Non-adiabatic Dynamics

Trajectory Surface Hopping

And Beyond

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Beijing, 05, 2024

Life Trajectory (Nonlinear Dynamics)

**Lanzhou→ Hefei → Beijing →
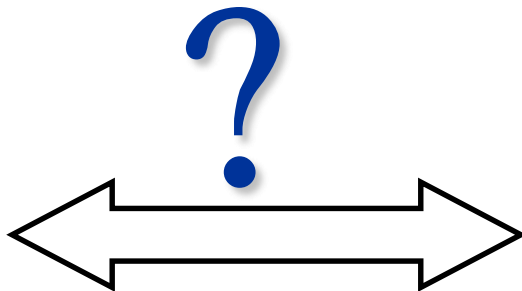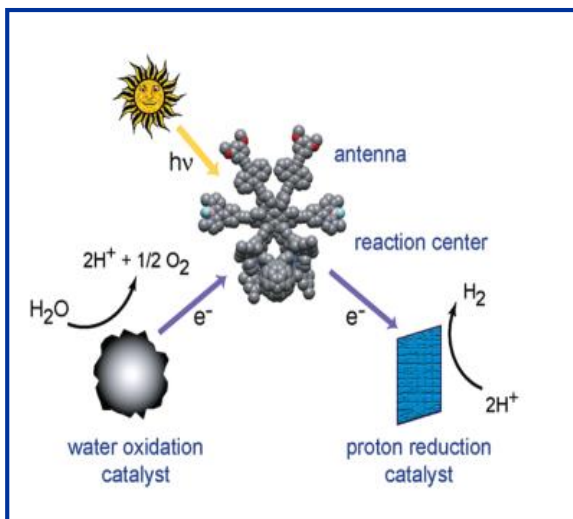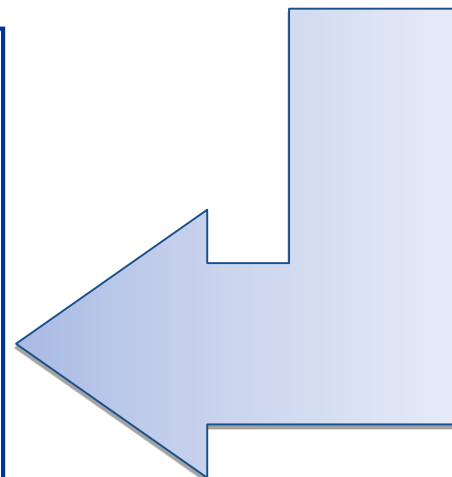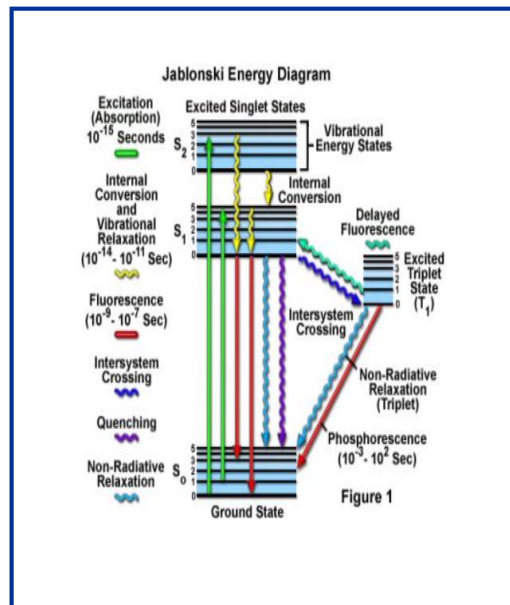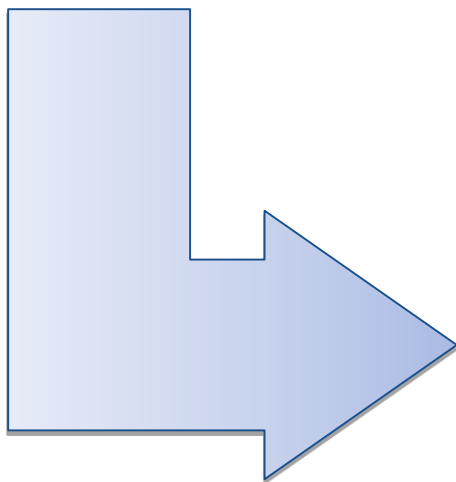Munich → Muelheim an der Ruhr
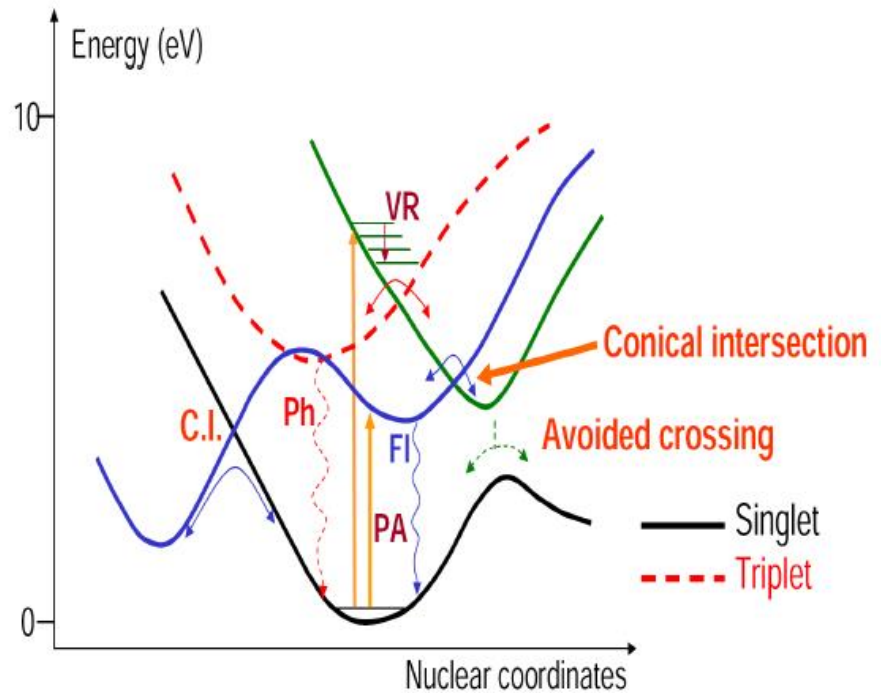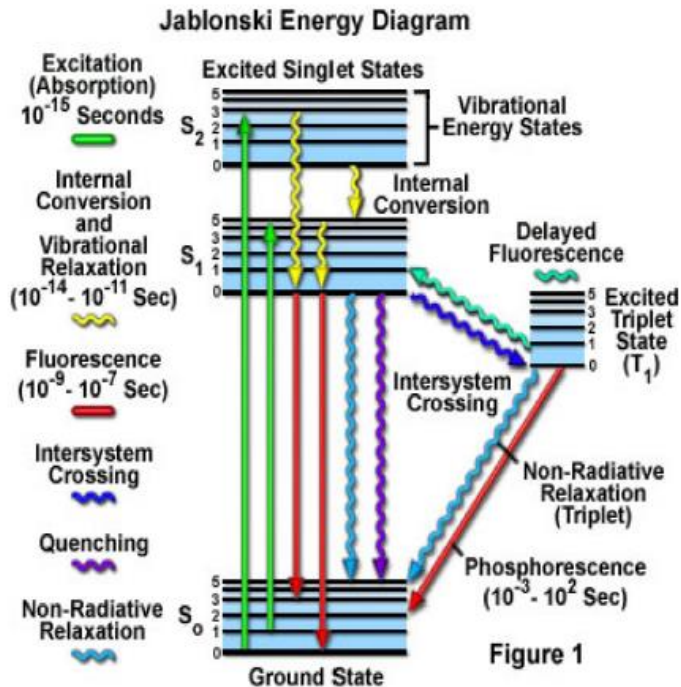→ Qingdao → Guangzhou**
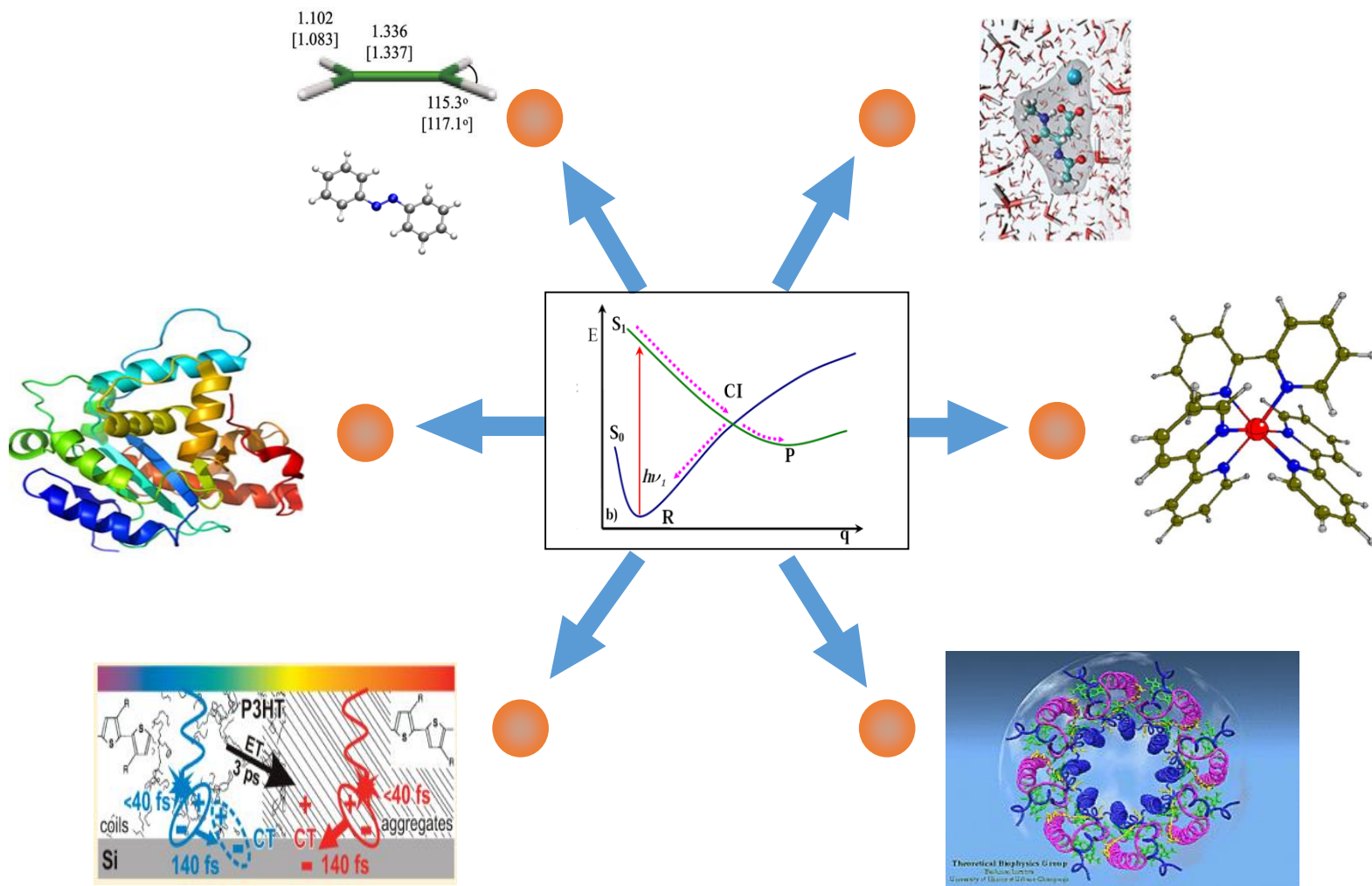
Part I:
Introduction to
Nonadiabatic Dynamics
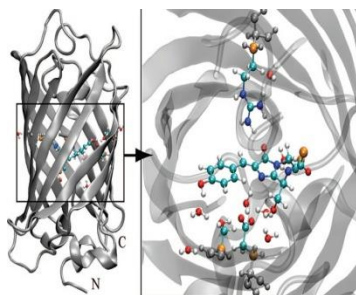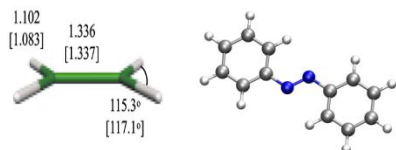
Introduction

Photophysics and photochemistry

Jablonski Energy Diagram

Figure 1

Nonadiabatic dynamics

Nonadiabatic dynamics

Conical intersections

Intersystem crossing
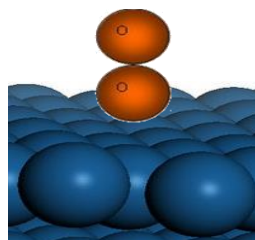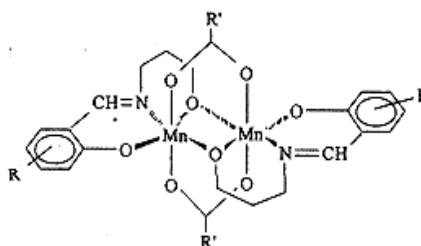
Avoid crossings
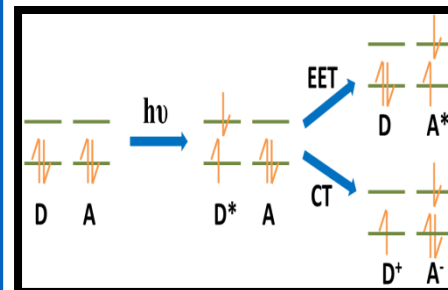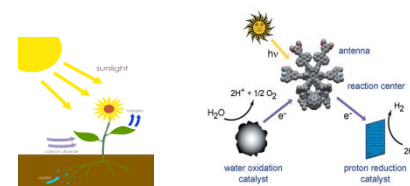
Adiabatic representations

Adiabatic basis: eigenstates of electronic Hamiltonian

$$\hat{H}_e(\mathbf{R_n})\Phi_i^a(\mathbf{r_e}, \mathbf{R_n}) = V_i^a(\mathbf{R_n})\Phi_i^a(\mathbf{r_e}, \mathbf{R_n}),$$

Born-Oppenheimer-Huang expansions

$$\Psi(\mathbf{r_e}, \mathbf{R_n}) = \sum_i \Phi_i^a(\mathbf{r_e}, \mathbf{R_n})\chi_i^a(\mathbf{R_n}).$$

Coupled equations for nuclear motions

$$[-\frac{1}{2}\nabla^2 + V_i(\mathbf{R_n})]\chi_i^a(\mathbf{R_n}) - \frac{1}{2}\sum_j [2\vec{F}_{ij}^a(\mathbf{R_n}) \cdot \nabla + G_{ij}^a(\mathbf{R_n})]\chi_j^a(\mathbf{R_n})$$

$$= E\chi_i^a(\mathbf{R_n}),$$

Nonadiabatic couplings
(Kinetic couplings)

$$\vec{F}_{ij}^a(\mathbf{R_n}) = \langle i(\mathbf{R_n})| \nabla |j(\mathbf{R_n})\rangle. \qquad G_{ij}^a(\mathbf{R_n}) = \langle i(\mathbf{R_n})| \nabla^2 |j(\mathbf{R_n})\rangle.$$

$$\vec{F}_{ij}^a = \frac{\langle i(\mathbf{R_n})| \nabla\hat{H}_e(\mathbf{r_e}, \mathbf{R_n}) |j(\mathbf{R_n})\rangle}{V_i^a(\mathbf{R_n}) - V_j^a(\mathbf{R_n})}$$

At conical intersections the coupling goes to infinity

Diabatic representations

Diabatic basis: smooth electronic functions of nuclear geometry

$$\Psi(\mathbf{r_e}, \mathbf{R_n}) = \sum_i \Phi_i^d(\mathbf{r_e}, \mathbf{R_n})\chi_i^d(\mathbf{R_n}),$$

Strict diabatic basis: nonadiabatic (kinetic) couplings vanish

$$\vec{F}_{ij}^d(\mathbf{R_n}) = 0,$$

Coupled equations for nuclear motions

$$-\frac{1}{2}\nabla^2\chi_i^d(\mathbf{R_n}) + \sum_j V_{ij}(\mathbf{R_n})\chi_j^d(\mathbf{R_n}) = E\chi_i^d(\mathbf{R_n}).$$

Diabatic couplings
(Potential couplings)

Concept of conical intersection
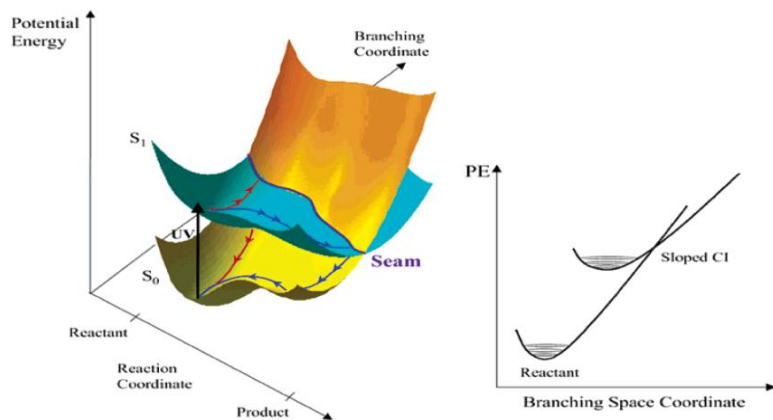
$$\psi = c_1\phi_1 + c_2\phi_2,$$

$$\begin{bmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0,$$

$$H_{11} = H_{22},$$

$$H_{12} = H_{21} = 0.$$
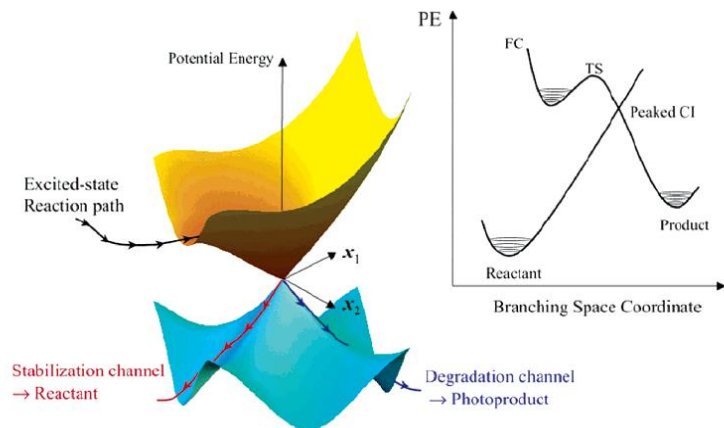
$$\begin{bmatrix} W + h_1 x - E & ly \\ ly & W + h_2 x - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0.$$

[1] Conical intersections, edited by W. Domcke, D. R. Yarkony,H. Koeppel, World Scuientific, (2004)
[2] M. J. Paterson, et. al. , *J. Phys. Chem. A*, **109,** 7527 (2005).

Adiabatic .vs. diabatic representations
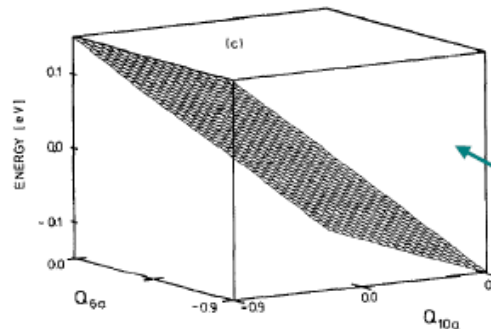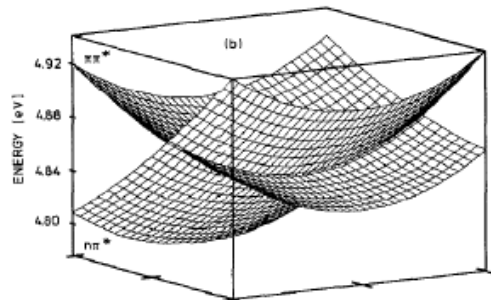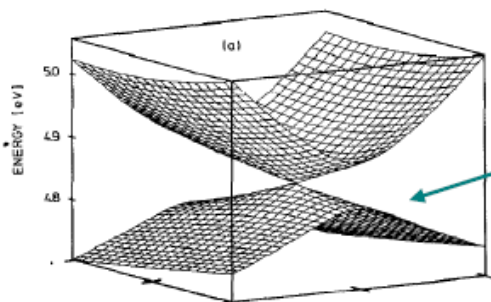
Adiabatic
representations
Nonsmooth potential
Nonsmooth
wavefunctions
Kinetic couplings F_{ij}
E2-E1=0 F_{ij} -> infinity

Diabatic
representations
Smooth potential
Smooth wavefunctions
Potential couplings V_{ij}
No singularity

Adiabatic .vs. diabatic representations
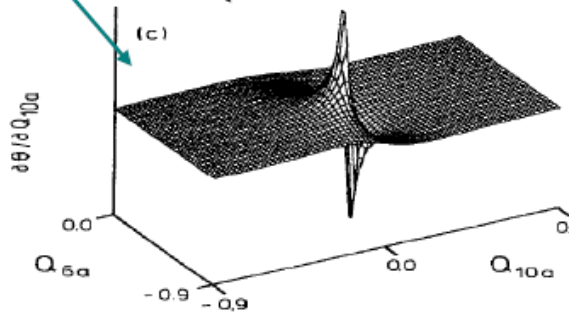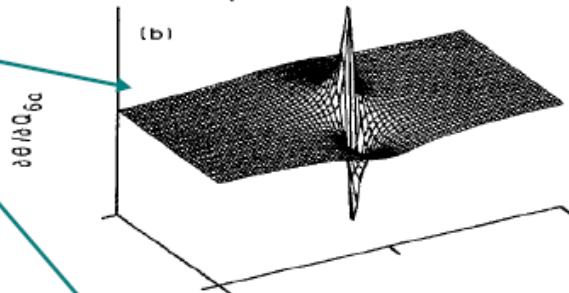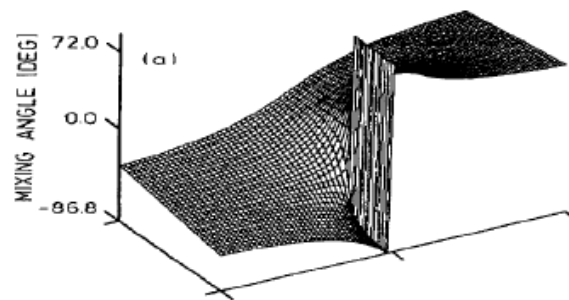
Adiabatic representations	Diabatic representations
Nonsmooth Electronic wavefunctions Nonsmooth dipole (transition) moments	Smooth Electronic wavefunctions Smooth dipole (transition) moments
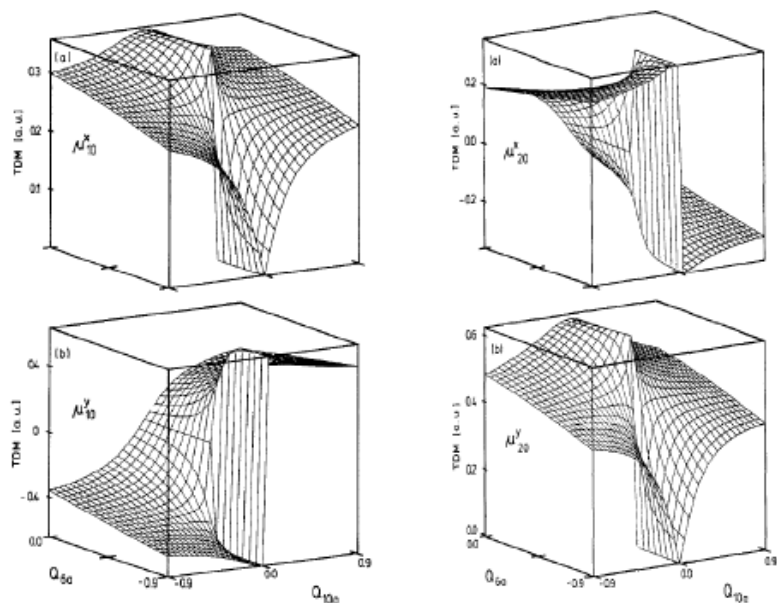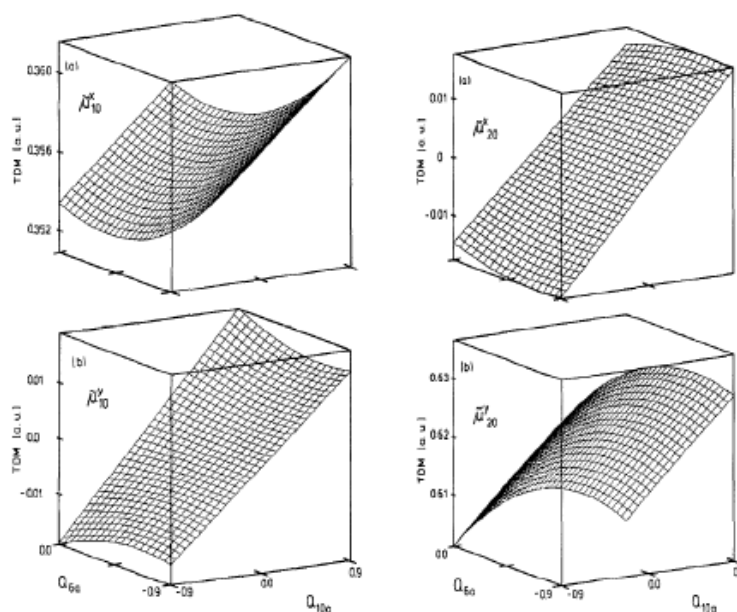
Books

