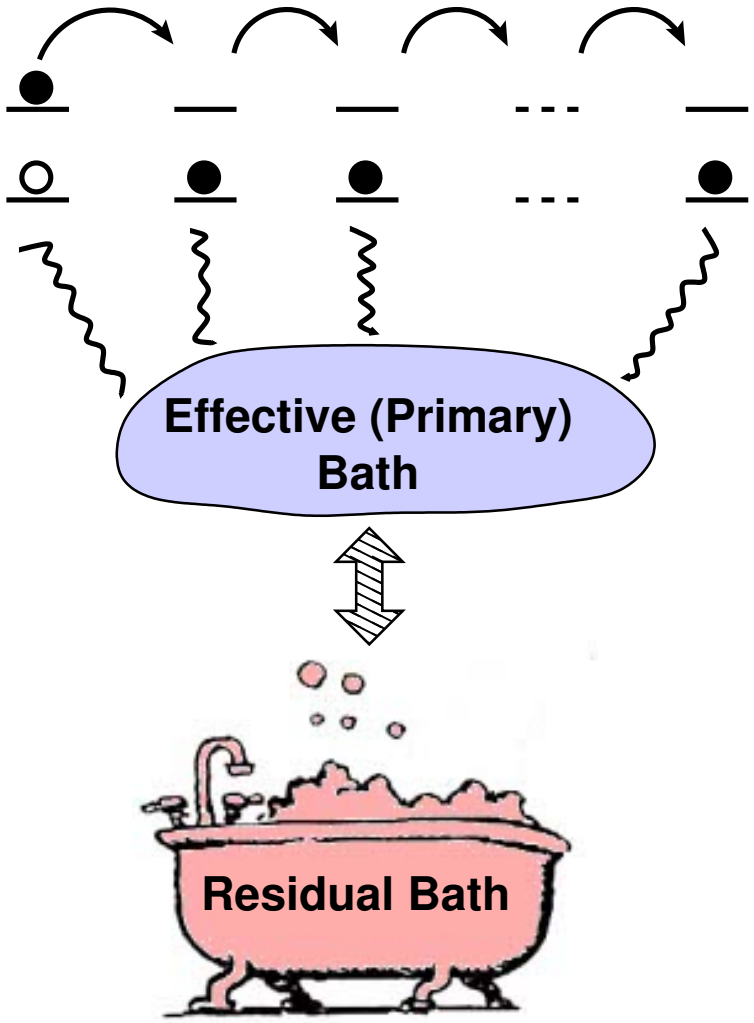
$$\mathscr{C}^{(2,2n)}(t) = \int_{-\infty}^{\infty} d\omega \; J_{\text{eff}}^{(M=n+1)}(\omega) \frac{\exp(-i\omega t)}{\exp\left(\frac{\omega}{2k_B T}\right) - 1}$$

- correlation functions appear in a 2nd-order master equation for the subsystem density operator, here for the interaction $\hat{H}_{SB} = \sum_i^N c_i \hat{x}_i \hat{\sigma}_z \equiv D\hat{X}_1 \hat{\sigma}_z$,

$$\begin{aligned}\frac{\partial \hat{\rho}_S}{\partial t} &= -i\hat{\hat{L}}_S(t)\hat{\rho}_S(t) - \int_{t_0}^{t} dt' \left[\hat{\sigma}_z(t), \hat{\sigma}_z(t')\hat{\rho}_S(t')\right] \mathscr{C}_B^{(2,k)}(t,t';t_0) \\ &\quad + \int_{t_0}^{t} dt' \left[\hat{\sigma}_z(t), \hat{\rho}_S(t')\,\hat{\sigma}_z(t')\right] \mathscr{C}_B^{(2,k)}(t',t;t_0)\end{aligned}$$

- beyond 2nd order, memory kernel can be developed in a double perturbation theory, w.r.t. the interaction strength and the Mori-chain order