Conical intersections
Edited by
Wolfgang Domcke
David. R. Yarkony
Horst Koeppel

Wolfgang Domcke
David R Yarkony
Horst Köppel
Editors

CONICAL
INTERSECTIONS

ELECTRONIC STRUCTURE,
DYNAMICS & SPECTROSCOPY

Advanced Series in Physical Chemistry Vol. **15**
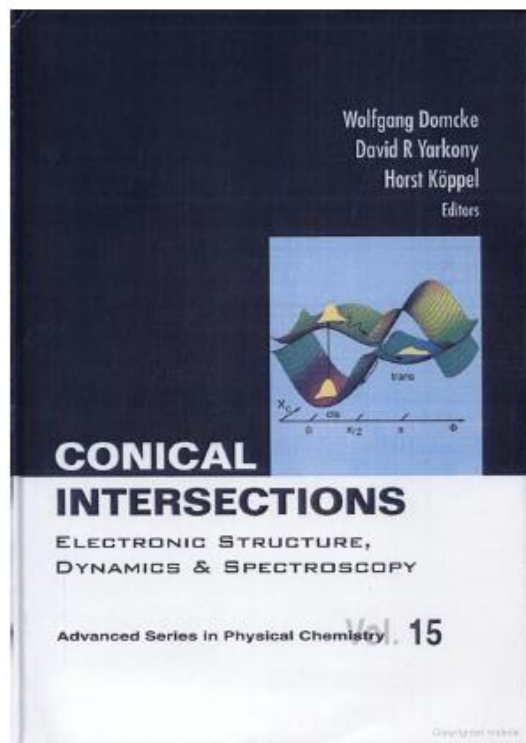
Beyond
Born-Oppenheimer

Michael Baer

WILEY

BEYOND
BORN–OPPENHEIMER
Electronic Noradiabatic Coupling Terms
and Conical Intersections

MICHAEL BAER
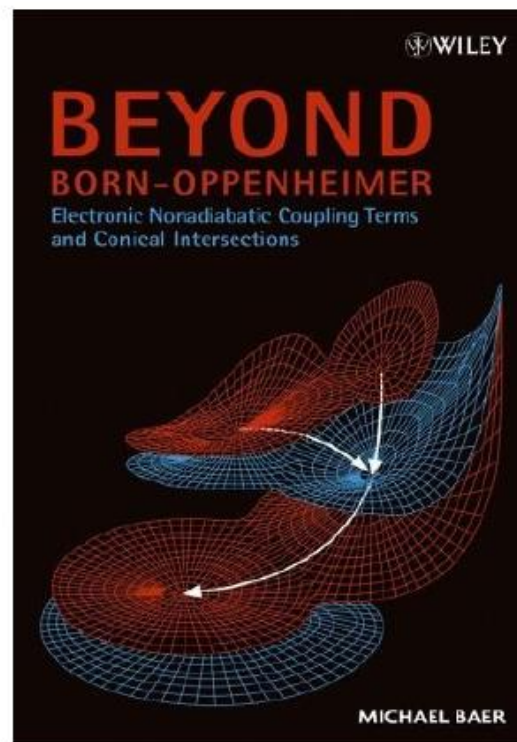
We should remember:

Edward Teller   *John Von Neumann* *Eugene Wigner*

Nonadiabatic dynamics
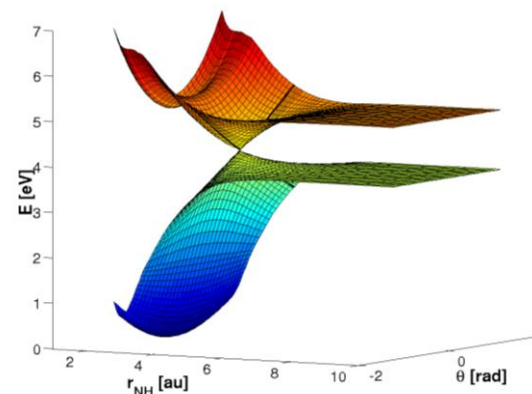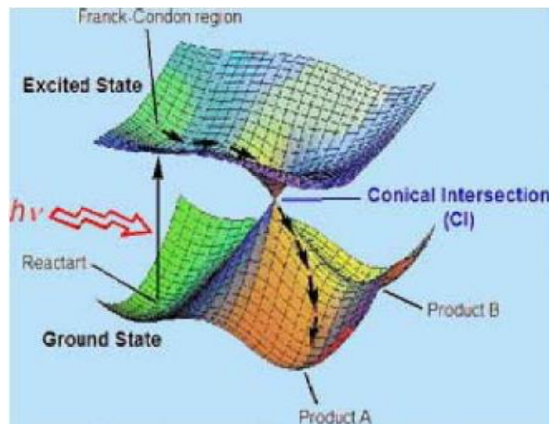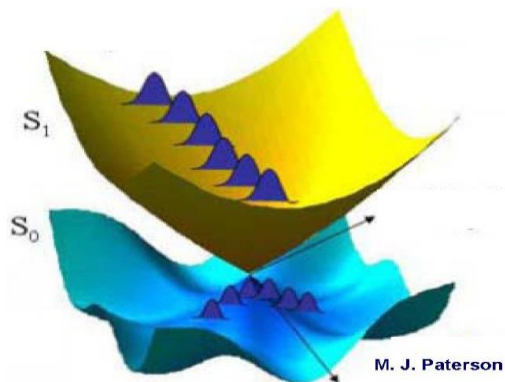
Born-Oppenheimer approximation breaks down !!
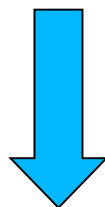
A self-consistent treatment of nuclear and electronic degrees of freedom is needed.

Dynamics methods

Quantum Dynamics
Quantum wavepacket
MCTDH, ML-MCTDH

?

Surface Hopping
Tully fewest switches
Landau-Zener and Zhu-Nakamura
Exact factorization (Gross)
Pechukas' force
Others.

Quantum dissipative dynamics
Redfiled
HEOM

Ehrenfest

Bohmian dynamics

Phase-space branching ...

Gaussian Wavepacket
Multiply spawning
Multiconfiguational Ehrenfest

Semiclassical Monte-Carlo

Mapping Hamiltonian
Semiclassical IVR
Quasiclassical Dynamcis
Symmetrical quasi-classical dynamics

Time-dependent DMRG

Quantum Classical Liouville Equation

E, S₁, S₀, CI, R, P, hν₁, q, b), C
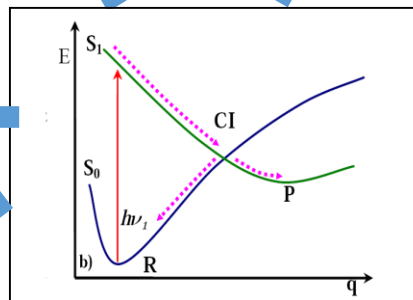
Quantum dynamics

Why Quantum wavepacket dynamics
- Exact treatments of the nonadiabatic transitions
- Hydrogen motions
- Quantum phase (Berry phase)
- Physical insight

Quantum dynamics
- Quantum wavepacket dynamics
    Reduced dimensional model
    Propagations of the nuclear wavepackets
- Multi-configuration time-dependent Hartree
    Many degrees of freedom in MCTDH

Quantum dynamics

- Nuclear Wavefunctions in diabatic picture

$$\Psi(\mathbf{r_e}, \mathbf{R_n}) = \sum_i \Phi_i^d(\mathbf{r_e}, \mathbf{R_n})\chi_i^d(\mathbf{R_n}),$$

$$i\frac{\partial}{\partial t}\chi^{\mathbf{d}}(t) = (\mathbf{T} + \mathbf{V^d(R)})\chi^{\mathbf{d}}(t),$$

- Electronic populations

$$P_i^d(t) = \int dR_1 \int dR_2...|\chi_i^d(t, R_1, R_2, ...)|^2.$$

$$P_i^a(t) = \int dR_1 \int dR_2...|\chi_i^a(t, R_1, R_2, ...)|^2.$$

- Flux

$$F_i^D(t) = \int dt \, \langle \chi_i(R_1, R_2, ..., t)| \, \hat{F} \, |\chi_i(R_1, R_2, ..., t)\rangle \Big|_{R_1=R_f}$$

$$= \int dt Im \left[\left\langle \chi_i(R_1, R_2, ..., t) \, \Big| \, \frac{\partial \chi_i(R_1, R_2, ..., t)}{\partial R_1} \right\rangle \Big|_{R_1=R_f} \right]$$
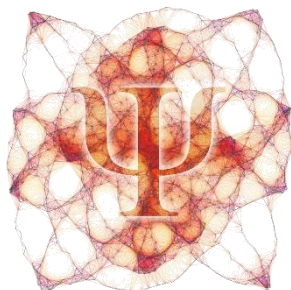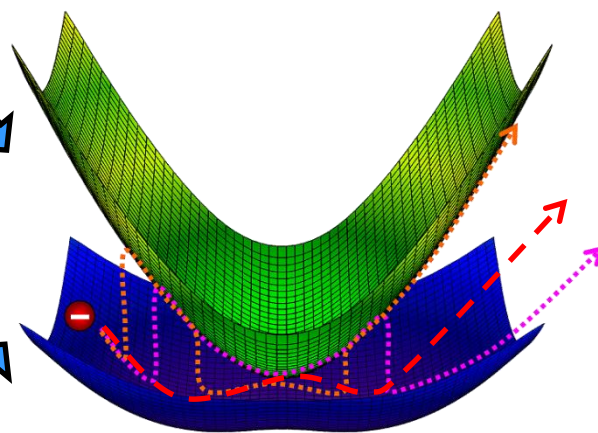
混合量子-经典动力学

分子动力学

量子动力学

混合量子-经典动力学

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Mean-Field and Surface Hopping

■ **Mean field :**

■ **Surface hopping :**

$$\frac{\partial |\psi\rangle}{\partial t} = \frac{\mathbf{H}|\psi\rangle}{i\hbar} \qquad m_i \ddot{x}_i = -\frac{\partial \langle \psi | \mathbf{H} | \psi \rangle}{\partial x_i}$$
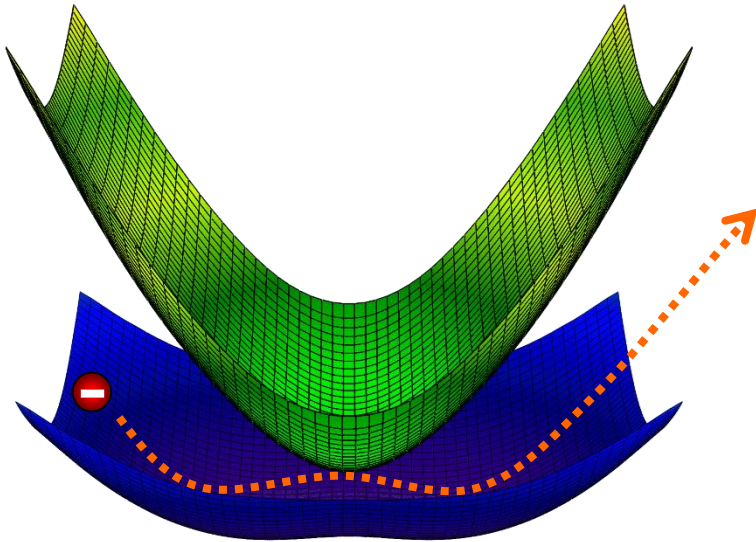
$$\frac{\partial |\psi\rangle}{\partial t} = \frac{\mathbf{H}|\psi\rangle}{i\hbar} \qquad m_i \ddot{x}_i = -\frac{\partial \langle \psi_k | \mathbf{H} | \psi_k \rangle}{\partial x_i}$$

Ehrenfest Dynamics
Ehrenfest, Z. Phys. 45, 445 (1927)
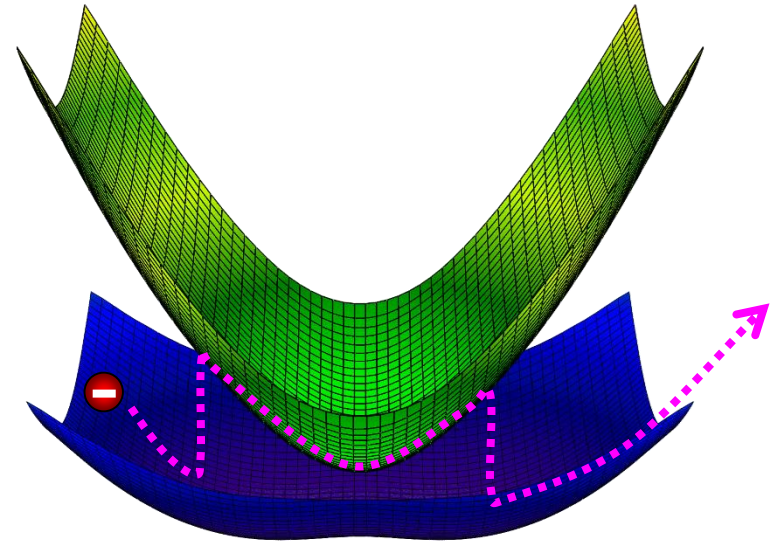
Fewest Switches Surface Hopping
Tully, J. Chem. Phys. 93, 1061 (1990)

Mean-Field Dynamics

- **Clear physical picture:**

  The classical part experiences average forces from the quantum part

- **Representation independence:**

$$\frac{\partial |\psi\rangle}{\partial t} = \frac{\mathbf{H}|\psi\rangle}{i\hbar} \qquad m_i \ddot{x}_i = -\frac{\partial \langle \psi | \mathbf{H} | \psi \rangle}{\partial x_i}$$

  Diabatic and adiabatic representations give the same results

- **High efficiency:**

  Only one trajectory is used to describe the classical dynamics
  The statistical error is minimized

Mean-Field Dynamics

■ **Detailed balance :**
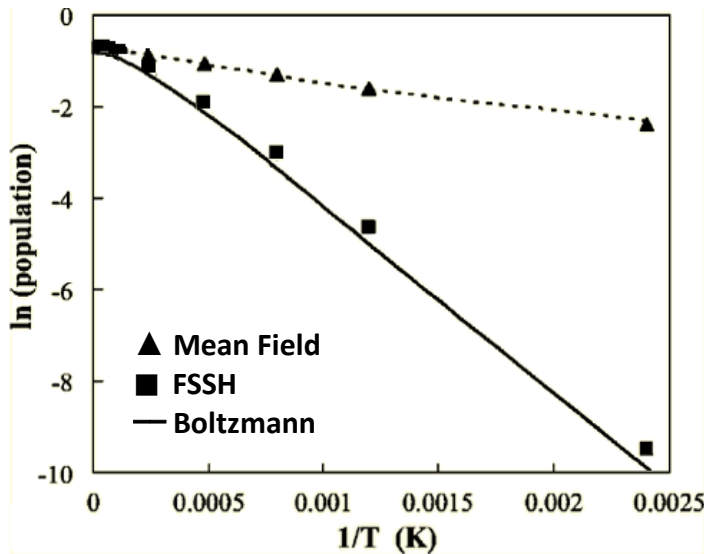
■ **Polaronic effect :**

Parandekar and Tully
J. Chem. Phys. 122, 094102 (2005)
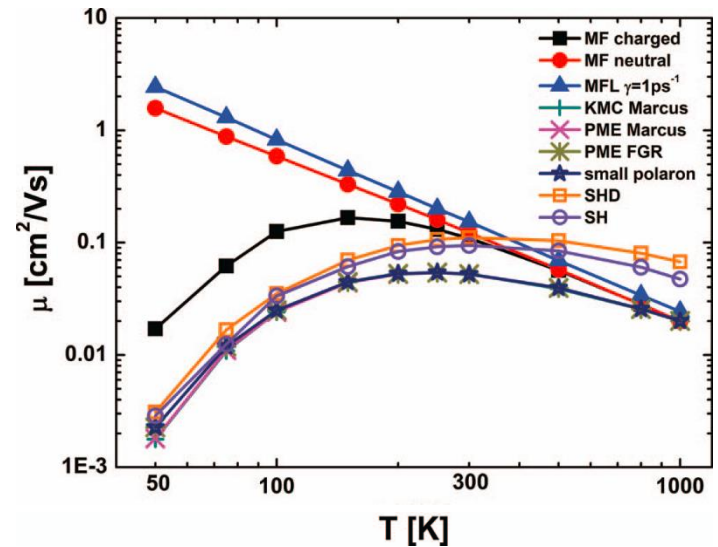
Wang* and Beljonne
J. Chem. Phys. 139, 064316 (2013)

Feedback between the electron and nuclei is not properly described

Part II:
Theoretical Framework
of
Surface Hopping

Surface-hopping dynamics

Why surface-hopping dynamics

- All degrees of freedom
- Low computational cost to propagate trajectories
- Good descriptions of the nonadiabatic transitions

Tully's approach

- Classical trajectories to describe the nuclear motions in the single surfaces
- On-the-fly calculations of potentials, gradients and nonadiabatic couplings
- Propagate the quantum amplitude (electronic populations) along each trajectory
- Fewest switch

Concept of trajectory surface hopping
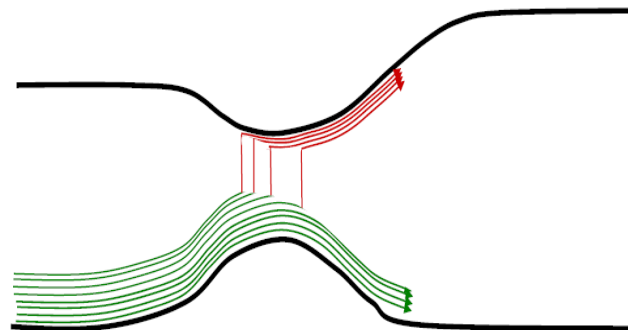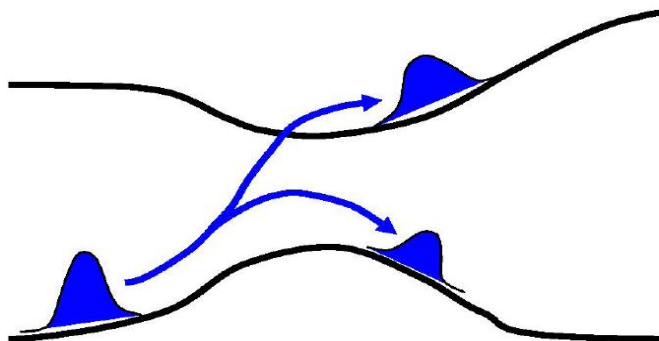
Methodology

A swarm of trajectories is considered for nuclear motions.
    (Why? Ensemble average)

Each trajectory mainly evolves on a single potential energy surface.
    (How? Solving Newton equations)

Sudden hops between different potential energy surfaces are allowed.
    (A central question: how to treat hopping events?)

Concept of trajectory surface hopping

Nuclear motion on a single surface:

Newton equations (or Hamilton equations)

$$\frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{M}$$

$$\frac{1}{M}\frac{d\mathbf{P}}{dt} = -\frac{dV}{d\mathbf{R}}$$

CI
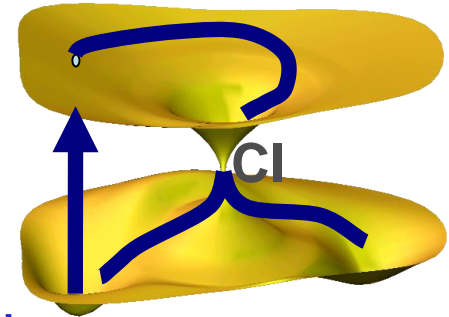
Sudden hops between different electronic states

Stochastic approaches

Define the hopping probability $P(i \to j)$

Compare $P(i \to j)$ with a random number $\xi \in [0, 1]$

A two-state example: (trajectory starting from S_1 state)

$S_1 \longrightarrow S_0$ hopping probability $P(1 \to 0)$

$\xi < P(1 \to 0) \longrightarrow$ Hops from S_1 to S_0

$\xi > P(1 \to 0) \longrightarrow$ Stay on the S_1 surface

Different surface-hopping approaches

A central question

"how to calculate the hopping probability?"

Three types of approaches

(1) Using predefined criteria

Landau-Zener

Massey parameters

Tracing electronic wavefunctions

(2) Solving the time-dependent Schrödinger equations for

electronic motion

Following the change of electronic population

Tully's fewest switching algorithm

(3) Computing the Pechukas' force

[1]   A. Bjerre and E. E. Nikitin, Chem. Phys. Lett. **1**, 179 (1967).
[2]   F. Bernardi, M. Olivucci and M. A. Robb, Chem. Soc. Rev. **25**, 321 (1996).
[3]   N. C. Blais and D. G. Truhlar, J. Chem. Phys. **79**, 1334 (1983).
[4]   J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[5]   F. Webster, P. J. Rossky and R. A. Friesner, Comp. Phys. Comm. **63**, 494 (1991).

Landau-Zener formula

Landau-Zener approximations

Landau-Zener formula is written in "__diabatic__" representation, not in "__adiabatic__" representation !
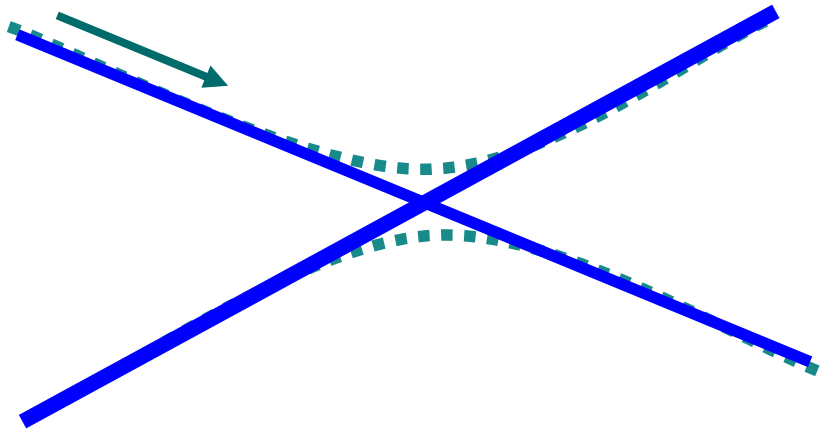
Assumptions:

1. One-dimensional model
2. Linear H_{11} and H_{22}
3. Constant H_{12}
4. Constant velocity

Limitations:

1. Very simple Hamiltonian
2. One-dimensional case
3. Diabatic representation

$$P = exp\left[\frac{-2\pi H_{12}^2}{\hbar \dot{\mathbf{R}} \frac{\partial(H_{11}-H_{22})}{\partial \mathbf{R}}}\right]$$

[1]   A. Bjerre and E. E. Nikitin, Chem. Phys. Lett. **1**, 179 (1967).

Massey parameter

Desouter-Lecomte / Lorquet approach

Nonadiabatic transition rate in "<u>adiabatic</u>" representation !
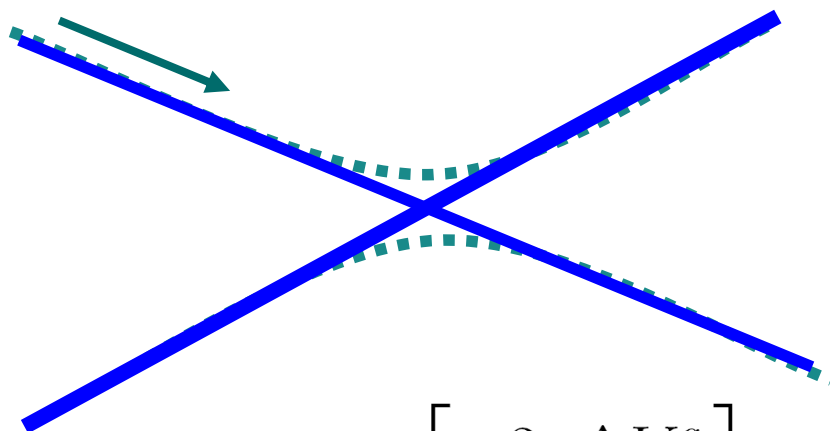
$$P = exp \left[\frac{-2\pi \Delta V^a}{\hbar \dot{\mathbf{R}} \, \mathbf{d_{ij}}} \right]$$

Adiabatic energy gap	ΔV^a

Nonadiabatic coupling	$\mathbf{d_{ij}} = \langle \Psi_i^a | \frac{\partial}{\partial \mathbf{R}} | \Psi_j^a \rangle$

Assumptions:

1 One-dimensional model
2. $H_{11}=H_{22}$
   (minimum energy gap)
3. Energy gap $2H_{12}$
4. Constant velocity

Limitations:

1. Very simple Hamiltonian
2. One-dimensional model
3. Underestimate nonadiabatic transition probability

[1]   M. Desouter-Lecomte and J. C. Lorquet, J. Chem. Phys. **71**, 4391 (1971).
[2]   F. Bernardi, M. Olivucci and M. A. Robb, Chem. Soc. Rev. **25**, 321 (1996).

Electronic Schrödinger equation

Electronic Hamiltonian

$$H_e(\mathbf{r}, \mathbf{R}) = -\frac{\hbar^2}{2}\sum_l \frac{1}{m_l}\nabla_{\mathbf{r}_l}^2 + V_{rR}(\mathbf{r}, \mathbf{R})$$

Kinetic energy
of electrons

Total potential
energy

Nuclei-nuclei
Coulomb interactions

Electron-nuclei
Coulomb interactions

Electron-electron
Coulomb interactions

Time-dependent electronic Schrödinger equation

$$i\hbar\frac{\partial\Phi(\mathbf{r}, \mathbf{R}, t)}{\partial t} = H_e\Phi(\mathbf{r}, \mathbf{R}, t)$$

Expansion of total electronic wavefunction

$$\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_i c_i(t)\phi_i(\mathbf{r}, \mathbf{R})$$

Any basis:
adiabatic or diabatic

Coefficient:
quantum amplitude

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Electronic Schrödinger equation

Coupled equations for electronic motion

Coefficient:
quantum amplitude

Nuclear velocity

Effective Hamiltonian

$$i\hbar \frac{dc_j(t)}{dt} = \sum_i c_i(t) \left[H_{ji} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{ji} \right]$$

Electronic Hamiltonian
matrix in the selected basis

$$H_{ji} \equiv \int d\mathbf{r}\, \phi_j^*(\mathbf{r}, \mathbf{R})\, H_e\, \phi_i(\mathbf{r}, \mathbf{R})$$

Derivative couplings

$$\mathbf{d}_{ji} \equiv \int d\mathbf{r}\, \phi_j^*(\mathbf{r}, \mathbf{R}) \left[\nabla_{\mathbf{R}} \phi_i(\mathbf{r}, \mathbf{R}) \right]$$

Derivative coupling term

(derivative of electronic wavefunction with respect to time)

$$F_{ji} = \dot{\mathbf{R}} \cdot \mathbf{d_{ji}} = \int dr\, \phi_j^*(t) \frac{\partial \phi_i^*(t)}{\partial t} \qquad \frac{\partial}{\partial t} = \frac{\partial}{\partial \mathbf{R}} \frac{d\mathbf{R}}{dt}$$

[1] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

31
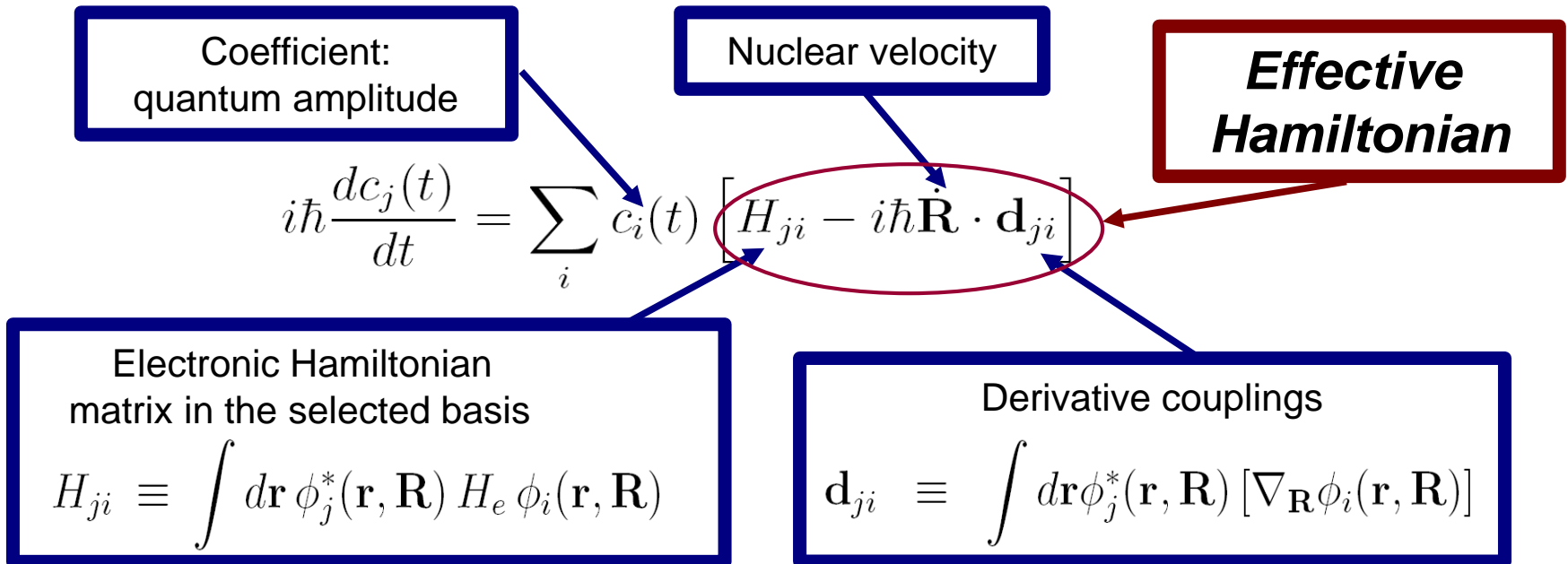
Electronic density matrix

Electronic density matrix

$$\rho_{ij}(t) = c_i^*(t)c_j(t)$$

ρ_{ii} Diagonal elements: populations

ρ_{ij} Offdiagonal elements: coherence

Equation of motions for electronic density matrix

$$\frac{d\rho_{ij}}{dt} = -\frac{i}{\hbar}\left(\sum_m H_{im}^{eff}\rho_{mj} - \sum_m \rho_{im}H_{mj}^{eff}\right)$$

Effective Hamiltonian for electronic motion

$$H_{im}^{eff} = H_{im} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{d}_{im}$$

[1] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

Example: A two-state model

Adiabatic basis (eigenstates of electronic Hamiltonian)

$$H_{ij} = V_i^a \delta_{ij} \qquad \mathbf{d_{ij}} \text{ (nonadiabatic couplings)}$$

Coupled equations for electronic motion

$$\frac{d}{dt} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} = -\frac{i}{\hbar} \begin{bmatrix} V_1^a & -i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{12} \\ -i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{21} & V_2^a \end{bmatrix} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix}$$

Two situations

Far away from conical intersections

$\phi_i(\mathbf{r}, \mathbf{R})$ changes smoothly over t and R

$\mathbf{d_{ij}} \sim 0, \quad F_{ij} \sim 0$ $\longrightarrow$ No adiabatic population transfer

In vicinity of conical intersections

$\phi_i(\mathbf{r}, \mathbf{R})$ changes dramatically over t and R

$\mathbf{d_{ij}} \sim \infty, \ F_{ij} \sim \infty$ $\longrightarrow$ Adiabatic population transfer

Example: A two-state model

Diabatic basis

Basis functions $\phi_i(\mathbf{r}, \mathbf{R})$ changing smoothly over R

No derivative couplings $\quad \mathbf{d_{ij}} \sim 0, \quad F_{ij} \sim 0$

Smooth diabatic potential couplings

$$\frac{d}{dt} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} = -\frac{i}{\hbar} \begin{bmatrix} V_{11}^d & V_{12}^d \\ V_{21}^d & V_{22}^d \end{bmatrix} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix}$$

Interesting questions

(1) *Which representation should we use for the surface-hopping calculations? Adiabatic or diabatic?*
(2) *Do the calculations in two different representations provide the same results?*

Early approximate methods
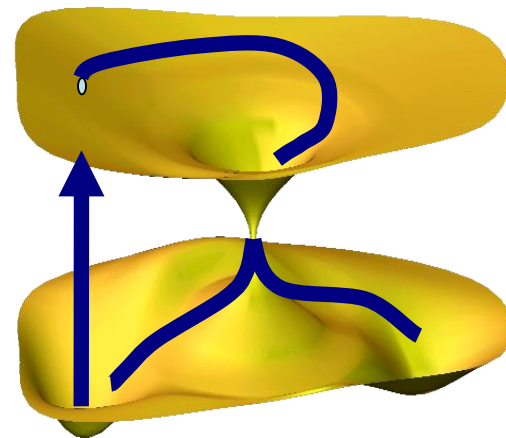
Approximations in early days

- Only considering electronic populations
- When the population of the current state is lower than a threshold, perform hop to other states.

A two-state example

(trajectory starting from the S_1 state)

$$\rho_{22}(t) = c_2^*(t)c_2(t) > 0.5 \rightarrow \text{Stay on the } S_1 \text{ state}$$

$$\rho_{22}(t) = c_2^*(t)c_2(t) < 0.5 \rightarrow \text{Hop from } S_1 \text{ to } S_0 \text{ state}$$

[1]   N. C. Blais and D. G. Truhlar, J. Chem. Phys. **79**, 1334 (1983).
[2]   O. Weingart, A. Migani, et. al. J. Phys. Chem. A, **108**, 4685 (2004).

Fewest switches algorithm

Occupation probability of the state i $\dfrac{N_i(t)}{N(t)}$

Electronic population probability of state i for a trajectory $\left|c_i(t)\right|^2$

Averaged electronic population probability $< \left|c_i(t)\right|^2 >$

Example: (time t, five trajectories, two electronic states)

	c_1	c_2	Current state
Traj 1	0.4	0.6	State 2
Traj 2	0.45	0.55	State 2
Traj 3	0.35	0.65	State 2
Traj 4	0.4	0.6	State 1
Traj 5	0.4	0.6	State 1

$$< c_1 > = 0.4, \quad < c_2 > = 0.6$$

$$\frac{N_1}{N} = 0.4, \quad \frac{N_2}{N} = 0.6,$$
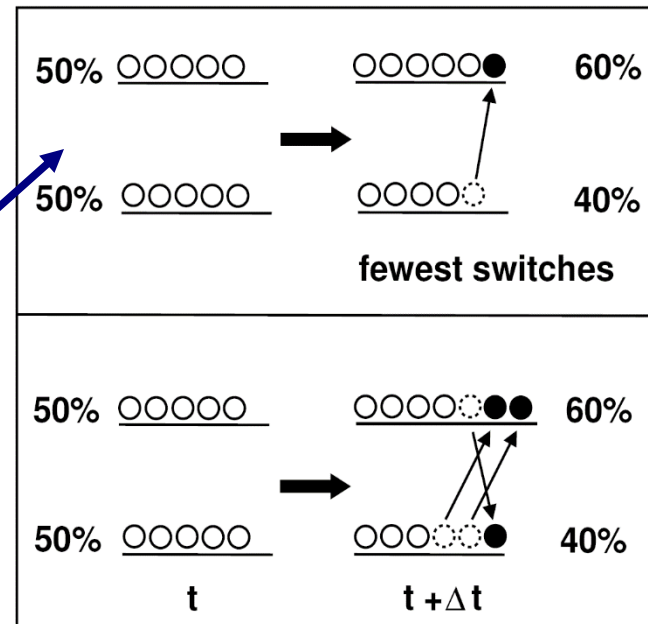
Fewest switches algorithm

Assumptions

(1) At any time, the occupation probability of trajectories evolving on the state i should be equal to the averaged electronic populations probability of state i.

(2) A swarm of trajectories have the same electronic populations.

(3) The overall change of the electronic populations should be achieved by the **minimum number** of trajectory hops.

$$(1) \quad < |c_i(t)|^2 > = \frac{N_i}{N}$$

$$(2) \quad < |c_i(t)|^2 > = |c_i(t)|^2$$

$$\frac{N_i(t)}{N} = |c_i(t)|^2$$

Fewest switches

50% OOOOO → OOOOO● 60%

50% OOOOO → OOOO◌ 40%

fewest switches

50% OOOOO → OOOO◌●● 60%

50% OOOOO → OOO◌◌● 40%

t   t + Δt

[1] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[2] N. L. Doltsinis, in "Quantum Simulations of Complex Many-Body systems: From Theory to Algorithms", http://www.fz-juelich.de/nic-series/volume10

Fewest switches algorithm

Occupation number and electronic population probability

$$\frac{N_i(t)}{N} = |c_i(t)|^2$$

Changes of occupation number and electronic population probability

$$N_i(t) \qquad P_i(t)dt = \frac{N_i(t) - N_i(t+dt)}{N_i(t)} \qquad N_i(t+dt)$$

$$t \longrightarrow t+dt$$

$$c_i(t) \qquad P_i(t)dt = \frac{|c_i(t)|^2 - |c_i(t+dt)|^2}{|c_i(t)|^2} \qquad c_i(t+dt)$$

Changing rate (hopping probability)

$$P_i = -\sum_j \frac{2\int_t^{t+\Delta t} dt \left[\hbar^{-1}\text{Im}(c_i^* c_j H_{ij}) - \text{Re}(c_i^* c_j \dot{\mathbf{R}} \cdot \mathbf{d}_{ji})\right]}{|c_i(t)|^2}$$

[1]   J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

Fewest switches algorithm
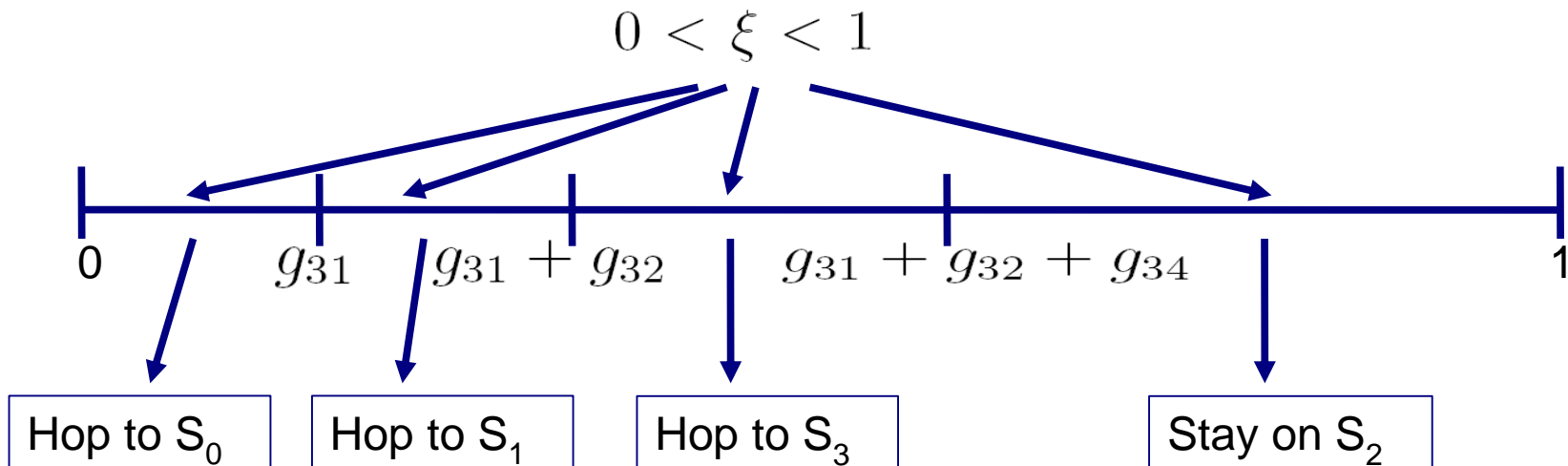
Hopping probability from state i to state j

$$P_{ij} = -\frac{2 \int_t^{t+\Delta t} dt \left[\hbar^{-1} \text{Im}(c_i^* c_j H_{ij}) - \text{Re}(c_i^* c_j \dot{\mathbf{R}} \cdot \mathbf{d}_{ji}) \right]}{|c_i(t)|^2}$$

$$g_{ij} = \max(P_{ij}, 0)$$

Compare the hopping probability and a random number $0 < \xi < 1$

$$\sum_{j=1}^{k} g_{ij} < \xi < \sum_{j=1}^{k+1} g_{ij} \quad \longrightarrow \quad \textit{Hop from state i to state k}$$

Example: Four-state model [The current state is S_2, (state 3)]

$$0 < \xi < 1$$

g_{31} $\quad$ $g_{31} + g_{32}$ $\quad$ $g_{31} + g_{32} + g_{34}$

Hop to S_0 $\quad$ Hop to S_1 $\quad$ Hop to S_3 $\quad$ Stay on S_2

Fewest switches algorithm

Adiabatic representation

$$P_{ij} = -\frac{2\int_t^{t+\Delta t} dt \left[-\text{Re}(c_i^* c_j \dot{\mathbf{R}} \cdot \mathbf{d}_{ji})\right]}{|c_i(t)|^2}$$

Hopping probability from state i to j

Coherence between state i and state j
Off-diagonal elements of density matrix

$$P_{ij} = 2\frac{\text{Re}(\rho_{ij}\dot{\mathbf{R}} \cdot \mathbf{d}_{ji})}{\rho_{ii}}\Delta t$$

Small time interval

Electronic probability in state i
Diagonal elements of density matrix

Nonadiabatic coupling between state i to j

Diabatic representation

$$P_{ij} = -\frac{2\hbar^{-1}\text{Im}(\rho_{ij}V_{ji}^d)}{\rho_{ii}^2}\Delta t$$

Velocity adjustment

Adjust velocity at hops

$$\dot{\mathbf{R}}'_\beta = \dot{\mathbf{R}}_\beta - \gamma_{ij}\frac{\mathbf{w}_{ij}^\beta}{M_\beta}$$

Kinetic energy change

$$
\begin{aligned}
\Delta T &= \frac{1}{2}\sum_\beta M_\beta \left(\dot{\mathbf{R}}'_\beta\right)^2 - \frac{1}{2}\sum_\beta M_\beta \left(\dot{\mathbf{R}}_\beta\right)^2 = \\
&= \frac{1}{2}\sum_\beta M_\beta \left[\gamma_{ij}^2 \frac{\mathbf{w}_{ij}^{\beta\,2}}{M_\beta^2} - 2\gamma_{ij}\frac{\dot{\mathbf{R}}_\beta \cdot \mathbf{w}_{ij}^\beta}{M_\beta}\right] = \\
&= \gamma_{ij}^2 a_{ij} - \gamma_{ij} b_{ij}
\end{aligned}
$$

$$
\begin{aligned}
a_{ij} &\equiv \frac{1}{2}\sum_\beta \frac{\mathbf{w}_{ij}^{\beta\,2}}{M_\beta} \\
b_{ij} &\equiv \sum_\beta \dot{\mathbf{R}}_\beta \cdot \mathbf{w}_{ij}^\beta \;.
\end{aligned}
$$

Total energy conversion

$$\gamma_{ij}^2 a_{ij} - \gamma_{ij} b_{ij} - (\epsilon_i - \epsilon_j) = 0 \;.$$

$$\gamma_{ij} = \frac{b_{ij} + \sqrt{b_{ij}^2 + 4a_{ij}(\epsilon_i - \epsilon_j)}}{2a_{ij}} \qquad \text{if } b_{ij} < 0 \;,$$
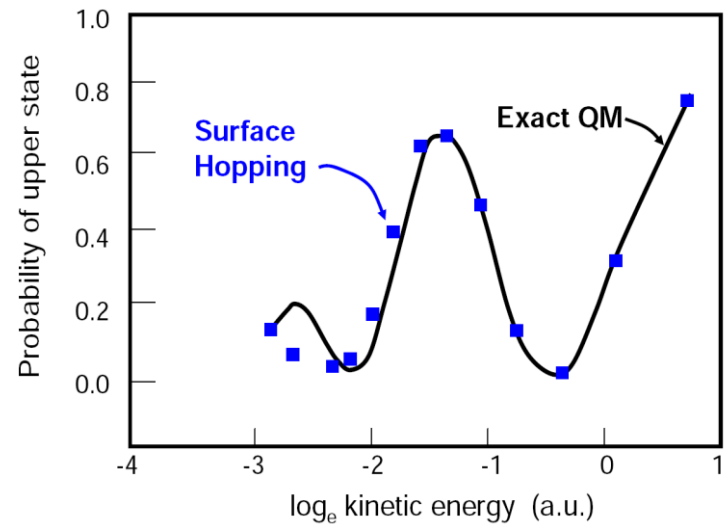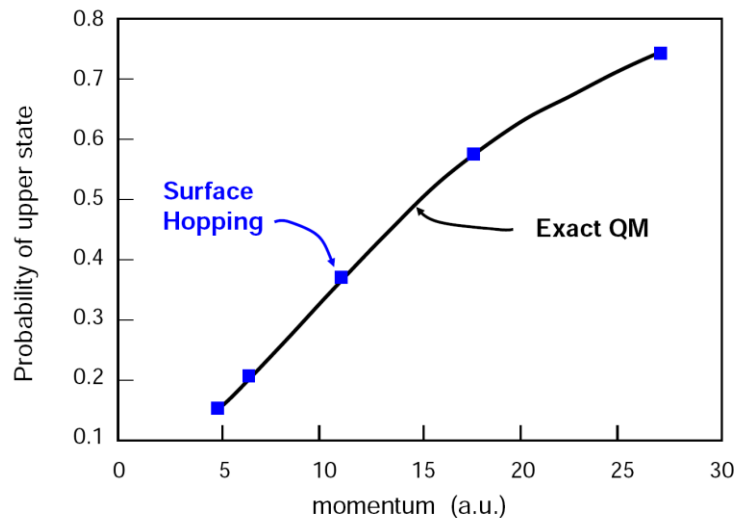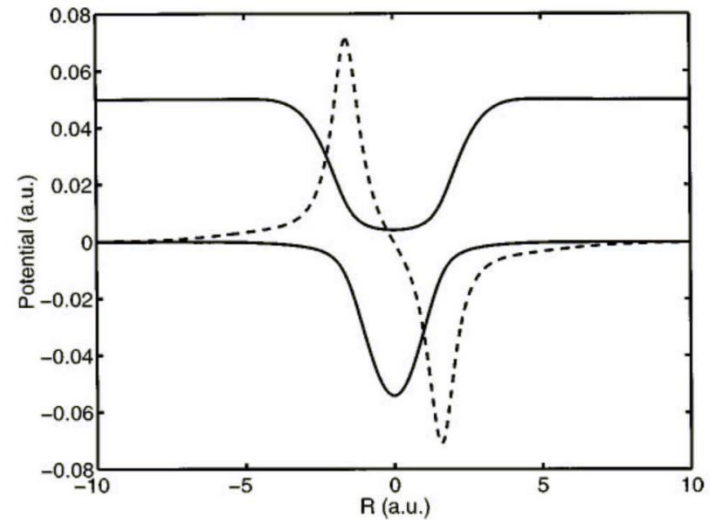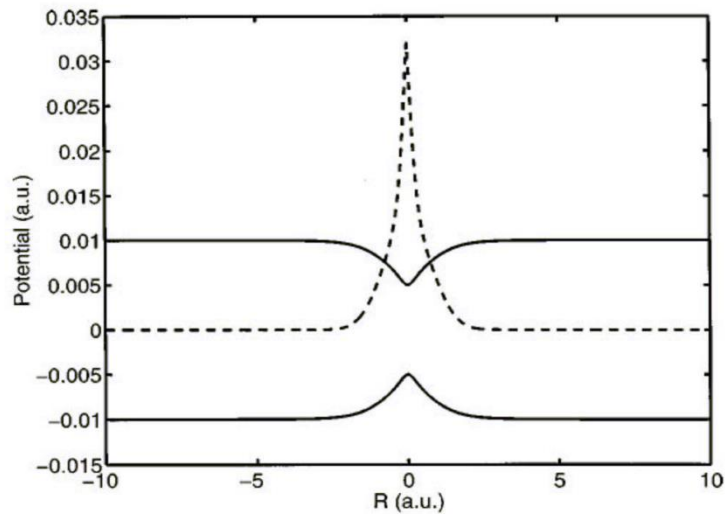
$$\gamma_{ij} = \frac{b_{ij} - \sqrt{b_{ij}^2 + 4a_{ij}(\epsilon_i - \epsilon_j)}}{2a_{ij}} \qquad \text{if } b_{ij} \geq 0 \;.$$