Transfer Processes in Fluctuating Environments



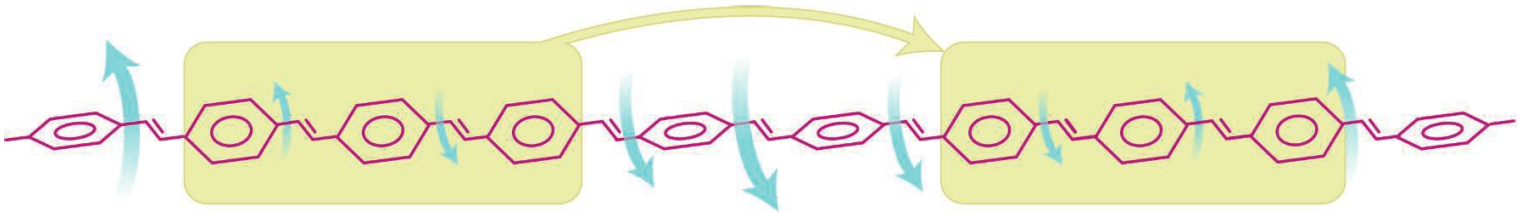
Martelli & Hughes & Burghardt, to be submitted

Excitation transfer vs. trapping
& dissipation & decoherence

- transition between coherent and non-coherent (Förster) transfer
- long-lived excitonic coherences?
- site-local vs. shared (correlated) modes: significant differences
- extend to include thermal gradients

Bittner, Goj, Burghardt, Chem. Phys., in press.

Exciton Migration & Long-Lived Coherences

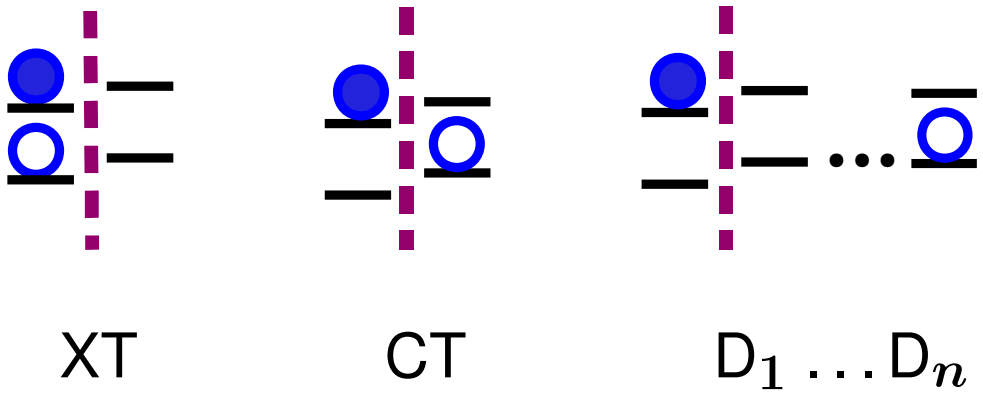


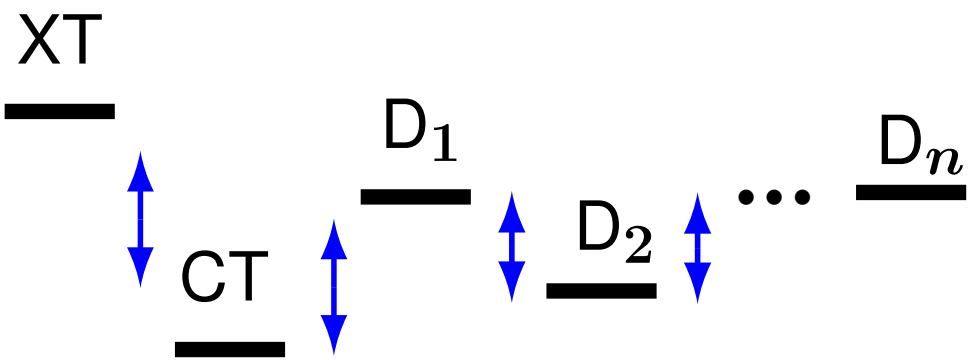
Collini, Scholes, Science 323, 369 (2009), Bredas & Silbey, Science 323, 348 (2009)

$$V^{\text{lin}} = \sum_i \begin{pmatrix} \kappa_i^{(1)} x_i & \lambda_i^{(12)} x_i & & & \\ \lambda_i^{(12)} x_i & \kappa_i^{(2)} x_i & \lambda_i^{(23)} x_i & & \\ & \lambda_i^{(23)} x_i & \kappa_i^{(3)} x_i & \lambda_i^{(34)} x_i & \\ & & \lambda_i^{(43)} x_i & \kappa_i^{(3)} x_i & \lambda_i^{(45)} x_i \\ & & & \ddots & \ddots & \ddots \end{pmatrix}$$

- coherent "surfing" rather than Förster-type hopping?
- role of site-local vs. shared (correlated) modes
- do shared modes contribute to the conservation of electronic coherence?

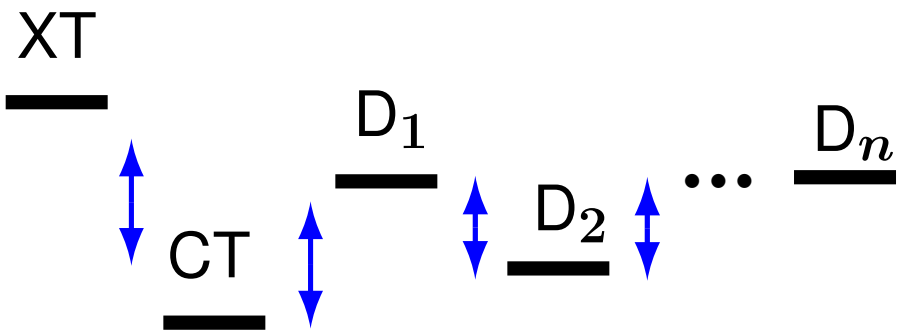
Heterojunction Dynamics: Charge Separation + Photocurrent



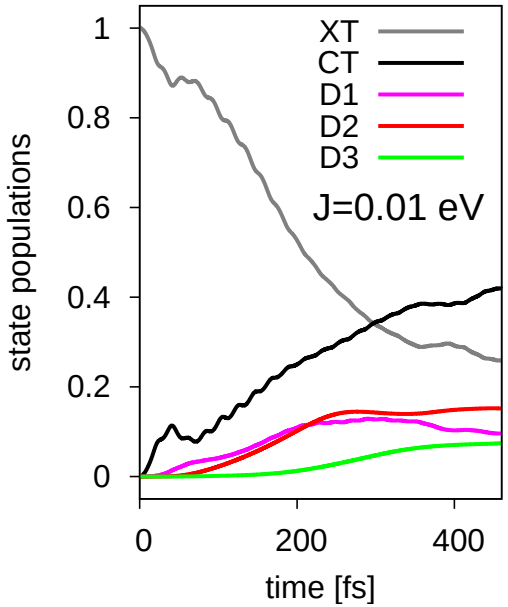


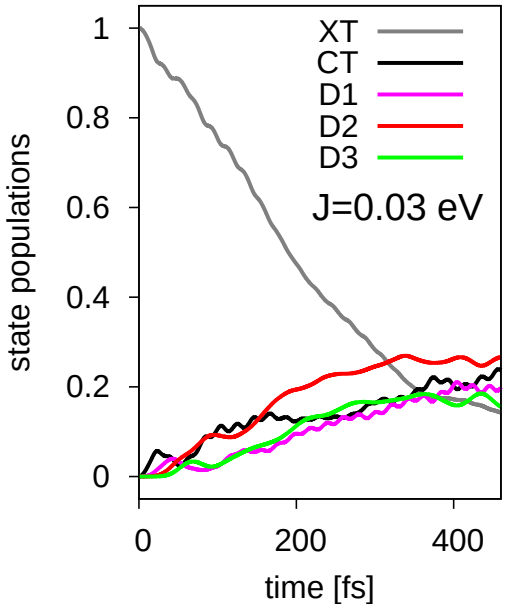
- tuning by low-frequency modes
- tuning by conformational fluctuations
- both factors could on average ensure transfer efficiency