Which direction ?
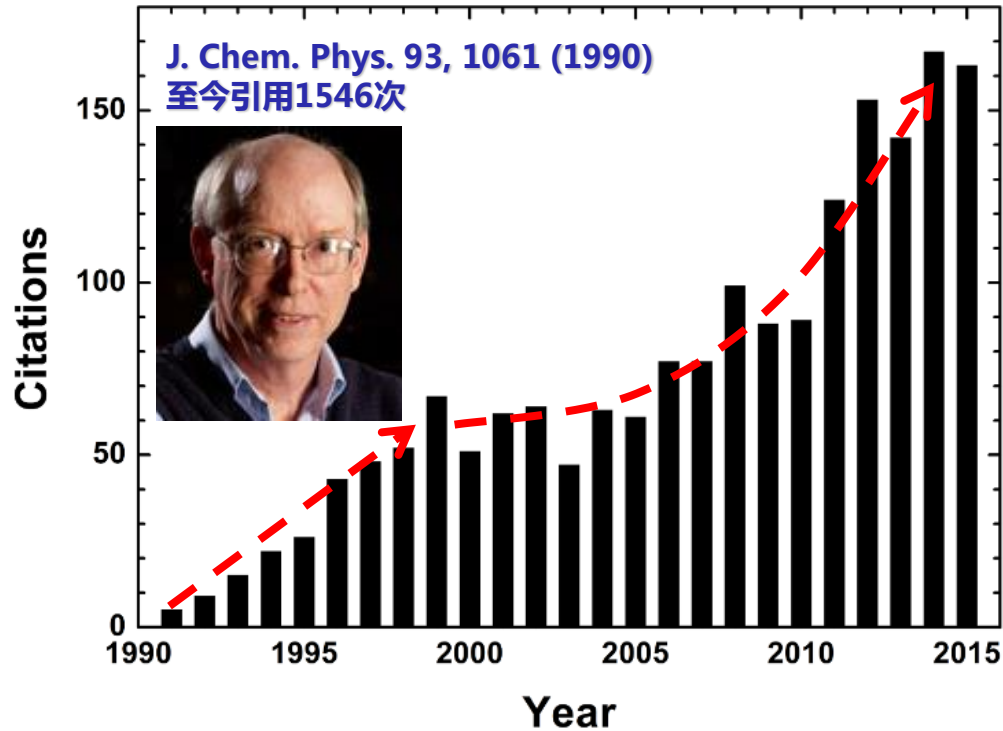
Along nonadiabatic coupling vector $\mathbf{d_{ij}}$

[1] M. F. Herman, J. Chem. Phys. **81**, 754 (1984).
[2] M. F. Herman, J. Chem. Phys. **82**, 3666 (1985).
[3] J. C. Tully, Int. J. Quantum Chem. **25**, 299 (1991).

Tully's examples (fewest switches algorithm)

[1]   J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

FSSH的关注度变化

J. Chem. Phys. 93, 1061 (1990)
至今引用1546次

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Surface Hopping的应用领域
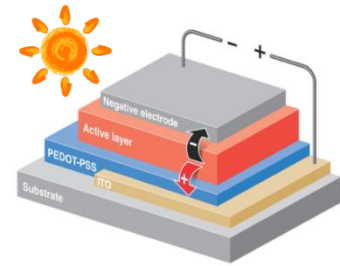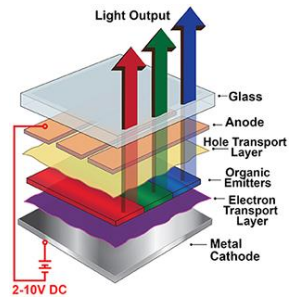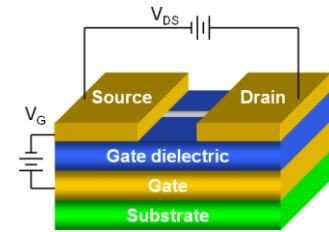
太阳能电池　场效应晶体管
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单分子导电　光合作用
光化学
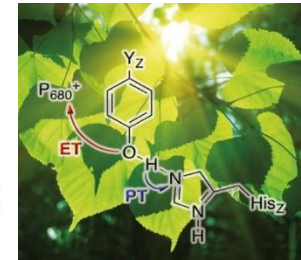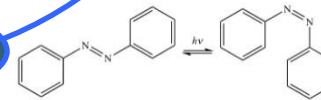
电子注入　电子转移　激子扩散　激子分离　激子弛豫
电子导出　电子传输　激子聚变　电导控制　振动弛豫
电子俘获　激子产生　激子裂变　激子复合　质子转移

化学、物理、生物、材料等多学科都有广泛应用前景

Shortcomings of fewest switches algorithm

- Trajectories are independent
- Trajectories should talk to each other.
- All trajectories may not have the same quantum amplitude.

$$(1) \quad < |c_i(t)|^2 > = \frac{N_i}{N} \quad \text{???}$$
$$(2) \quad < |c_i(t)|^2 > = |c_i(t)|^2$$

- Too drastic hops

    Velocity changes suddenly at hops.

- Non-invariant to representation

    Adiabatic and diabatic representations give different results.
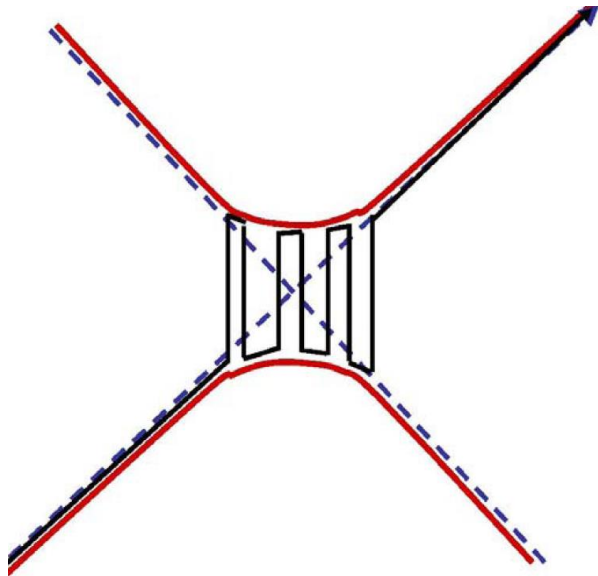
- No quantum interference
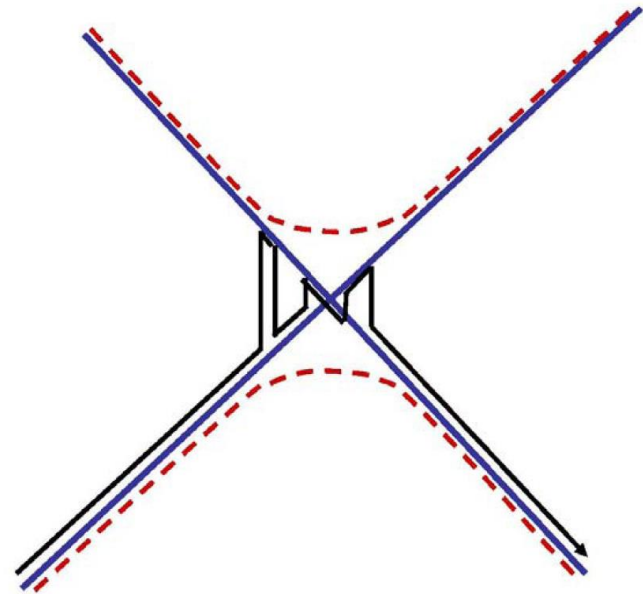- Decoherence is neglected
- Frustrated hops

    Kinetic energy is not large enough to compensate the energy change for the hop from the lower to upper state.

Choice of representations (shortcoming)

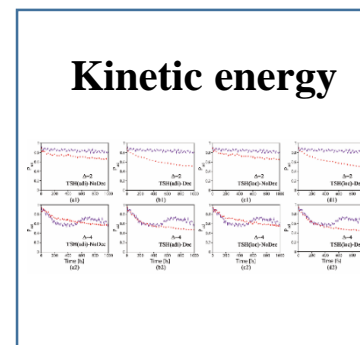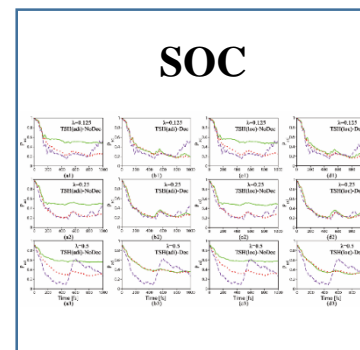- Not invariant to choice of representation in the fewest switches algorithm
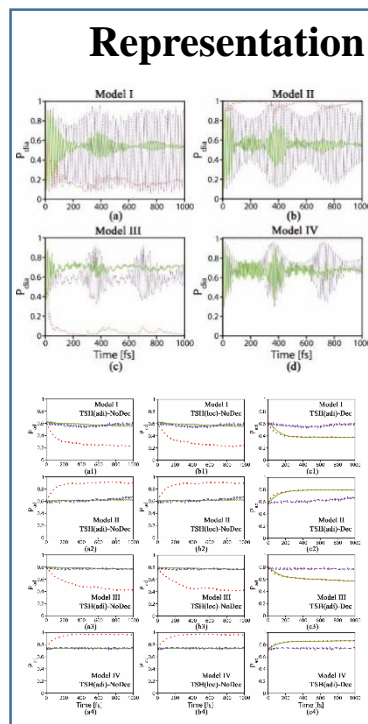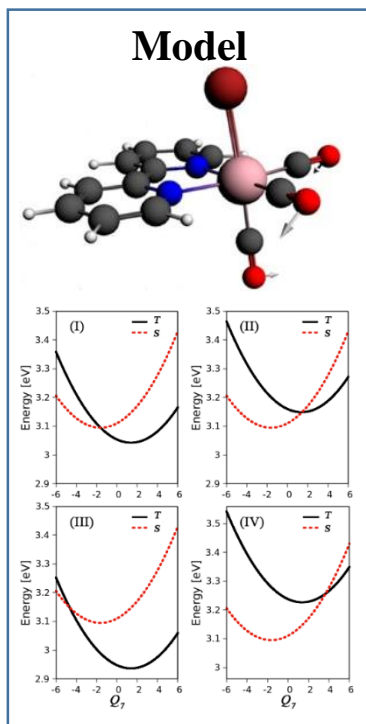

adiabatic representation   diabatic representation

The natural selection for surface-hopping calculations is the *adiabatic* representation.

Model

Representation

SOC

Kinetic energy

➤ The fewest switches TSH dynamics in the spin-adiabatic representation (TSH-adi) and by the local diabatization approaches (TSH-loc) produce very similar results.

➤ With the weak diabatic coupling (SOC) or high kinetic energy, the TSH-adi dynamics works well.

J. Eng, C. Gourlaouen, E. Gindensperger, C. Daniel. *Acc. Chem. Res.* 2015, 48, 809-817.
W. Peng, Y. Xie, Z. Lan, JCP, 2019 (Accepted)

Frustrated hops (shortcoming)

- For the hop from lower to upper state, the kinetic energy is not sufficient

- to compensate the change in the potential energy !!
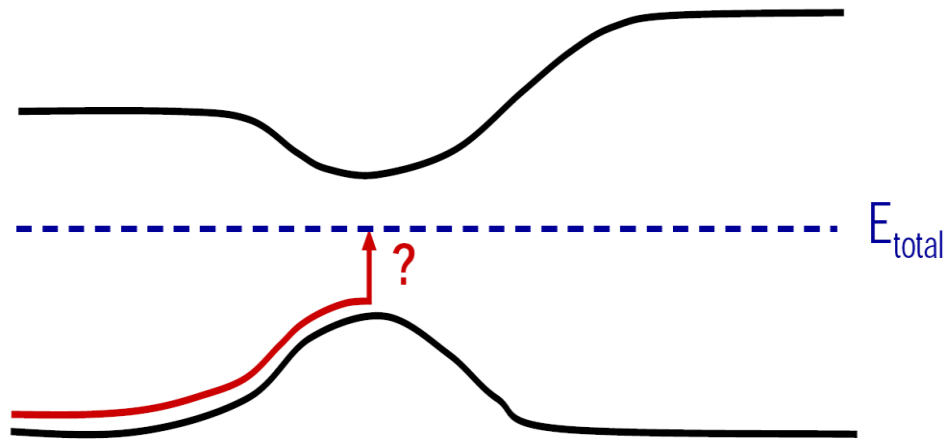
Internal consistency breaks down !!

$$(1) \quad < |c_i(t)|^2 > = \frac{N_i}{N} \qquad \text{???}$$

$$(2) \quad < |c_i(t)|^2 > = |c_i(t)|^2$$

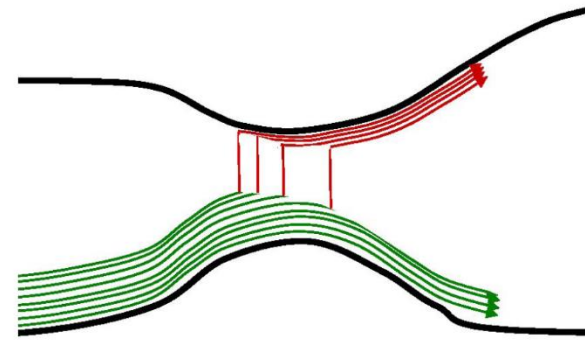[1] J.-Y. Fang and S. Hammes-Schiffer, J. Chem. Phys. **103**, 9309 (1999).
[2] G. Granucci and M. Persico, J. Chem. Phys. **126**, 134114 (2007).

Decoherence (shortcoming)
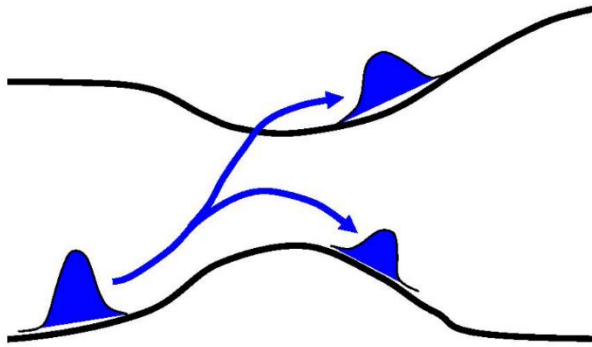
quantum wave packet

$$\rho_{ij}(t) = \int dR\, \chi_i^*(R,t)\chi_j(R,t)$$

surface hopping

$$\rho_{ij}(t) = C_i^*(t)C_j(t)$$

Quantum picture
The overlap of nuclear wavefunctions (on the ground state and excited state) should decay during time evolution, particularly for multi-dimensional systems. Therefore, off-diagonal elements of the electronic density matrix should quickly decay to zero.

Mixed quantum-classical picture
The off-diagonal elements of the electronic density matrix are not dependent on the nuclear wavefunctions. For classical nuclear motions, they retain too much "*coherence*".

[1] J.-Y. Fang and S. Hammes-Schiffer, J. Chem. Phys. **103**, 9309 (1999).
[2] G. Granucci and M. Persico, J. Chem. Phys. **126**, 134114 (2007).

Decoherence Correction and Existed Approaches

■ **Quantum decoherence:**

The decay of coherence with time when a quantum system is in contact with the environment
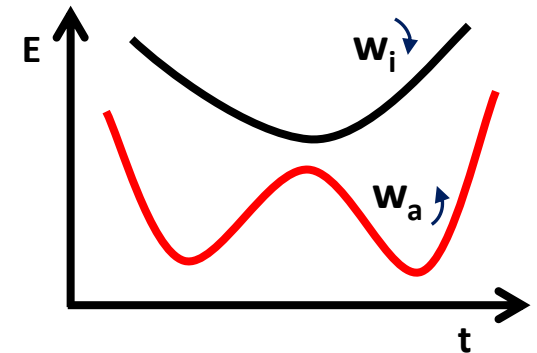
Decoherence correction

$$c_i' = c_i e^{-dt/\tau_i} \qquad c_a' = c_a \left[\frac{1 - \sum_{j \neq a} |c_j'|^2}{|c_a|^2} \right]^{\frac{1}{2}}$$

Force-based decoherence time

$$\tau_i^{-2} = \sum_j \frac{(F_a^j - F_i^j)^2}{4\hbar\sqrt{Km}}$$

Energy-based decoherence time

$$\tau_i = \frac{\hbar}{|E_i - E_a|}\left(1 + \frac{C}{E_{kin}}\right)$$

Bitter and Rossky, J. Chem. Phys. 103, 8130 (1995)
Schwartz, Bittner, Prezhdo, and Rossky, J. Chem. Phys. 104, 5942 (1996)
Wong and Rossky, J. Chem. Phys. 116, 8429 (2002)
Zhu, Nangia, Jasper, and Truhlar, J. Chem. Phys. 121, 7658 (2004)
Bedard-Hearn, Larsen, and Schwartz, J. Chem. Phys. 123, 234106 (2005)
Granucci and Persico, J. Chem. Phys. 126, 134114 (2007)
Subotnik, J. Phys. Chem. A 115, 12083 (2011)
Subotnik and Shenvi, J. Chem. Phys. 134, 024105 (2011)
Jaeger, Fischer, and Prezhdo, J. Chem. Phys. 137, 22A545 (2012)
Chen and Reichman, J. Chem. Phys. 144, 094104 (2016)

AFSSH decoherence time

$$\tau_i^{-1} = \sum_j Z_{ai}^j \Theta\left(Z_{ai}^j\right) \Theta\left[\left(\delta R_{aa}^j - \delta R_{ii}^j\right)\left(\delta P_{aa}^j - \delta P_{ii}^j\right)\right]$$
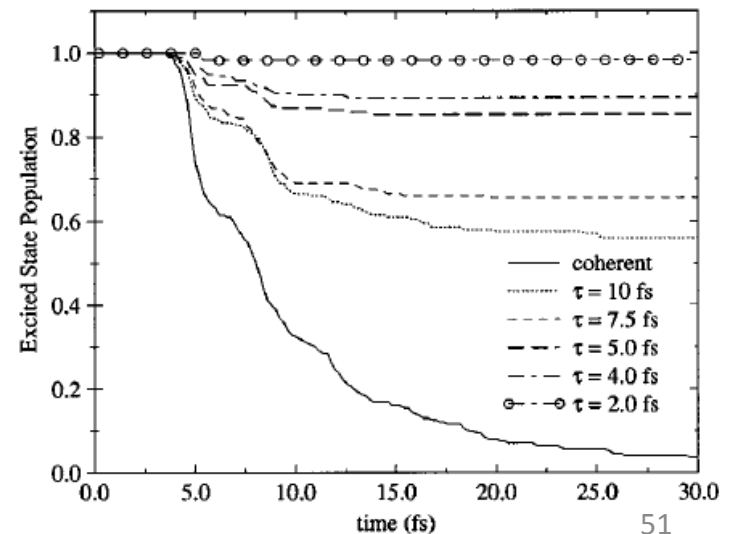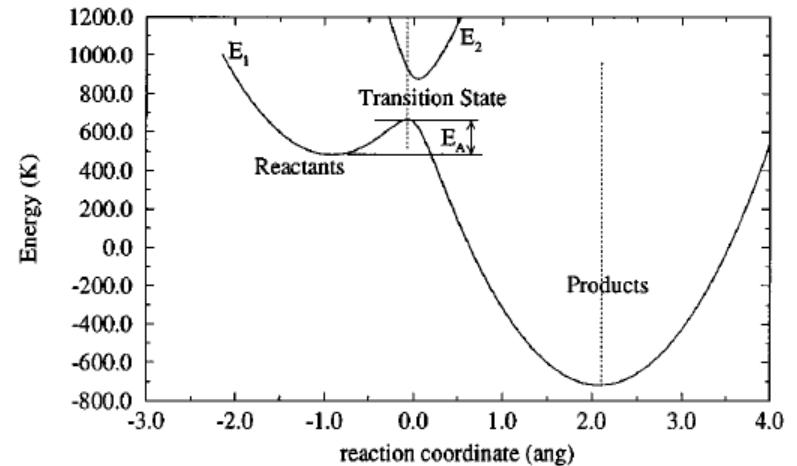
Decoherence corrections

$$H = H_0 + \sum_n \frac{m_n}{2} \dot{q}_n^2 + \frac{m_n \omega_n^2}{2} \left(q_n - x \frac{c_n}{\omega_n^2 m_n} \right)^2,$$

$$H_0 = \frac{p^2}{2m} + E_{\pm}(x) - \sum_n \frac{c_n^2}{2 m_n \omega_n^2} x^2.$$

$$J(\omega) = \frac{\pi}{2} \sum_n \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j).$$

$$V_i(x) = \frac{m \omega_i}{2} (x - x_i)^2 + bx, \quad \text{where} \quad i = 1, 2,$$

$$V_{12}(x) = c \exp(-dx^2).$$

Decoherence corrections

Quantum amplitude of other states

Other states K

$$C'_K = C_K e^{-\Delta t/\tau_{KM}}, \quad \forall\, K \neq M,$$

Quantum amplitude of current state

$$C'_M = C_M \left[\frac{1 - \sum\limits_{K \neq M} |C'_K|^2}{|C_M|^2} \right]^{1/2},$$