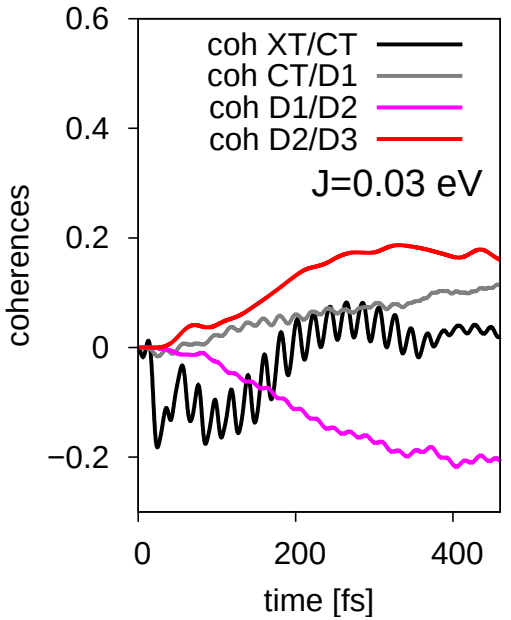
Detailed Picture of Exciplex Break-Up



- 5 states: XT, CT, $D_1 \ldots D_3$
- 4 effective tuning modes
- 30-mode residual bath







Summary

1. Molecular-Level Approaches for Extended Systems
   - charge transfer, excitation energy transfer
   - combine model Hamiltonians & electronic structure information
   - alternative/complementary to QM/MM + on-the-fly approaches

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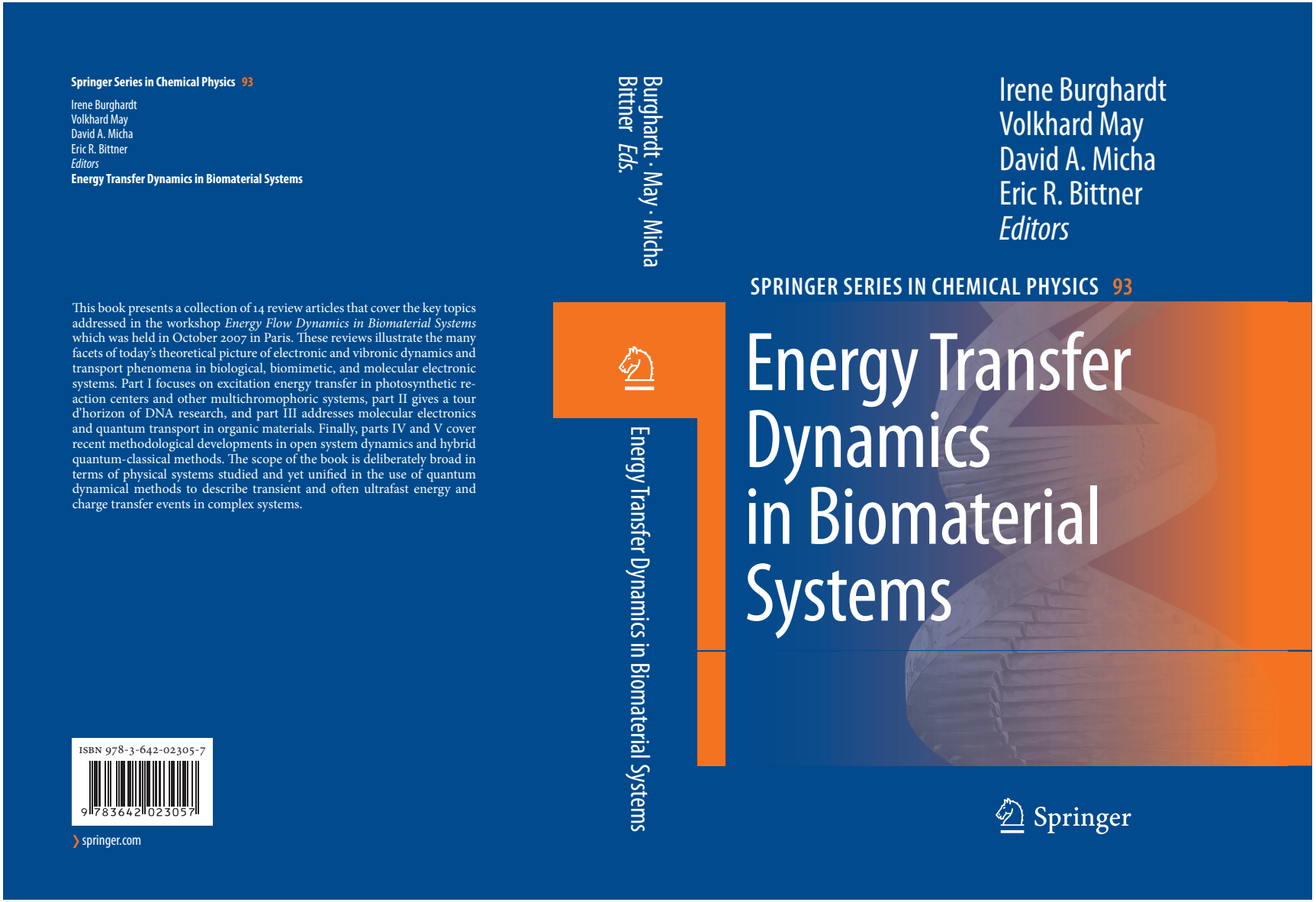
Just Appeared



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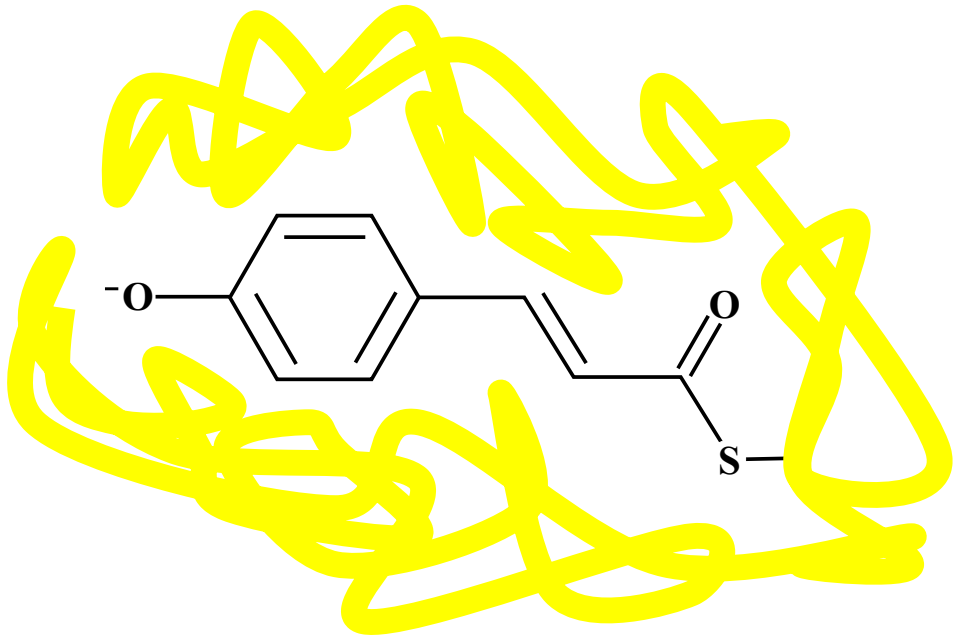
Appendix