Current state M

$$\tau_{KM} = \frac{\hbar}{|E_K - E_M|} \left(1 + \frac{C}{E_{\text{kin}}} \right),$$
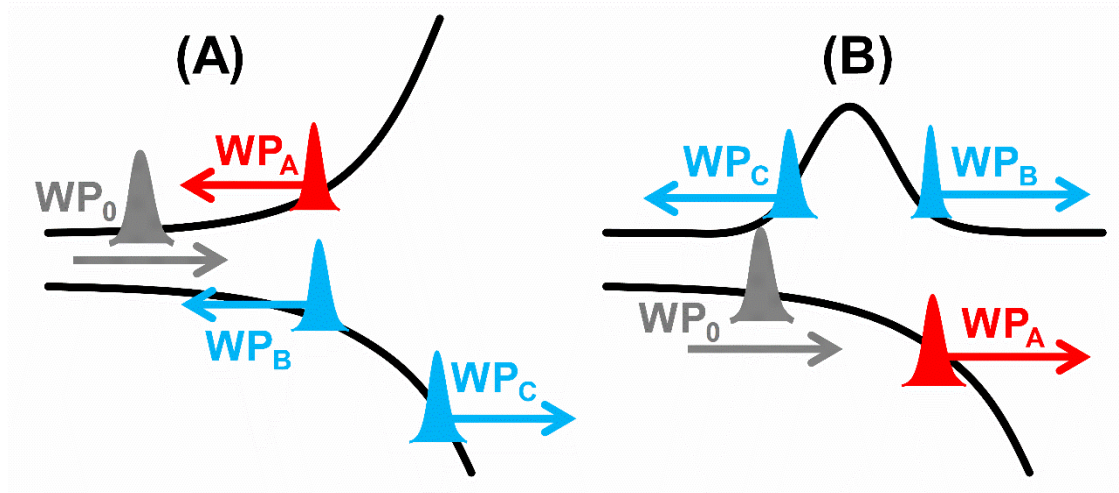
Parameter C=0.1 Hartree

Potential energy of state K

Potential energy of current state

Kinetic energy

[1] C. Zhu, S. Nangia, A. W. Jasper and D. G. Truhlar, J. Chem. Phys. **121**, 7658 (2004).
[2] G. Granucci and M. Persico, J. Chem. Phys. **126**, 134114 (2007).
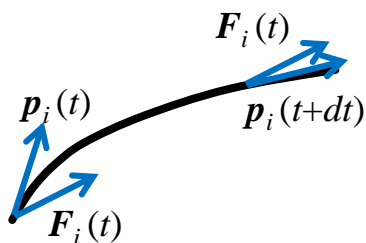
■ **Multiple Gaussian WPs generated due to reflection:**

$$|\psi\rangle = c_A |g_A(x);1\rangle + c_B |g_B(x);2\rangle + c_C |g_C(x);2\rangle \qquad |\psi\rangle = c_A |g_A(x);2\rangle + c_B |g_B(x);1\rangle + c_C |g_C(x);1\rangle$$

Multiple Gaussian WPs are necessary in certain cases
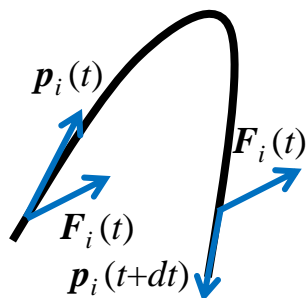**One WP needs to be eliminated, which gives decoherence correction**

Branching Corrected Surface Hopping (BCSH)

- **Resetting wavefunction by judgment of trajectory reflection:**

no reflection

$$\text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t) \right\} = \text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t+dt) \right\}$$

reflection

$$\text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t) \right\} = -\text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t+dt) \right\}$$

When either the active or one of the non-active surfaces is reflected, the wave function is collapsed to the active state (c_a = 1 and c_{na} = 0)

Xu and Wang*, J. Chem. Phys. 150, 164101 (2019)

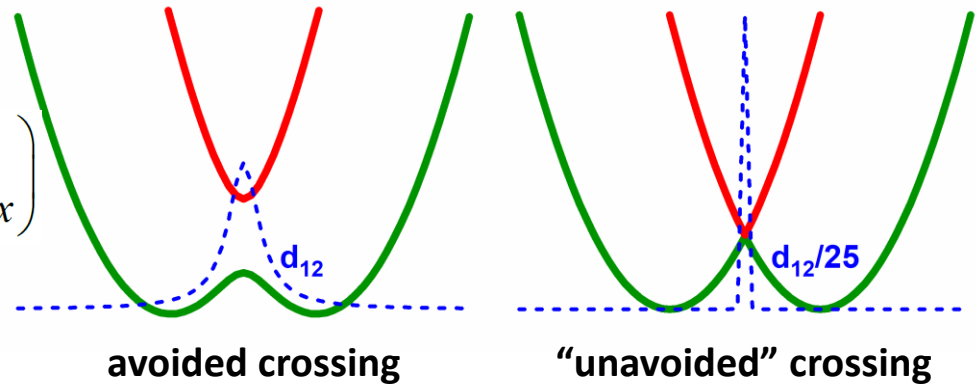# Avoided and "Unavoided" Surface Crossings

■ **Hellmann-Feynman theorem:**

$$d_{ij} = \frac{\langle \phi_i | \frac{\partial H}{\partial x} | \phi_j \rangle}{E_j - E_i}$$

■ **Spin-boson model:**

$$\hat{H}(x) = \begin{pmatrix} Kx^2/2 + \alpha x & V \\ V & Kx^2/2 - \alpha x \end{pmatrix}$$

$$d_{12}(x) = \frac{\alpha V}{2\alpha^2 x^2 + 2V^2}$$

avoided crossing   "unavoided" crossing

Different time intervals are needed for different surface crossings

Granucci, Persico, and Toniolo, J. Chem. Phys. 114, 10608 (2001)
Fernandez-Alberti, Roitberg, Nelson, and Tretiak, J. Chem. Phys. 137, 014512 (2012)
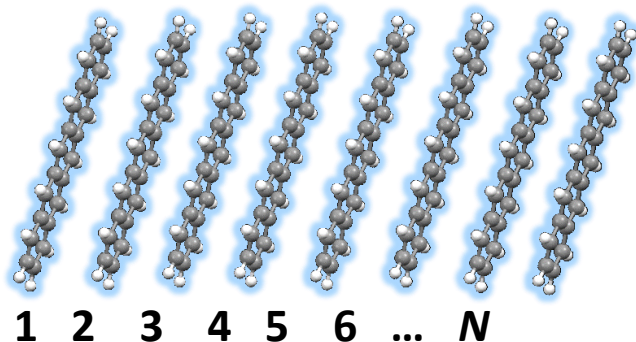Wang* and Beljonne, J. Phys. Chem. Lett. 4, 1888 (2013)
Meek and Levine, J. Phys. Chem. Lett. 5, 2351 (2014)
Wang* and Prezhdo*, J. Phys. Chem. Lett. 5, 713 (2014)
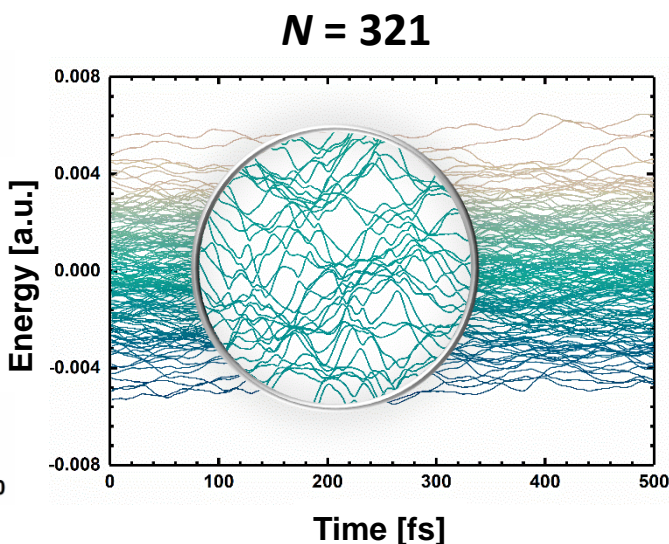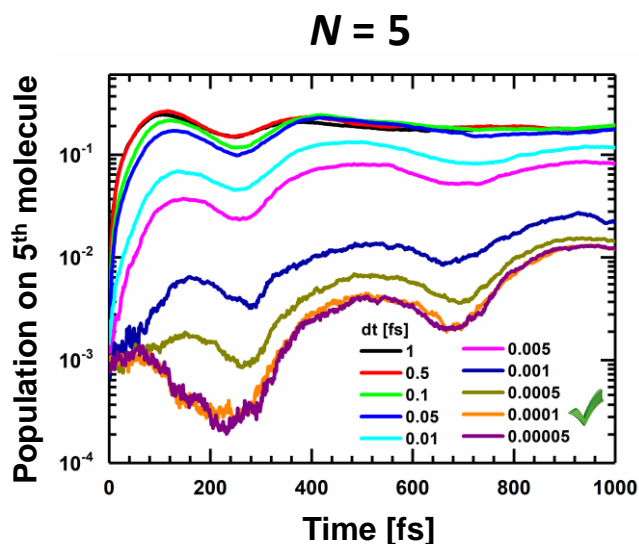Spörkel and Thiel, J. Chem. Phys. 144, 194108 (2016)
Bai, Qiu, and Wang*, J. Chem. Phys. 148, 104106 (2018)

1 2 3 4 5 6 … *N*

■ **Holstein Hamiltonian：**

$$\hat{H} = \sum_{i=1}^{N-1} V\left(|i\rangle\langle i+1| + |i+1\rangle\langle i|\right) + \sum_{i=1}^{N} \frac{1}{2}\left(Kx_i^2 + mv_i^2\right) + \sum_{i=1}^{N} \alpha x_i |i\rangle\langle i|$$

electron   **phonon**   **coupling**

N = 5

N = 321

An extremely small time interval is needed to study extended systems

dt [fs]
1	0.005
0.5	0.001
0.1	0.0005 ✓
0.05	0.0001
0.01	0.00005

Wang* and Prezhdo*, J. Phys. Chem. Lett. 5, 713 (2014)

Artificial Long-Range Population Transfer

■ **Distribution of the energy gap:**
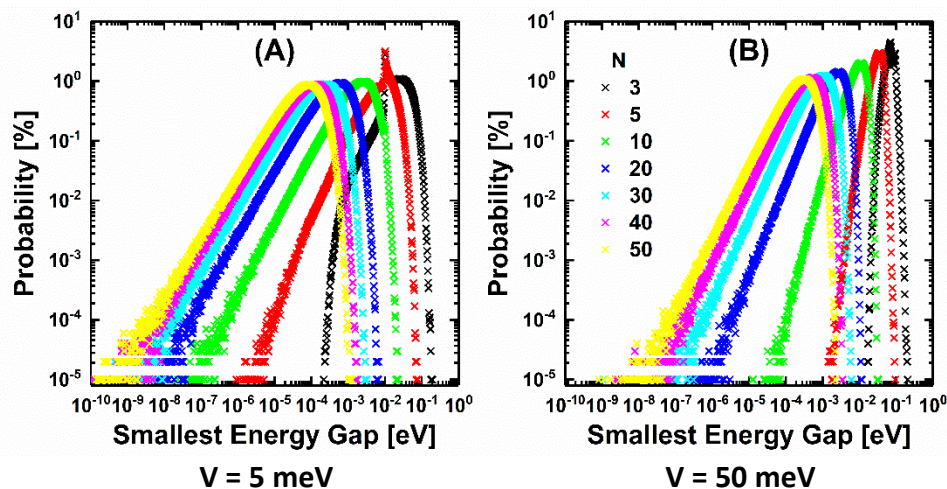
■ **Artificial population transfer:**
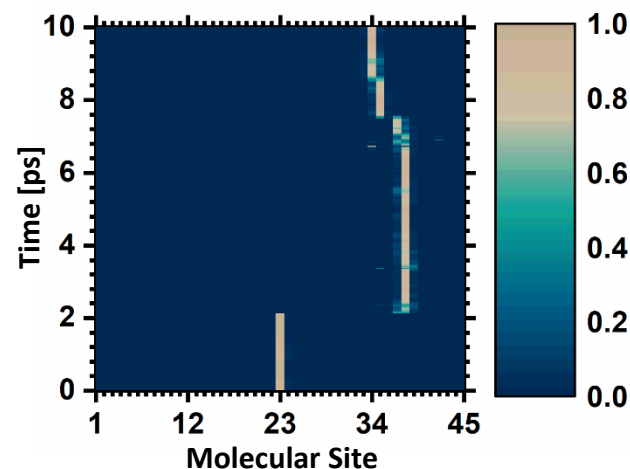
Improper treatment of even one single trivial crossing could easily
lead to artificial long-range population transfer

Wang* and Prezhdo*, J. Phys. Chem. Lett. 5, 713 (2014)
Bai, Qiu, and Wang*, J. Chem. Phys. 148, 104106 (2018)

Self-Consistency of Hopping Probabilities and Self-Consistent Correction

- **Exact total probability:**

$$\frac{\left|c_a(t)\right|^2 - \left|c_a(t+dt)\right|^2}{\left|c_a(t)\right|^2}$$

- **FSSH probabilities:**

$$b_{ij} = 2\hbar^{-1}\,\mathrm{Im}\left(a_{ij}^* V_{ij}\right) - 2\,\mathrm{Re}\left(a_{ij}^* \sum_k v_k \cdot d_{ij}^k\right)$$

$$g_{ij} = -\frac{\Delta t\, b_{ij}}{a_{ii}}$$

- **Self-consistent correction:**
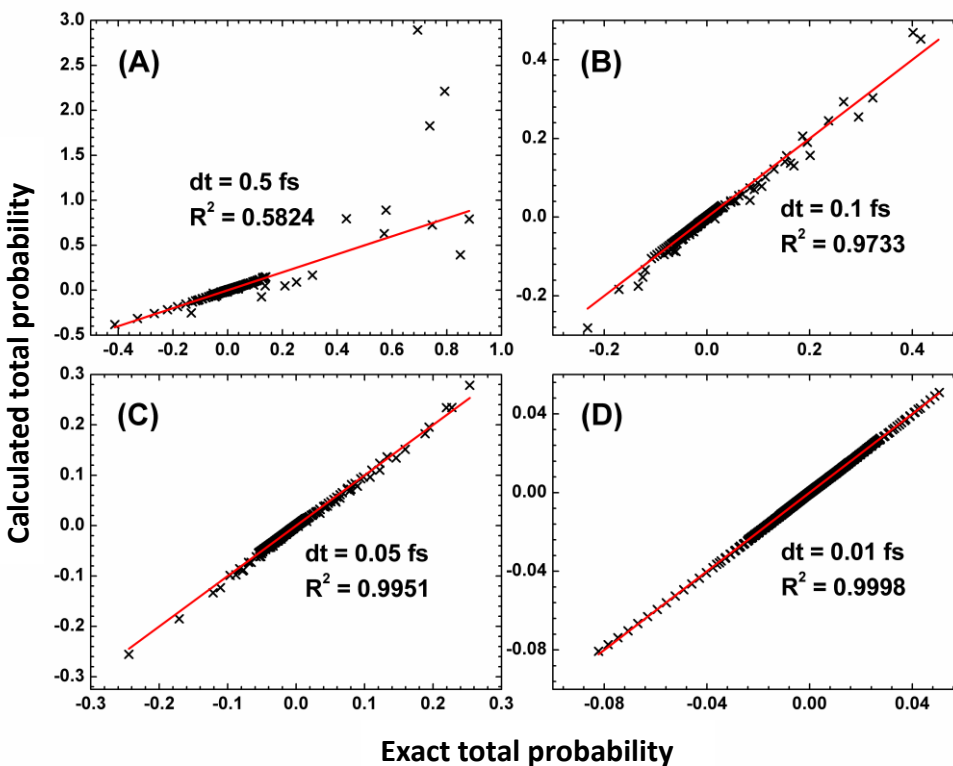
$$g_{aj} = \frac{\left|c_a(t)\right|^2 - \left|c_a(t+dt)\right|^2}{\left|c_a(t)\right|^2} - \sum_{i\neq j} g_{ai}$$

Wang* and Prezhdo*, J. Phys. Chem. Lett. 5, 713 (2014)

Liouville Space Surface Hopping

Hilbert Space

$$\left|\psi(t)\right\rangle = \sum_i c_i(t)\left|i\right\rangle$$

$$\frac{\partial\left|\psi(t)\right\rangle}{\partial t} = \frac{\hat{H}}{i\hbar}\left|\psi(t)\right\rangle$$

$$\rho_{ii} \equiv \left|c_i\right|^2 \qquad \sum_i \rho_{ii} = 1$$

$$\dot{\rho}_{ii} = \sum_{j\neq i} b_{ij}$$

Liouville Space

$$\left|\rho(t)\right\rangle\rangle = \sum_{ij} \rho_{ij}(t)\left|ij\right\rangle\rangle$$

$$\frac{\partial\left|\rho(t)\right\rangle\rangle}{\partial t} = \frac{\hat{\hat{L}}}{i\hbar}\left|\rho(t)\right\rangle\rangle$$

$$p_{ij} \equiv \left|\rho_{ij}\right|^2 \qquad \sum_{ij} p_{ij} = 1$$

$$\dot{p}_{ij} = \sum_{k\neq i \text{ or } l\neq j} b_{ij,kl}$$

Similar Formalism

Surface hopping can be extended to the Liouville space

Three-Level Superexchange Model
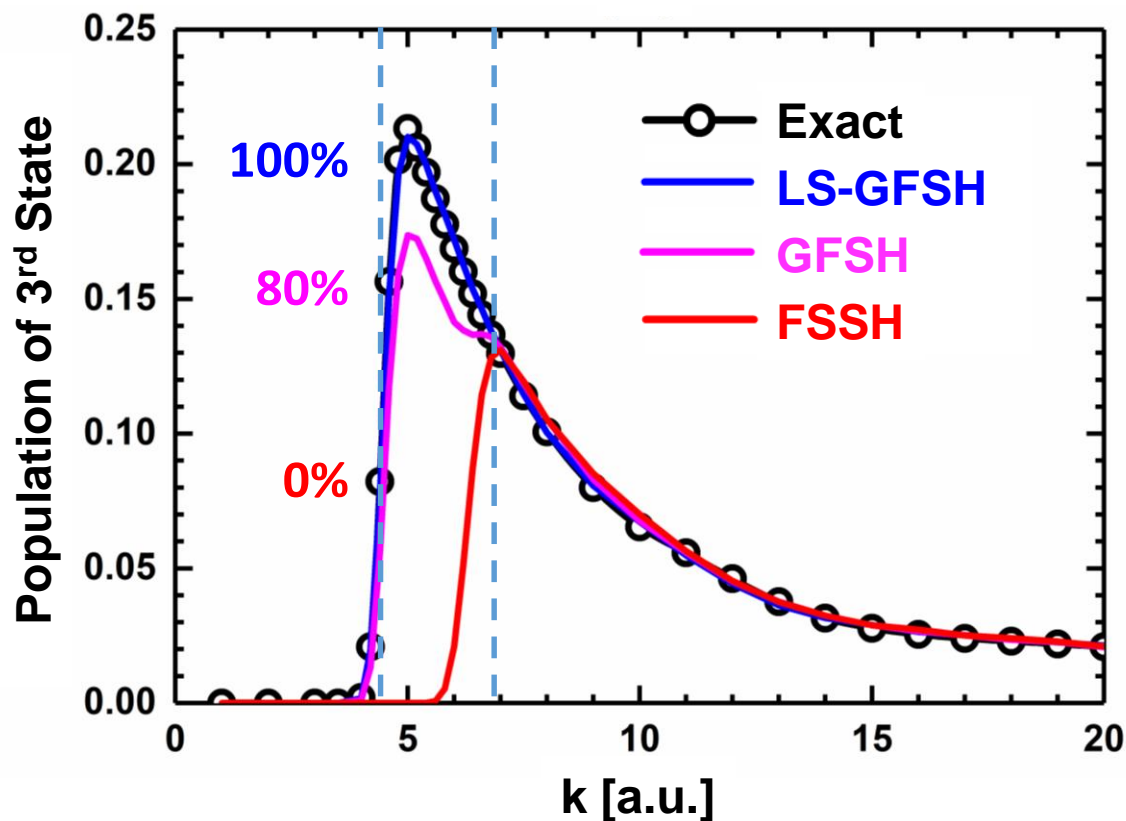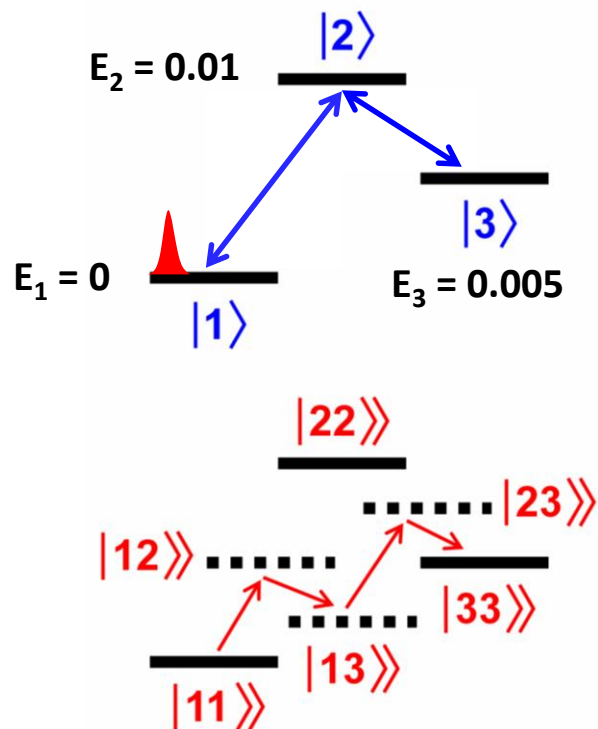
LS-GFSH reproduces the exact solution for superexchange

Wang*, Sifain, and Prezhdo*, J. Chem. Phys. 143, 191102 (2015)

More theoretical insight (further reading)

- Mean-field dynamics

[1] K. Drukker, J. Comp. Phys. 153, 225 (1999).

[2] J. C. Tully, J. Chem. Phys. 93, 1061 (1990).

[3] J. C. Tully, Int. J. Quantum Chem. 25, 299 (1991).

[4] J. C. Tully, Faraday Disc. 110, 407 (1998).

- Pechukas force

[1] F. Pechukas, Phys. Rev. 181, 174, (1969).

[2] W. H. Miller and T. George, J. Chem. Phys. 56, 5637 (1972).

[3] M. F. Herman, J. Chem. Phys. 81, 754 (1984).

[4] M. F. Herman, J. Chem. Phys. 82, 3666 (1985).

[5] F. Webster, P. J. Rossky and R. A. Friesner, Comp. Phys. Comm. 63, 494 (1991).

[6] D. F. Coker and L. Xiao, J. Chem. Phys. 102, 496 (1995).

[7] B. J. Schwartz, E. R. Bittner, O. V. Prezhdo and P. Rossky, J. Chem. Phys. 104, 5942 (1996).

More theoretical insight (further reading)

- Hamilton-Jacobi equations

[1] K. Drukker, J. Comp. Phys. 153, 225 (1999).

[2] J. Tully, Faraday Disc. 110, 407 (1998).

- Decay of mixing (Decoherence)

[1] K. Drukker, J. Comp. Phys. 153, 225 (1999).

[2] B. J. Schwartz, E. R. Bittner, O. V. Prezhdo and P. Rossky, J. Chem. Phys. 104, 5942 (1996).

[3] C. Zhu, S. Nangia, A. W. Jasper and D. G. Truhlar, J. Chem. Phys. 121, 7658 (2004).

[4] A. W. Jasper, S. Nangia, C. Zhu and D. G. Truhlar, Acc. Chem. Res. 39, 101, (2006).

[5] M. J. Bedard-Hearn, R. E. Larsen and B. Schwartz, J. Chem. Phys. 123, 234106 (2005).

[6] J.-Y. Fang and S. Hammes-Schiffer, J. Chem. Phys. 103, 9309 (1999).

[7] G. Granucci and M. Persico, J. Chem. Phys. 126, 134114 (2007).