Quantum Solute + Classical Mesoscopic Environment

Quantum-Classical, Multi-Scale Approach

quantum solute + classical mesoscopic environment



- e.g., photoswitches in solution, EET in polar/polarizable environments, ...
- complementary approach to QM/MM-MD type methods

Quantum-Classical Liouville Equation

quantum solute + classical mesoscopic environment

- quantum-classical Liouville equation, for $\hat{f}_{\mathbf{rp}} = \sum_{nm} f_{nm}(\mathbf{r},\mathbf{p})|n\rangle\langle m|$,

$$\frac{\partial \hat{f}_{\mathbf{rp}}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{\mathbf{rp}}, \hat{f}_{\mathbf{rp}}] + \frac{1}{2}\left(\{\hat{H}_{\mathbf{rp}}, \hat{f}_{\mathbf{rp}}\} - \{\hat{f}_{\mathbf{rp}}, \hat{H}_{\mathbf{rp}}\} \right)$$

- propagate either the single-particle phase-space functions $f_{nm}(\mathbf{r},\mathbf{p},t)$
- or propagate the corresponding hydrodynamic quantities: local density $\rho_{nm}(\mathbf{r},t)$, current density $\boldsymbol{g}_{nm}(\mathbf{r},t)$[1]

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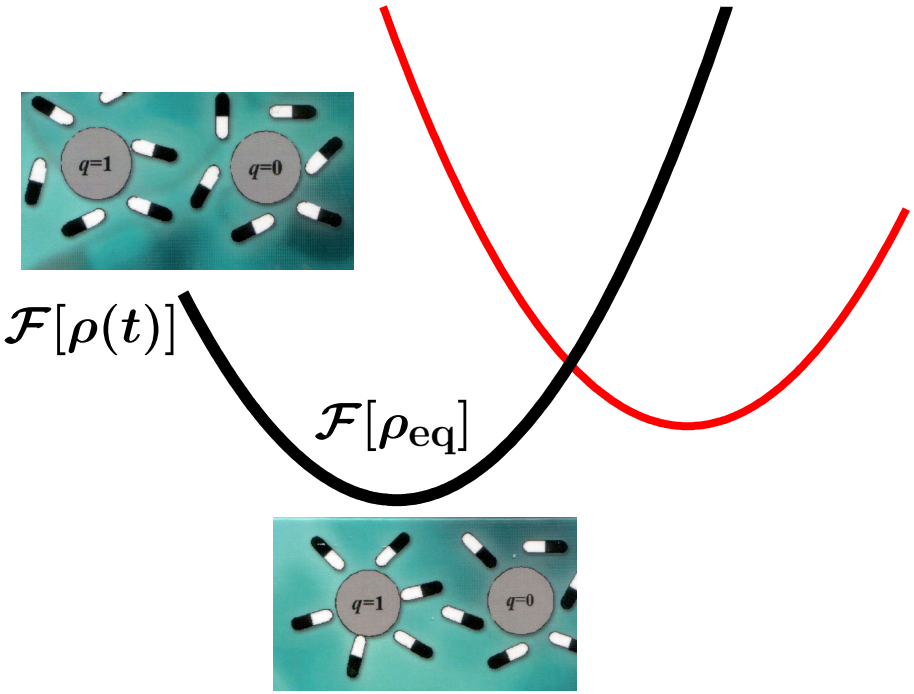
[1] local density: $\rho_{nm}(\mathbf{r},t) = \int d\mathbf{p} f_{nm}(\mathbf{r},\mathbf{p},t)$, current: $\boldsymbol{g}_{nm}(\mathbf{r},t) = \int d\mathbf{p}\, \mathbf{p} f_{nm}(\mathbf{r},\mathbf{p},t)$

Classical Dynamical Density Functional Theory (DDFT)

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = -\frac{1}{m}\nabla_r \cdot \boldsymbol{g}(\mathbf{r},t)$$

$$\frac{\partial}{\partial t}\boldsymbol{g}(\mathbf{r},t) = -\rho(\mathbf{r},t)\nabla_{\mathbf{r}}\frac{\delta\mathscr{F}[\rho]}{\delta\rho} + \Xi_{\text{diss}}[\boldsymbol{g}]$$