Surface Hopping方法评估

1971, Tully, Preston, **RSSH (1046)**
1990, Tully, **FSSH/MDQT (1573)**
1994, Webster, Rossky, Friesner, **SPSH (144)**
1997, Prezhdo, Rossky, **MF/SH (212)**
1998, Sholl, Tully, **GSH (96)**
1999, Fang, Hammes-Schiffer, **MDQT* (82)**
2000, Volobuev, Hack, Truhlar, **CSS (88)**
2001, Hack, Truhlar, **CSS2 (34)**
2001, Hack, Truhlar, **NDM (63)**
2002, Jasper, Truhlar, **FSTU (87)**
2003, Jasper, Truhlar, **FSTU▽V (46)**
2004, Zhu, Jasper, Truhlar, **SCDM (86)**
2004, Zhu, Jasper, Truhlar, **CSDM (116)**
2005, Zhu, Jasper, Truhlar, **LDM, PDDM (49)**
2007, Granucci, Persico, **EFS (122)**
2007, Lasser, Swart, Teufel, **SSSH (16)**
2008, Zhu, Truhlar, **CSDM-D (20)**
2009, Shenvi, Tully, **IESH (59)**
2009, Mitric, Petersen, B-Koutecky, **FISH (45)**

2011, Shenvi, Subotnik, Yang, **PC-FSSH (32)**
2011, Shenvi, Subotnik, Yang, **STSH (45)**
2011, Fischer, Chapman, Li, **SHEEP (22)**
2011, Subotnik, Shenvi, **A-FSSH (60)**
2012, Fernandez-Alberti, Tretiak, **Min-Cost (29)**
2012, Shushkov, Tully, **RPSH (5)**
2012, Jaeger, Fischer, Prezhdo, **DISH (43)**
2013, Wang, Beljonne, **FSH (35)** ✔
2013, Gorshkov, Tretiak, Mozyrsky, **SCMC (13)**
2014, Akimov, Prezhdo, **CPF (10)**
2014, Akimov, Prezhdo, **SQUASH (7)**
2014, Zheng, Truhlar, **AAT-CDSM (5)**
2014, Wang, Prezhdo, **SC-FSSH (28)** ✔
2014, Wang, Prezhdo, **GFSH (19)** ✔
2014, Feng, Li, Fang, Yan, **QTMF (3)**
2015, Ouyang, Subotnik, **SL-FSSH (7)**
2015, Sherman, Corcelli, **FSSH-L (2)**
2015, Wang, Prezhdo, **LS-FSSH (1)** ✔
2015, Wang, Prezhdo, **LS-GFSH (0)** ✔

Part III:
On-the-fly Implementation of
Surface Hopping

Implementation (direct dynamics "on-the-fly")

What is "on-the-fly" (Wikipedia)

In colloquial use, on-the-fly means something created when needed. The phrase is used to mean:
(1) something that was not planned ahead.
(2) changes that are made during the execution of some activity: ex tempore, impromptu.

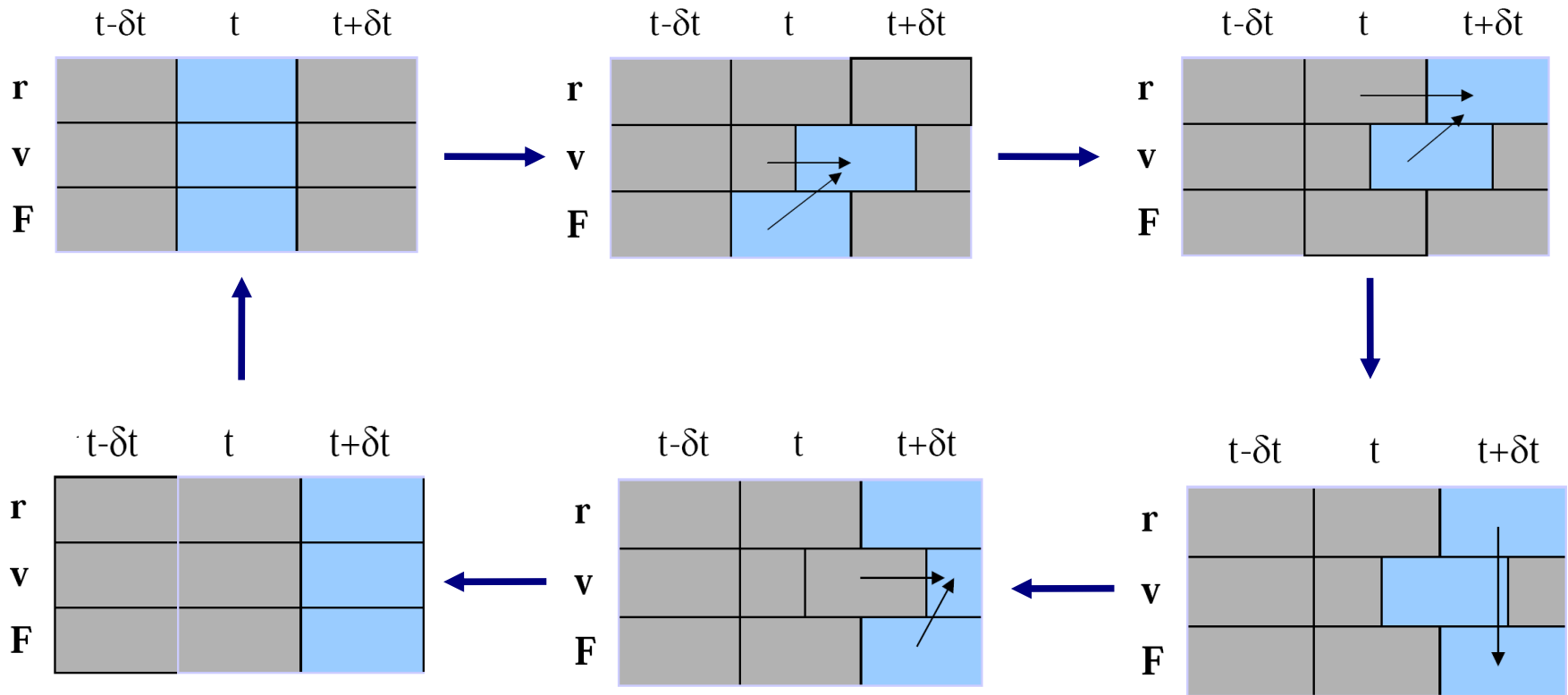### How to calculate direct (on-the-fly) nonadiabatic dynamics

All potential energies, gradients and interstate couplings are computed at each point along a classical trajectory, instead of being calculated before dynamics calculations.

(1) At time t and position R(t), calculate the potential energies, gradients and nonadiabatic couplings.

(2) Calculate the position R(t+dt) at next time step t+dt by solving the Newton equations.

(3) Calculate the quantum evolutions by solving the electronic Schrödinger equation.

(4) Back to (1) for time t+dt and R(t+dt).

Implementation (velocity Verlet)

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t - \frac{\nabla E(t) \cdot \mathbf{M}^{-1}}{2}\Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) - \frac{[\nabla E(t) + \nabla E(t + \Delta t)] \cdot \mathbf{M}^{-1}}{2}\Delta t$$

[1]   L. Verlet, J. Phys. Rev. **159**, 98 (1967).

Implementation (quantum propagation)

- ## Electronic Schrödinger equation

$$i\hbar\frac{dc_j(t)}{dt} = \sum_i c_i(t)\left[H_{ji} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{d}_{ji}\right]$$

Electronic Schrödinger equation in matrix form

$$\frac{d}{dt}\tilde{\mathbf{c}}(t) = i\underline{\mathbf{A}}(t)\tilde{\mathbf{c}}(t)$$

Short-time propagation

$$\tilde{\mathbf{c}}(t+dt) = exp(i\underline{\mathbf{A}}dt)\tilde{\mathbf{c}}(t)$$

Unitary propagator

$$\underline{\mathbf{A}} = \underline{\mathbf{U}}\begin{pmatrix}\omega_1 & 0 & \ldots & 0 \\ 0 & \omega_2 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & \omega_n\end{pmatrix}\underline{\mathbf{U}}^\dagger \qquad e^{i\underline{\mathbf{A}}dt} = \underline{\mathbf{U}}\begin{pmatrix}e^{i\omega_1 dt} & 0 & \ldots & 0 \\ 0 & e^{i\omega_2 dt} & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & e^{i\omega_n dt}\end{pmatrix}\underline{\mathbf{U}}^\dagger$$

Initial sampling

- Generate a large number of geometries
- (a) Normal modes
- (a1) Calculate the equilibrium geometry and normal modes
- (a2) For mode i, generate a pair of (x_i, p_i) in phase space
- (a3) Combine all (x_i, p_i) to get one initial condition
- (a4) Repeat (a2) and (a3)
- (b) Molecular-dynamics simulations
- (b1) Molecular dynamics run
- With fixed energy
- With fixed temperature
- (b2) Take many snapshots from production run.
- Select geometries
- (a) Energy window
- (b) Transition probability
-

[1] M. Barbatti, G. Granucci, et. al. J. Photochem. Photobiol. A **190**, 228 (2007).

Sampling of normal mode (Wigner distribution)

Wigner distribution function

$$W(q, p) = \frac{1}{\pi \hbar} \int_{-\infty}^{\infty} dy \langle q - y | \hat{\rho} | q + y \rangle e^{2ipy/\hbar},$$

$$W(q, p) = \frac{1}{\pi \hbar} \int_{-\infty}^{\infty} dy \psi^*(q + y) \psi(q - y) e^{2ipy/\hbar}$$

Expectation value of a physical observable

$$\int dq \int dp\, A(q, p) W(q, p) = Tr(\hat{\rho} \hat{A}(\hat{q}, \hat{p}))$$

Vibrational ground-state of a harmonic oscillator

$$W(P_i, Q_i) = N\, exp[-(P_i^2 + Q_i^2)]$$

(1) Approximated as a 2D Gaussian function

(2) In dimensionless normal coordinates
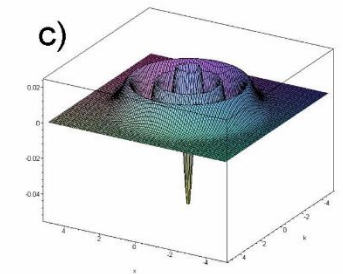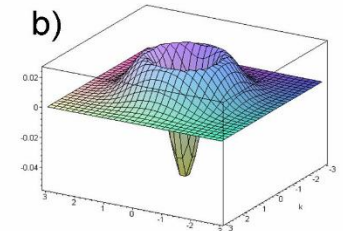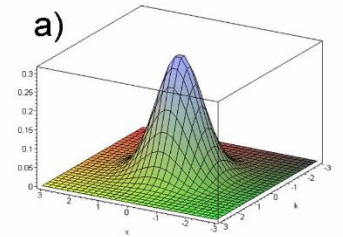
[1] E. Wigner, Phys. Rev. **40**, 749 (1932).
[2] "Conical Intersections: Electronic Structure, Dynamics and Spectroscopy", edited by W. Domcke, D. R. Yarkony, and H. Köppel (2004).

Sampling of normal mode (energy)

Action-angle variables

$$Q_i = \sqrt{2n_i + 1}\,\sin\alpha_i$$
$$P_i = \sqrt{2n_i + 1}\,\cos\alpha_i$$

$$\alpha_i \in [0, 2\pi]$$

(i*n dimensionless normal coordinates*)

$$E(n_i) = (n_i + \frac{1}{2})\omega_i = \frac{1}{2}\omega_i(P_i^2 + Q_i^2),\ (\hbar = 1)$$

Quantum number of a harmonic oscillator n_i

Boltzmann distribution

$$P(n_i) = exp(-n_i\omega_i/k_B T)$$

Specific vibrational level n_i

[1] U. Müller and G. Stock, J. Chem. Phys. 107, 6230 (1997).
[2] "Conical Intersections: Electronic Structure, Dynamics and Spec-
troscopy", edited by W. Domcke, D. R. Yarkony, and H. Köppel (2004).

Different ways of sampling

Wigner
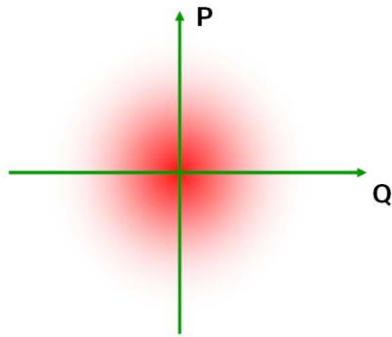
- Quantum distribution

- Energy fluctuations

- The calculation of Wigner function is not easy for vibrationally excited states.

Occupation
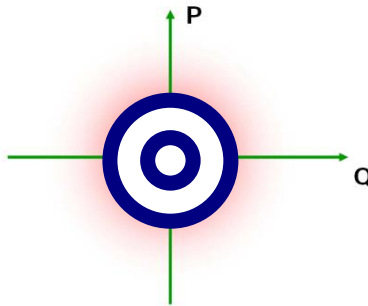
- Constant energy

- Zero-point energy

- Not related to quantum wavefunctions

Classical MD
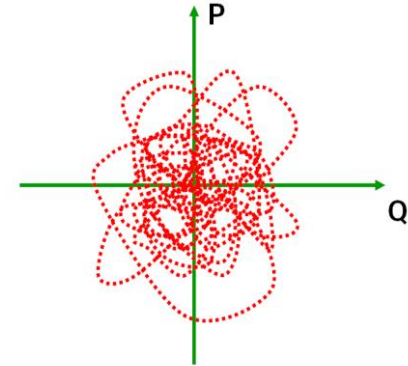
- Very simple

- No zero-point energy

- No detailed balance
  In thermal equilibrium, all modes have the same energy.

Selection of geometries (transition probability)

Transition probability $(S_0 \rightarrow S_k)$:

Transition probability	Oscillator strength	Transition energy	Transition dipole moment

$$P_{k0}^{(i)} = \frac{f_{k0}^{(i)}/\omega_{k0}^{(i)}}{max(f_{k0}^{(i)}/\omega_{k0}^{(i)})} = \frac{|\mu_{k0}^{(i)}|^2}{max(|\mu_{k0}^{(i)}|^2)}$$

Absorption spectra $(S_0 \rightarrow S_k)$:

For geometry i
$$I_{k0}^{(i)} = \frac{f_{k0}^{(i)}}{max(f_{k0}^{(i)})}\delta(\omega - \omega_{k0}^{(i)})$$

For all geometries
$$I_{k0} = \sum_{geom(i)} I_{k0}^{(i)}$$

Nonadiabatic couplings

Treatment of nonadiabatic couplings

Analytical

$$i\hbar \frac{dc_j(t)}{dt} = c_j(t)\epsilon_j - i\hbar \sum_i c_i(t)\dot{\mathbf{R}} \cdot \mathbf{d}_{ji}$$

- **Nonadiabatic coupling vectors (NAC)**

$$\mathbf{d}_{ji} \equiv \int d\mathbf{r}\phi_j^*(\mathbf{r},\mathbf{R})\left[\nabla_{\mathbf{R}}\phi_i(\mathbf{r},\mathbf{R})\right]$$

Numerical

- **No NAC available in many codes**

- **Numerical approaches** *Wavefunction overlap*

$$F_{ji} = \dot{\mathbf{R}} \cdot \mathbf{d_{ji}} = \int dr\phi_j^*(t)\frac{\partial \phi_i^*(t)}{\partial t}$$

$$F_{ji} = \frac{1}{\delta t} < \phi_j(t)|\phi_i(t+\delta t) >$$

Electronic Schrödinger equation
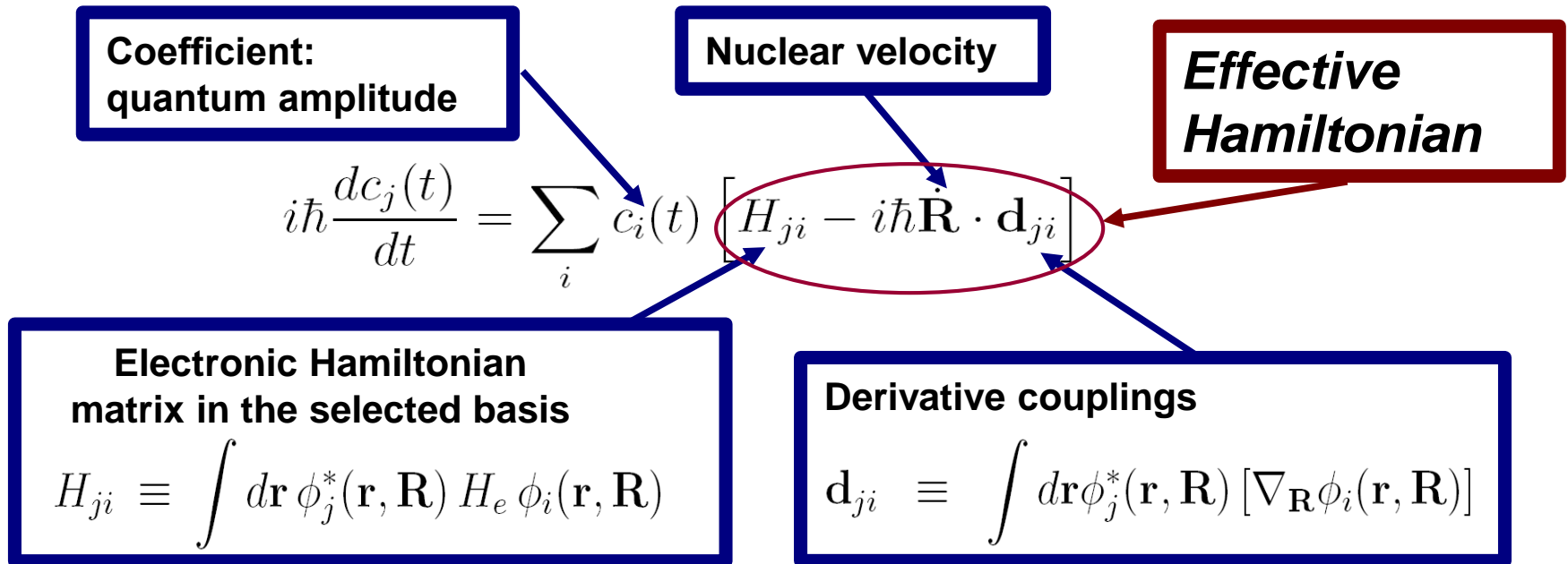
Coupled equations for electronic motion

Coefficient:
quantum amplitude

Nuclear velocity

Effective Hamiltonian

$$i\hbar\frac{dc_j(t)}{dt} = \sum_i c_i(t)\left[H_{ji} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{d}_{ji}\right]$$

Electronic Hamiltonian matrix in the selected basis

$$H_{ji} \equiv \int d\mathbf{r}\,\phi_j^*(\mathbf{r},\mathbf{R})\,H_e\,\phi_i(\mathbf{r},\mathbf{R})$$

Derivative couplings

$$\mathbf{d}_{ji} \equiv \int d\mathbf{r}\phi_j^*(\mathbf{r},\mathbf{R})\left[\nabla_\mathbf{R}\phi_i(\mathbf{r},\mathbf{R})\right]$$

Derivative coupling term

(derivative of electronic wavefunction with respect to time)

$$F_{ji} = \dot{\mathbf{R}}\cdot\mathbf{d_{ji}} = \int d\mathbf{r}\phi_j^*(t)\frac{\partial\phi_i(t)}{\partial t} \qquad \frac{\partial}{\partial t} = \frac{\partial}{\partial\mathbf{R}}\frac{d\mathbf{R}}{dt}$$

[1]   J. C. Tully, J. Chem. Phys. 93, 1061 (1990).

Numerical nonadiabatic couplings

CI form of electronic wavefunctions

$$|\phi_i(t)\rangle = \sum_k C_{ik}(t) \left|\psi_k^{CSF}(t)\right\rangle$$

Slater determinant:

Elements:
Molecular orbitals

$$\left|\psi_k^{CSF}\right\rangle = \begin{bmatrix} \kappa_1^{MO}(r_1) & \kappa_2^{MO}(r_1) & ... \\ \kappa_1^{MO}(r_2) & \kappa_2^{MO}(r_2) & ... \\ ... & ... & ... \end{bmatrix}$$

Overlap of electronic wavefunctions:
Overlap of Slater determinants

$$< \phi_j(t)|\phi_i(t+\delta t) > = \sum_{kl} C_{jk}(t) < \psi_k^{CSF}(t)|\psi_l^{CSF}(t+\delta t) > C_{il}(t+\delta t)$$

Numerical nonadiabatic couplings

Overlap of Slater determinants

$$< \psi_k^{CSF}(t) | \psi_l^{CSF}(t + \delta t) > = \quad \textbf{?}$$

Overlap of Molecular orbitals

$$< \kappa_m^{MO}(t) | \kappa_n^{MO}(t + \delta t) > = \quad \textbf{?}$$

MO -- AO $\quad |\kappa^{MO}(t) > = \sum_p B_{np}(t) | \mu_p^{AO}(t) >$

Overlap of Atomic orbitals

$$< \mu_p^{AO}(t) | \mu_q^{AO}(t + \delta t) >$$

Numerical nonadiabatic couplings

AO Overlap: $< \mu_p^{AO}(t)|\mu_q^{AO}(t + \delta t) >$

MO Overlap: $< \kappa_m^{MO}(t)|\kappa_n^{MO}(t + \delta t) >$

CSF Overlap (Overlap of Slater determinant)

$$< \psi_k^{CSF}(t)|\psi_l^{CSF}(t + \delta t) >$$

Overlap of Electronic Wavefunctions

$$< \phi_j(t)|\phi_i(t + \delta t) >$$

Nonadiabatic couplings

$$F_{ji} = \frac{1}{\delta t} \ < \phi_j(t)|\phi_i(t + \delta t) >$$

Trajectory surface hopping (direct dynamics)

- **Initial sampling**
- (1) Generate many geometries and velocities.
- (2) Select geometries for initial conditions.
- **Classical trajectories**
- (1) Calculate the gradient "on-the-fly".
- (2) Solve the Newton equations.
- **Electronic motion**
- (1) Calculate potential energies and nonadiabatic couplings.
- (2) Solve the time-dependent Schrödinger equation for the electrons.
- **Hopping events**
- (1) Calculate the hopping probability (Tully's approach).
- (2) Judge whether hop takes place or not.
- (3) At the hopping event, adjust the velocity.
- **Final results**
- (1) Average over all trajectories.