- coupled equations for local density $\rho(\mathbf{r},t)$ and current density $\boldsymbol{g}(\mathbf{r},t)$
- free energy functional $\mathscr{F}[\rho(\mathbf{r},t)] = kT\ln\Lambda^3\rho(\mathbf{r},t) - \int d\mathbf{r}' C_2(\mathbf{r}-\mathbf{r}')\delta\rho(\mathbf{r}',t)$
- transpose to quantum-classical setting: coupled equations for $\{\rho_{nm}, \boldsymbol{g}_{nm}\}$: dynamics on coupled Marcus parabolas!

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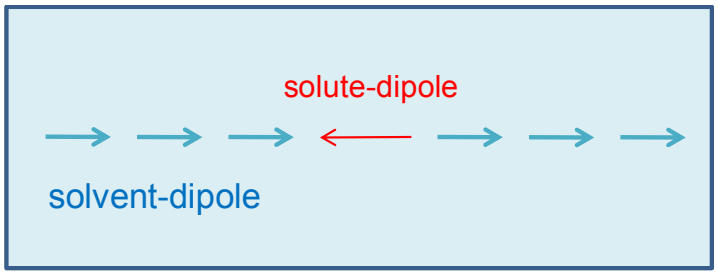
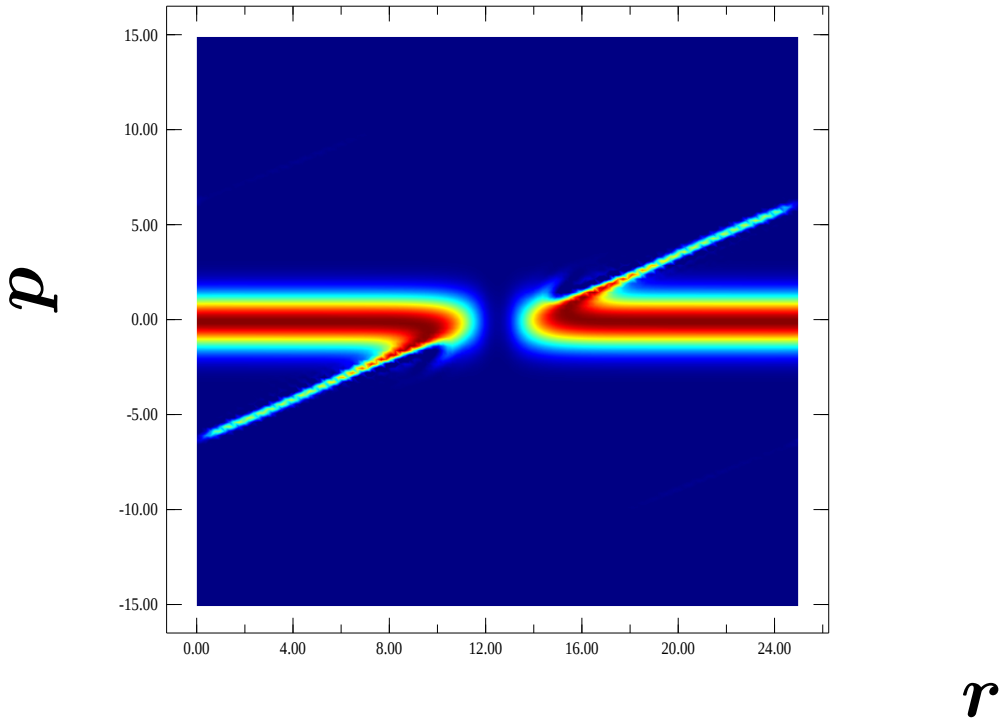
Translational Solvation in 1D: Classical



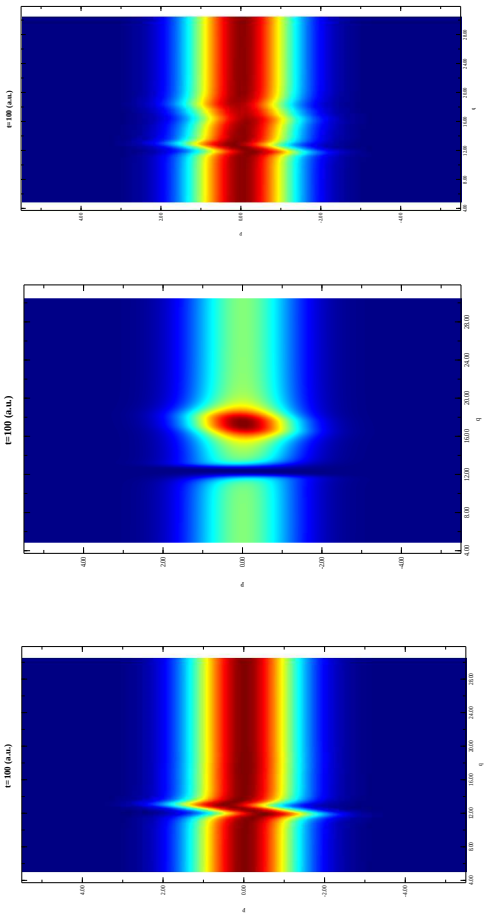
1D model: pure translational motion

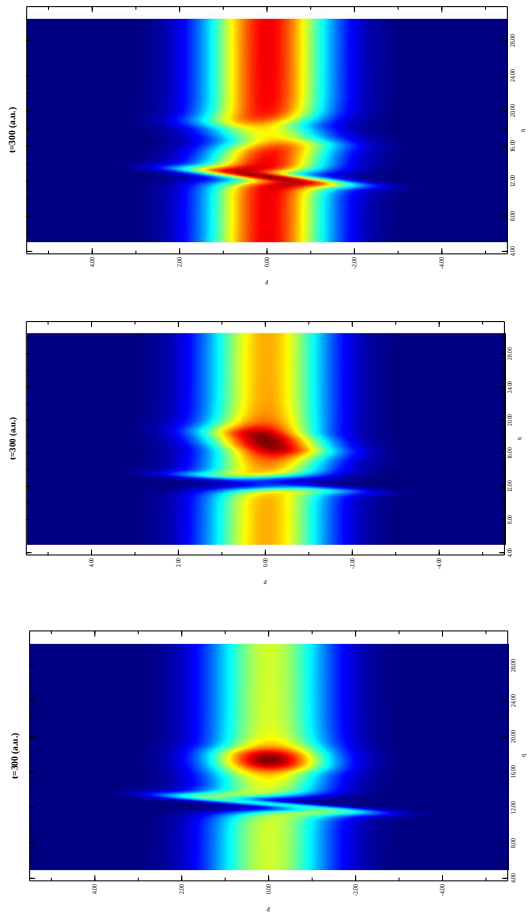


phase-space density $f(\boldsymbol{r},\boldsymbol{p},t)$

- initial condition: homogeneous density $f(\boldsymbol{r},\boldsymbol{p},0) = \rho_0 \exp(-\boldsymbol{p}^2/4mT)$
- repulsive electrostatic solute-solvent interaction: "dip" in solvent density

Translational Solvation in 1D: Quantum-Classical (2-State)





$\boldsymbol{r}$

$\boldsymbol{p}$

t = 100 fs

t = 300 fs

population $f_{22}(\boldsymbol{r},\boldsymbol{p},t)$

coherence $f_{12}(\boldsymbol{r},\boldsymbol{p},t)$

population $f_{11}(\boldsymbol{r},\boldsymbol{p},t)$

- initial condition: homogeneous density for state 1: $f_{11}(\boldsymbol{r},\boldsymbol{p},0) = \rho_0(\boldsymbol{r}) f_{\mathrm{M}}(\boldsymbol{p})$

Hughes, Ramanathan, Burghardt, to be submitted