Part IV:
On-the-fly Implementation of
Surface Hopping: QM/MM and beyond

QM/MM approach: General overview

QM: ab initio, DFT, semiempirical

MM: standard force field

QM – MM interactions:

„*electronic embedding*"

$$\hat{H}^{I,O}_{QM-MM} = -\sum_{i,J}\frac{q_J}{r_{iJ}} + \sum_{i,J}\frac{q_J Z_A}{R_{AJ}} + \sum_{A,J}\left(\frac{A_{AJ}}{R_{AJ}^{12}} - \frac{B_{AJ}}{R_{AJ}^{6}}\right)$$

QM-MM boundary region:

- **hydrogen link atoms L**

- **charge shift for q(M$_1$)**

Codes:

ChemShell as control module

Interfaces to standard QM and MM codes

H. M. Senn and W. Thiel, Top. Curr. Chem. **268**, 173-290 (2007).
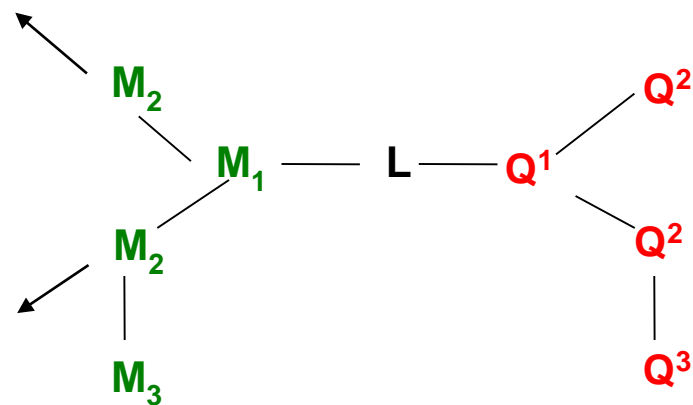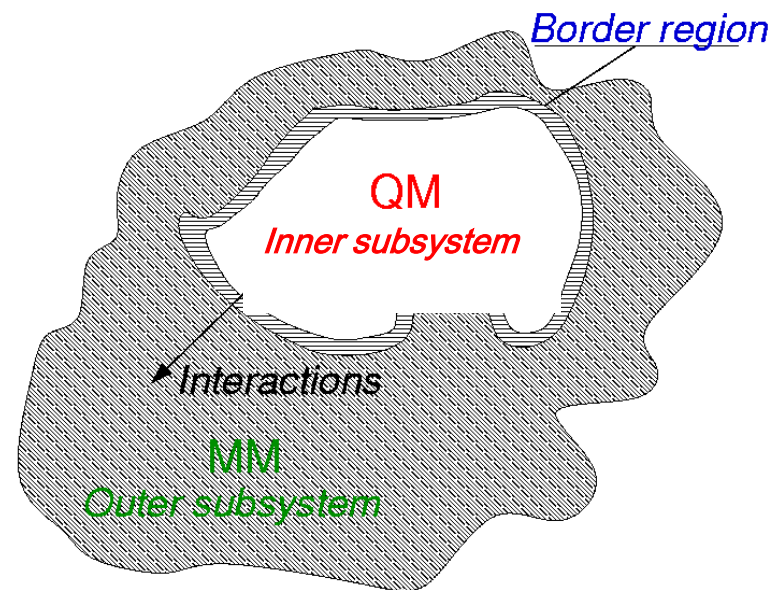
Overview & Timeline

QM/MM Dynamics with Surface Hopping

Keyword search (isiknowledge):

QM/MM   : >>**2500** hits

QM/MM + excited state   : **107** hits

QM/MM + excited state + dynamics : **57** hits

QM/MM + surface hopping   : **8** hits (!)
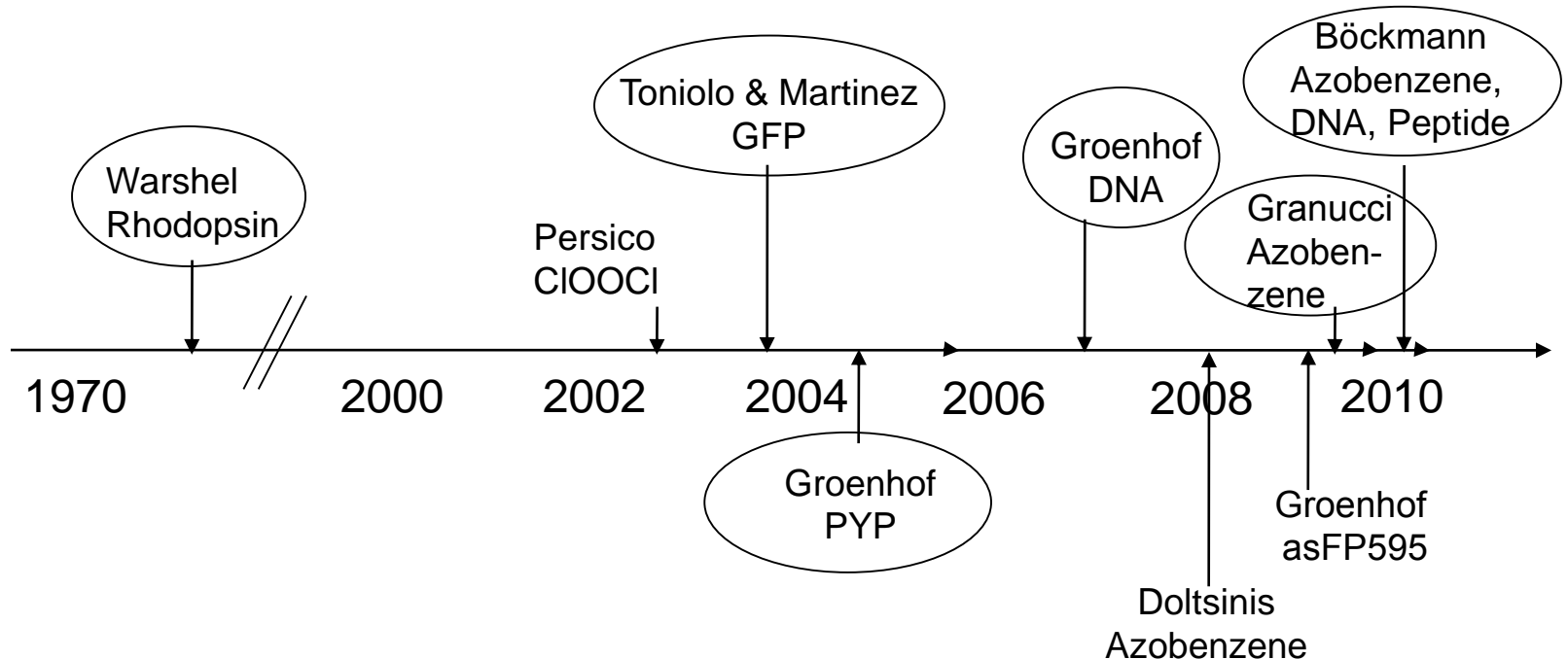
Isomerisation of Retinal in Rhodopsin

Rhodopsin
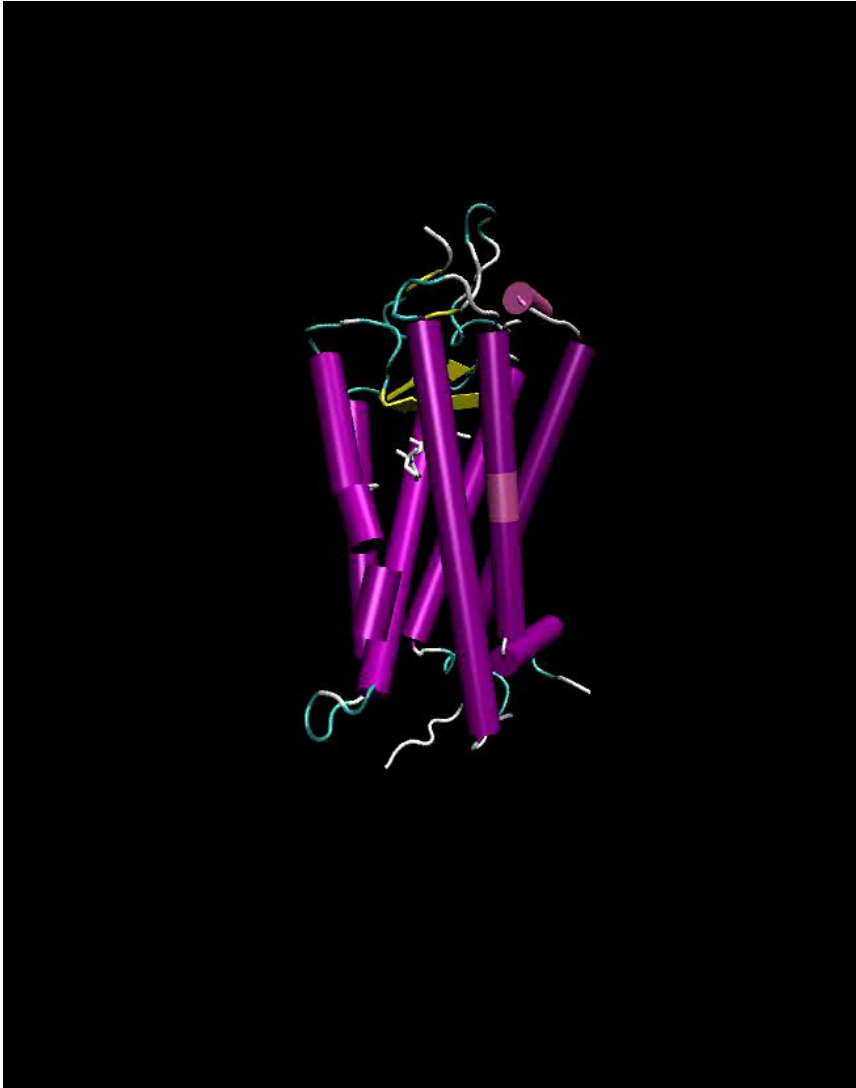
• visual pigment in vertebrate eyes

• transmembrane protein with seven α-helices

• light induces 11-cis to all-trans isomerization of retinal chromophore:
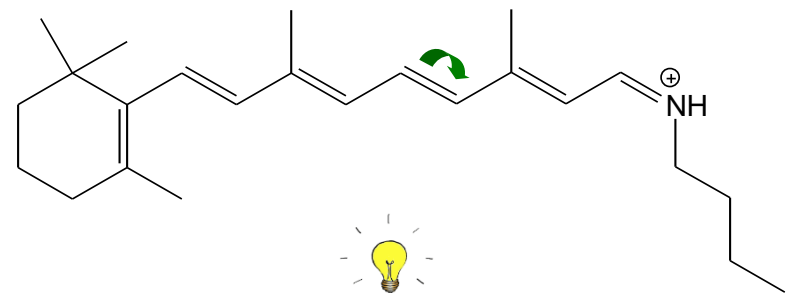
• complete within 200fs!!

Isomerisation of Retinal in Rhodopsin

Retinal: modified PPP Hamiltonian (QCFF/PI)

Protein modelling: steric restriction on retinal, electrostatic interactions by microscopic dielectric model representing average density of typical enzmye

Surface hopping using probabilities from timedependent Schrödinger equation

Warshel, Nature 260, 681 (1976)
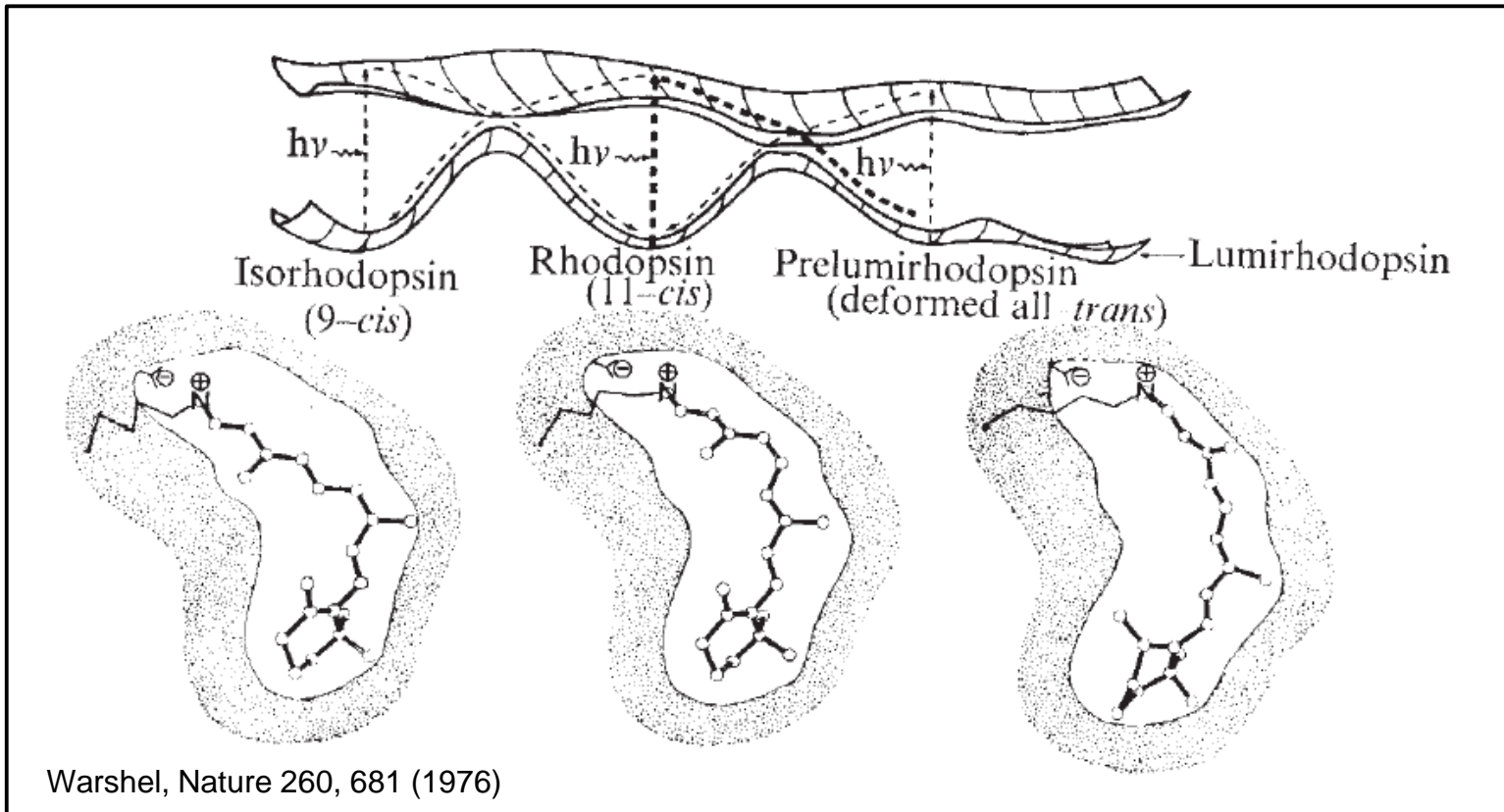
Isomerisation of Retinal in Rhodopsin

One trajectory started from 11-cis Retinal:
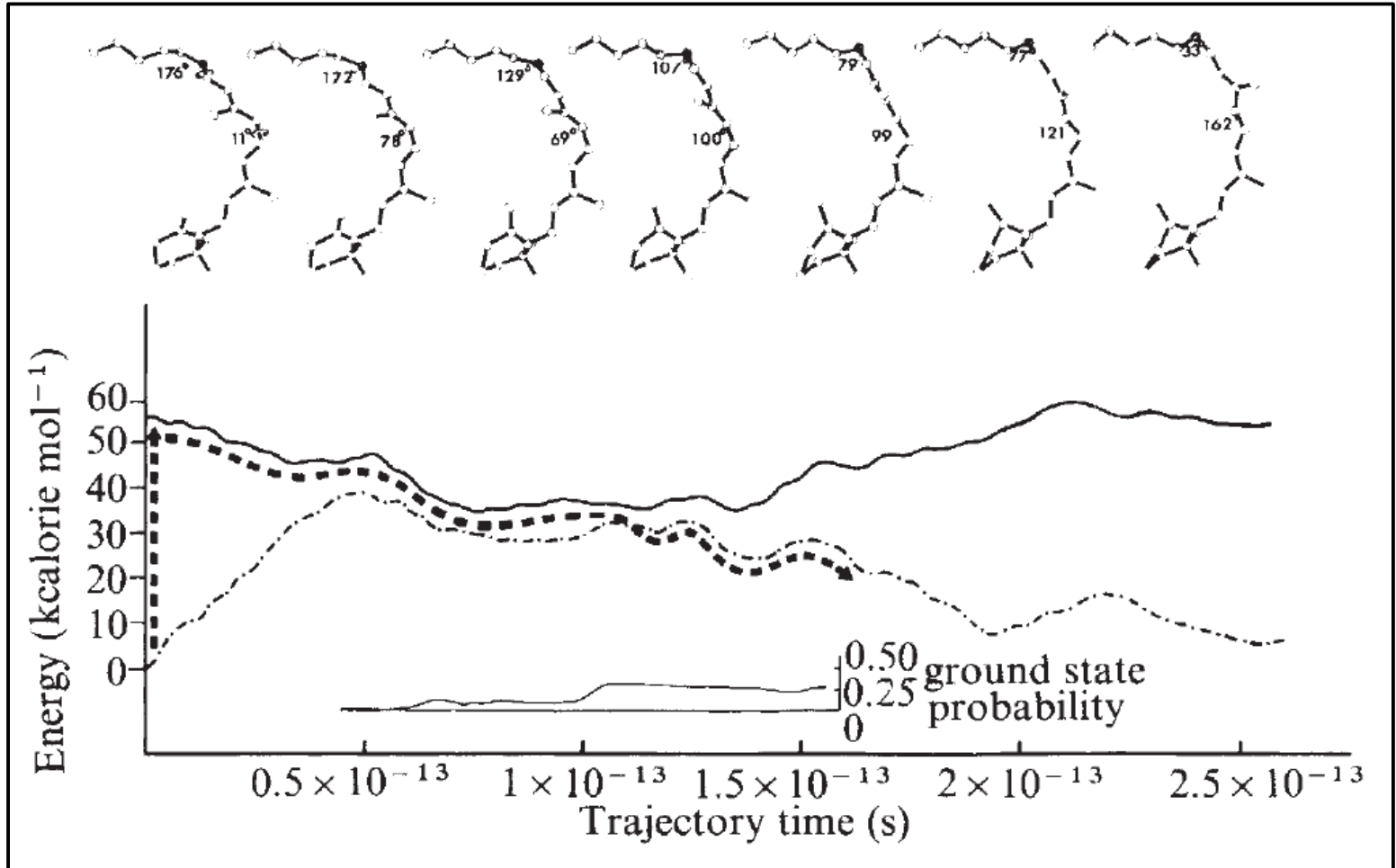
Recent Rh QM/MM SH studies:Martinez et al., J. Phys. Chem. B 2009, 113, 3280
Hayashi et al. (mechanical embedding) Biophys. J. 2009, 96, 403, Polli et al, submitted to nature
Warshel, Nature 260, 681 (1976)

Fluorescent Proteins
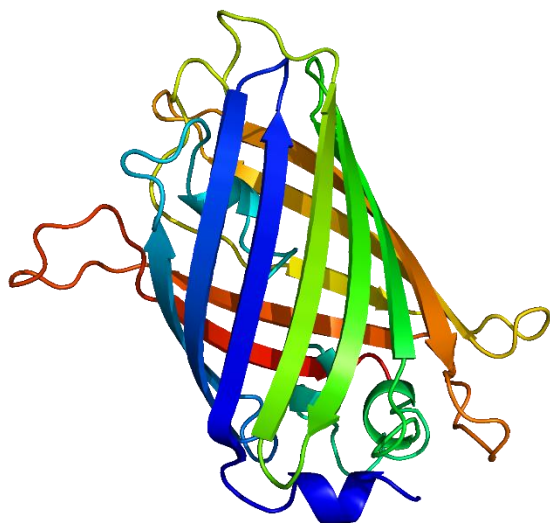
Green Fluorescent Protein

Aqueora – yellyfish

Renilla – soft corals

Red Fluorescent Protein

Antozoa, Discosoma - Sea anemons, corals

- Bioluminescence in invertebrates
- Functions not completely understood
- "Burglar alarm", pairing, communication

M. Zimmer, Chem. Rev. 2002, 102, 759; Gross et al.PNAS 2000, 97, 11990-95
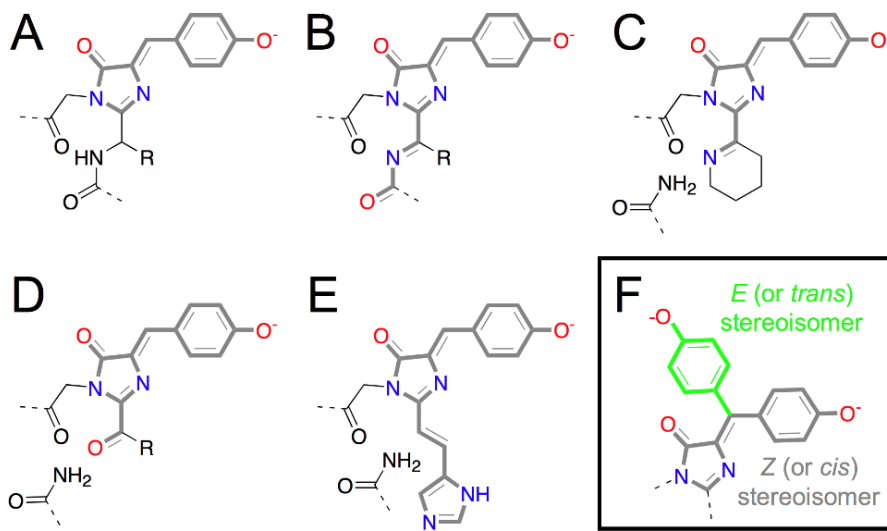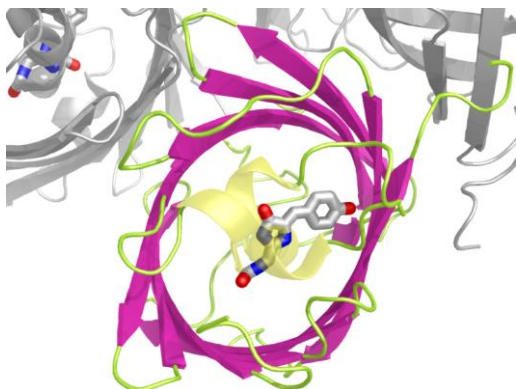
Photoactive Yellow Protein

PYP from Halorhodospira halophila: 14 kDa cytoplasmic photoreceptor protein
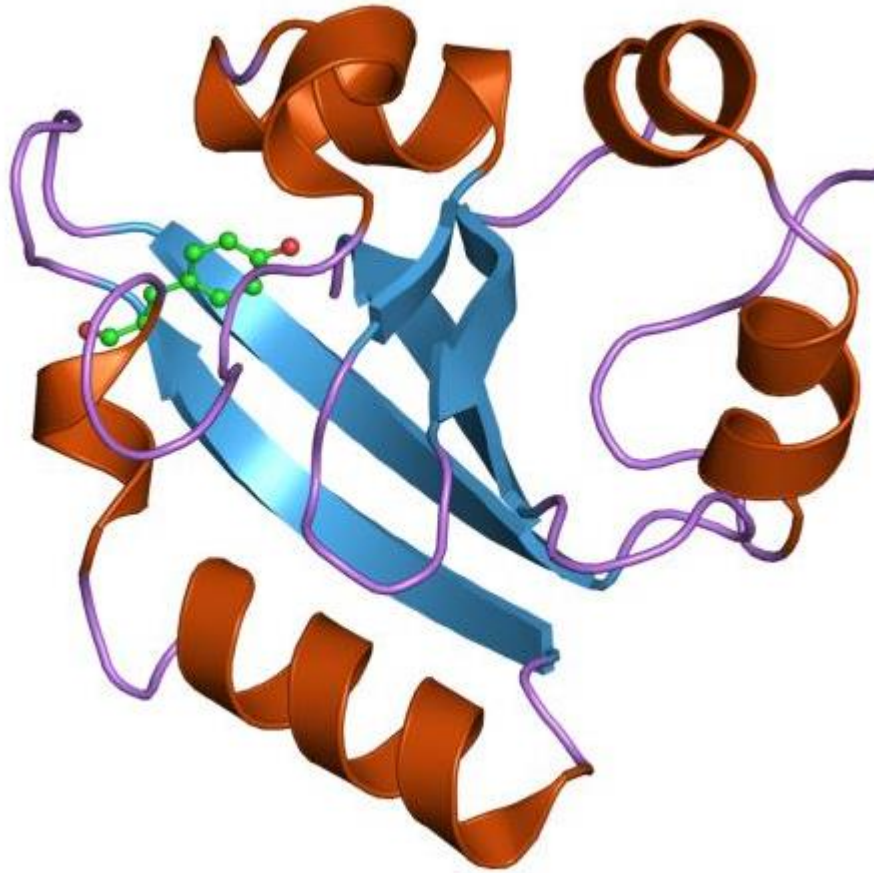
- Responsible for negative phototactic response

- Isomerisation of p-coumaric acid
- initiates partly unfolding →
- activation

$$pG_{446nm}$$

$$h\nu$$

$$\tau_1 = 0.21 \text{ ms}$$
$$\tau_2 = 1.23 \text{ ms}$$

$$\tau_3 = 405 \text{ ms}$$

$$pB_{355nm}$$

Hellingwerf et al J. Phys. Chem. A, 2003, 107, 1082
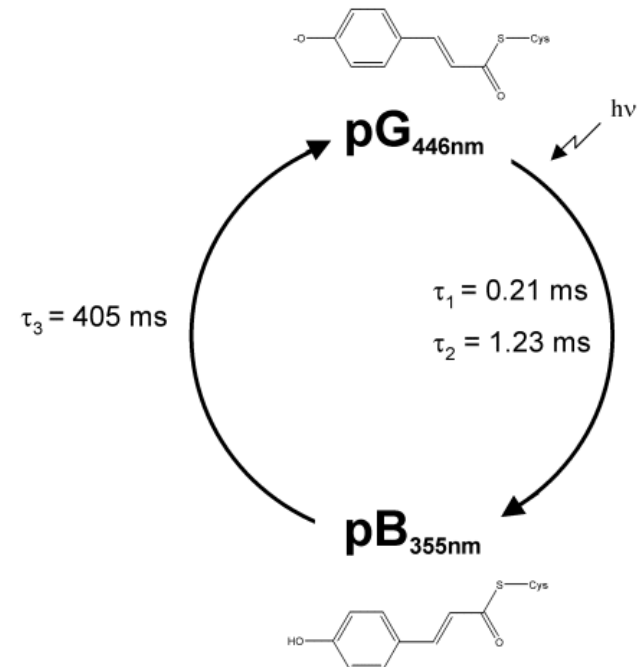
DNA Photoprotection

Ultrafast Proton Transfer in Cytosine-Guanine Base Pairs

Fully hydrated 22 base pair B-DNA

Link atom / hydrogen capping

20 Trajectories G03 CASSCF(8,8)/3-21G / Amber99ff

Initial conditions from 2 ps ground state run

Diabatic surface hopping by CI-vector following
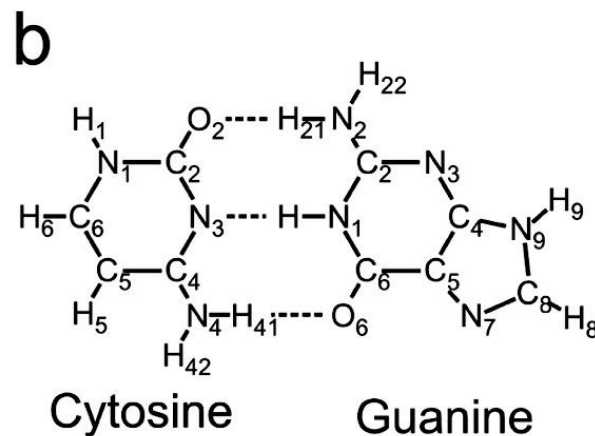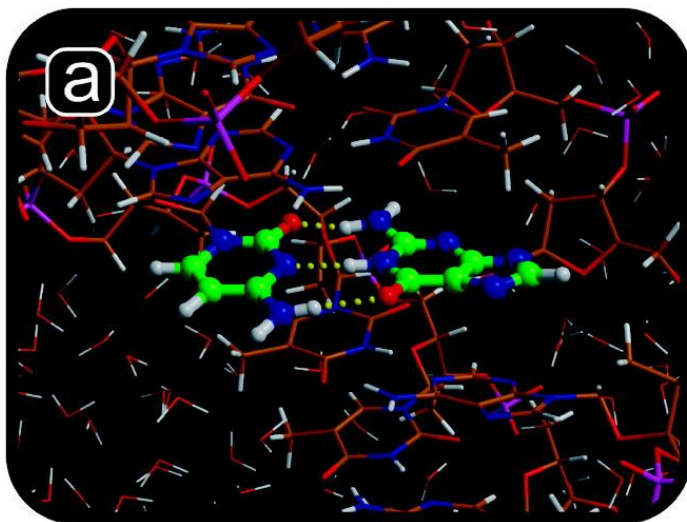
G. Groenhof et al., JACS 129,6812 (2007)

DNA Photoprotection

Scheme of photoinduced Proton transfer reactions

QM/MM excited-state dynamics: Solvated adenine

QM/MM treatments

QM part

Adenine

OM2

GUGA-CI

MM part

Water molecules

CHARMM force-field

TIP3P water

Freeze waters molecules
in outer shell
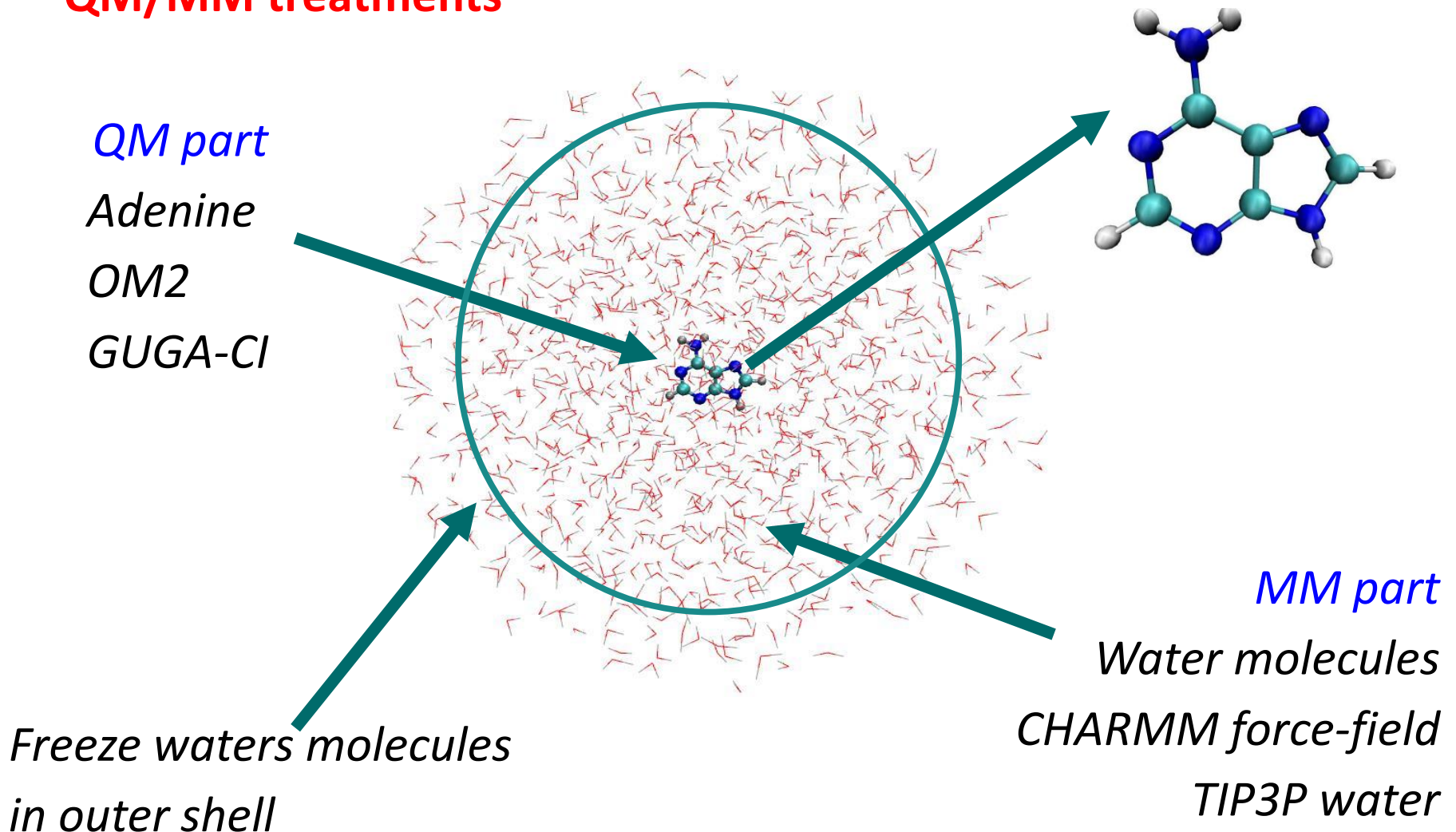
Decay dynamics of adenine in water

Absorption band
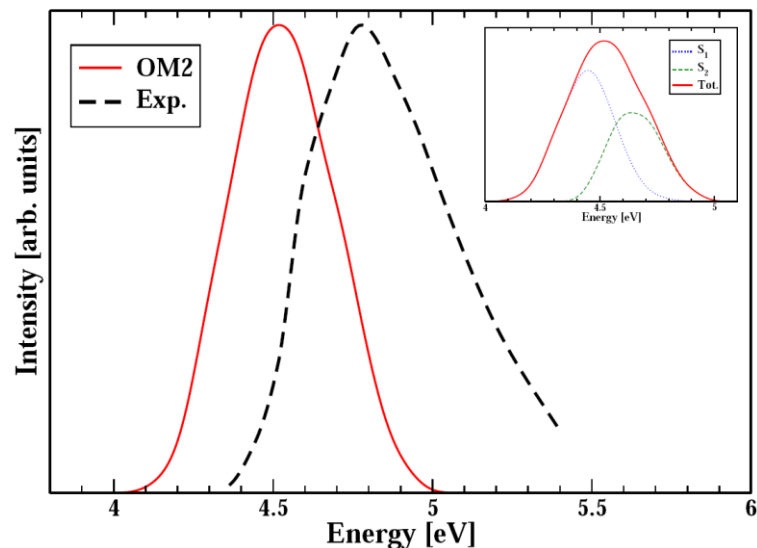
Adiabatic occupations
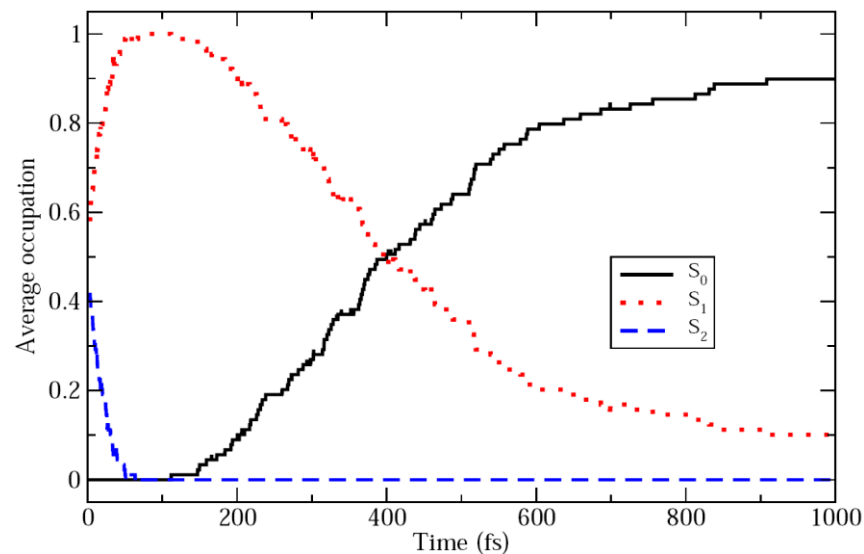
Absorption band:

Strong $\pi\pi^*/n\pi^*$ mixing in initial configurations.

Excitations to S_1 and S_2 states.

Dynamics

Two decay channels are observed.

Two decay time constants: 40 fs, 410 fs (exp: 300-500 fs)

The relaxation time to the ground state is overall reduced compared to the gas phase.
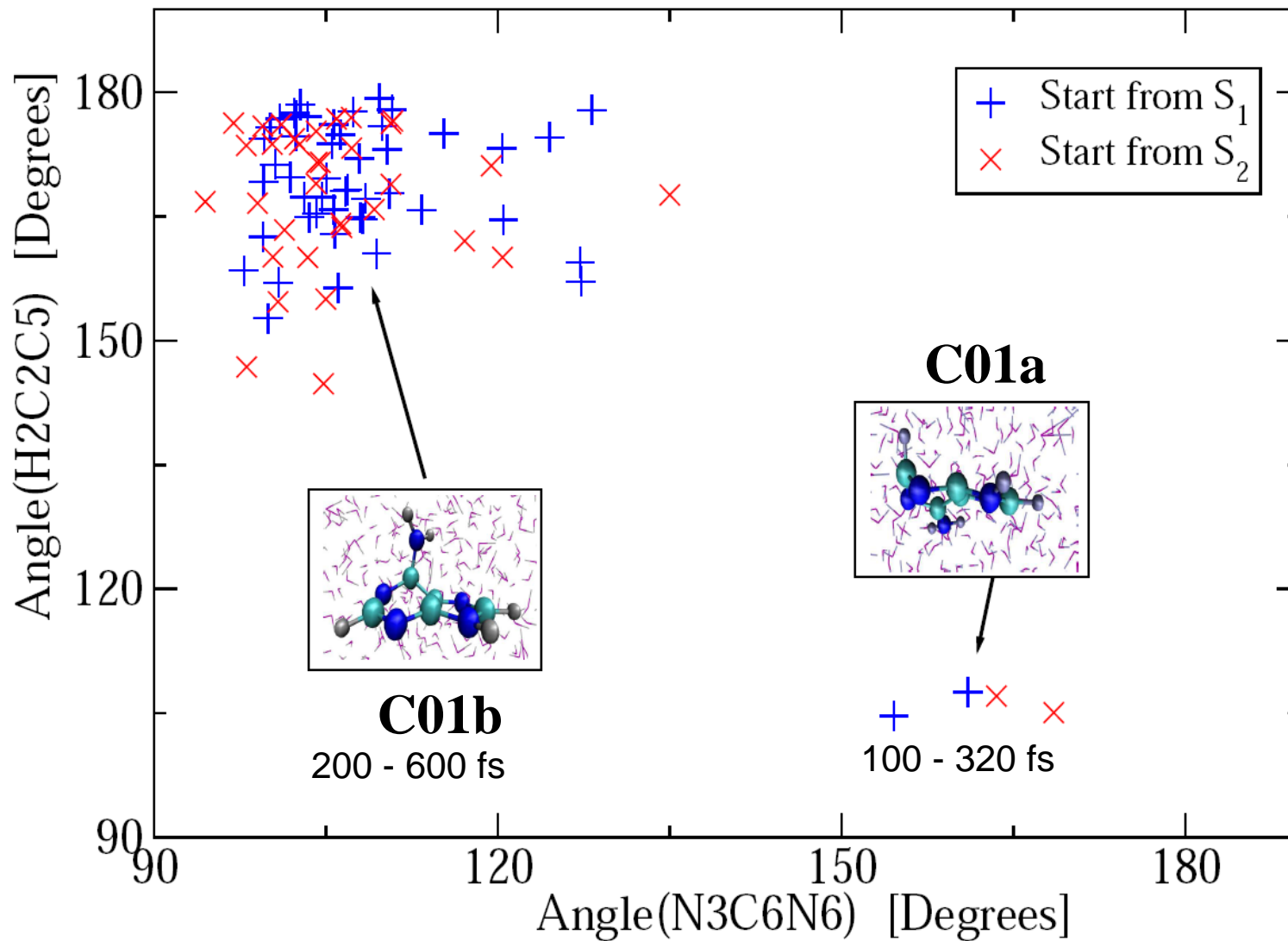
Excited-state dynamics: Adenine in DNA strands
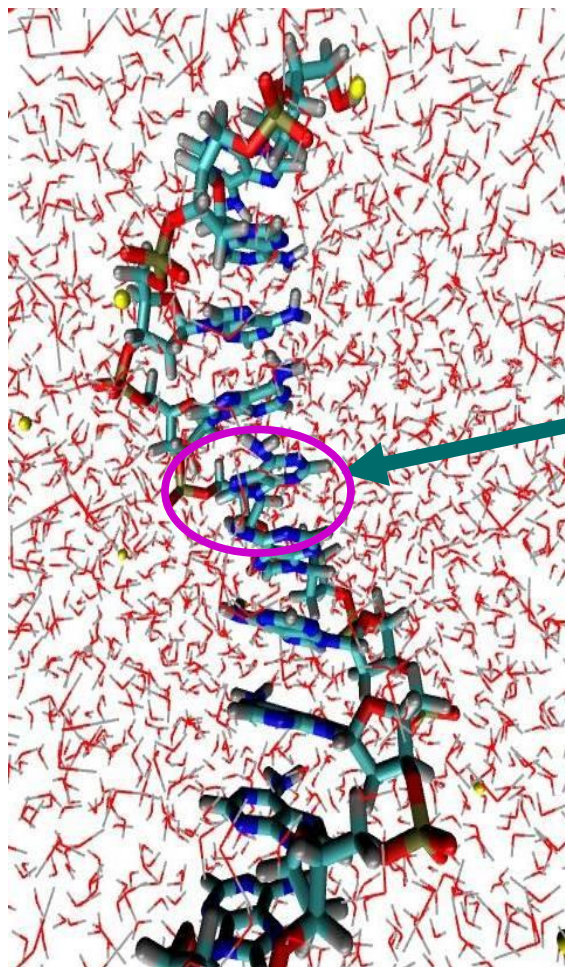
QM part
Single Adenine
OM2/GUGA-MRCI
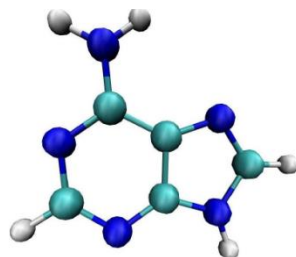
MM part
All other atoms
CHARMM force-field
TIP3P water model
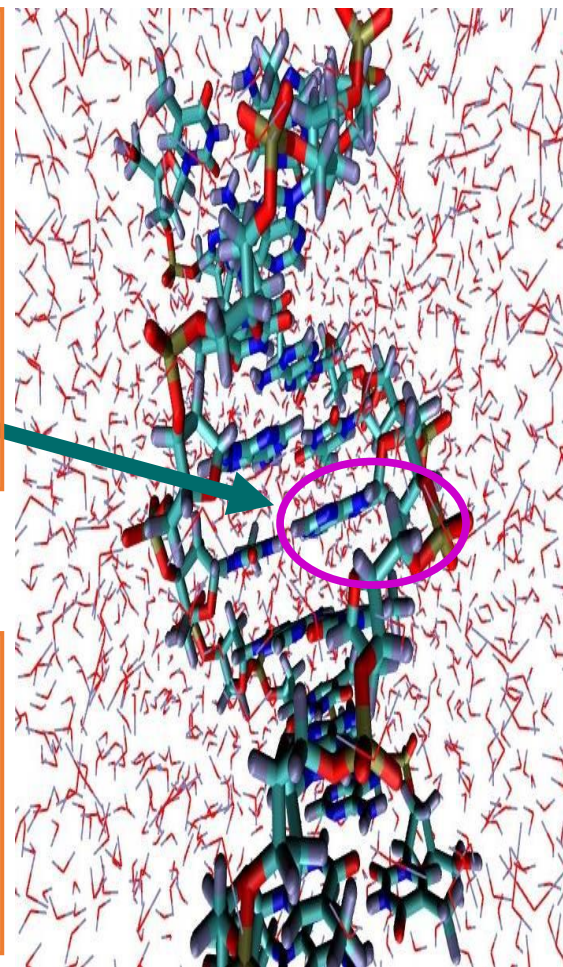
Decay dynamics of adenine in DNA strands

Adenine in single strand $(dA)_{10}$

Absorption maximum 4.63 eV

Adenine in double strands $(dA)_{10}(dT)_{10}$

Absorption maximum 4.69 eV

12% from S_2
88% from S_1
$S_2 \rightarrow S_1 \sim$ 7 fs
$S_1 \rightarrow S_0$ 5.7 ps
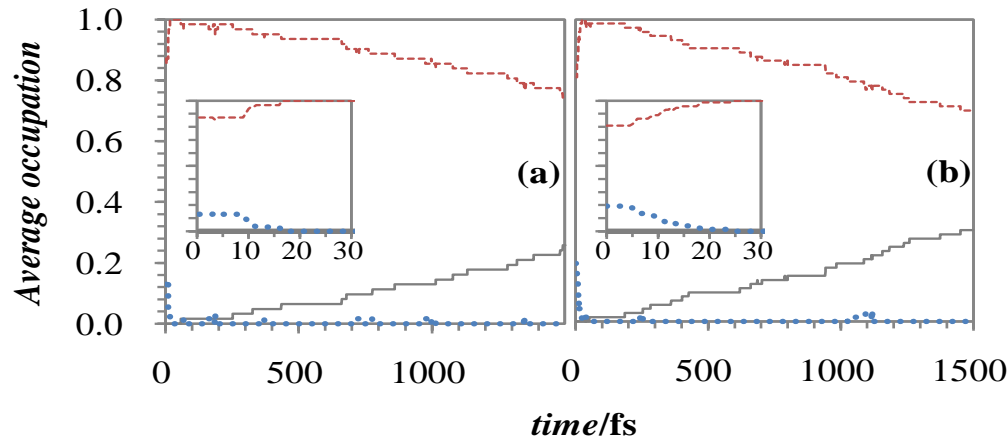
19% from S_2
81% from S_1
$S_2 \rightarrow S_1 \sim$ 7 fs
$S_1 \rightarrow S_0$ 4.1 ps

The internal conversion dynamics of adenine in DNA strands is much slower than the same decay in the gas phase and aqueous solution

Decay dynamics of adenine in DNA strands

Adenine in single strand $(dA)_{10}$

Major decay channel: $^6S_1$
Out-of-plane NH_2

Secondary decay channel: E_2
Out-of-plane H2
and C2 puckering

Adenine in double strands
$(dA)_{10}(dT)_{10}$

Major decay channel: E_2
Out-of-plane H2
and C2 puckering

The $^6S_1$ channel does not exist.
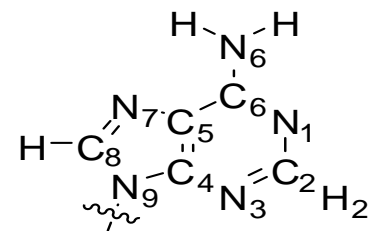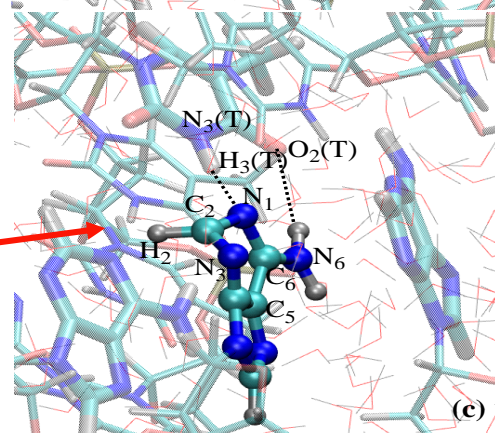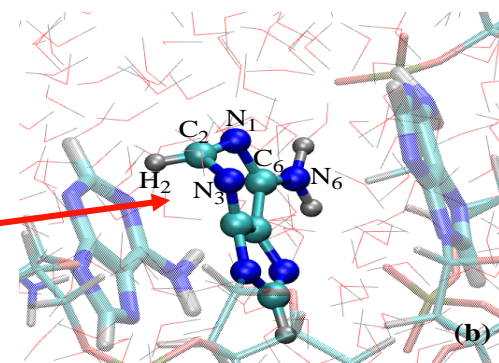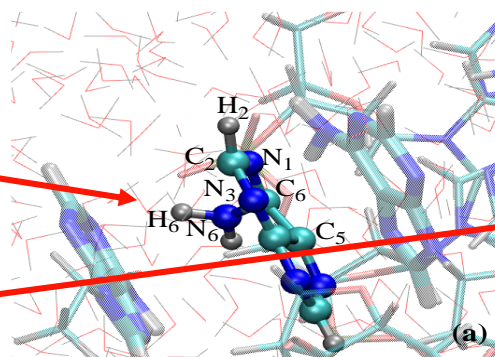
- **For the $S_1 \rightarrow S_0$ decay of adenine in the gas phase, aqueous solution and single DNA strand $(dA)_{10}$, the major channel is governed by the $^6S_1$ conical intersection.**
- **For the $S_1 \rightarrow S_0$ decay of adenine in double DNA strands $(dA)_{10}(dT)_{10}$, the $^6S_1$ channel (out-of-plane motion of NH_2) is hindered by the A-T hydrogen bond. The major channel is now the E_2 conical intersection.**

Photodissociation of ClOOCl

(a) $t = 0$

(b) $t = 7$ fs

(c) $t = 20$ fs
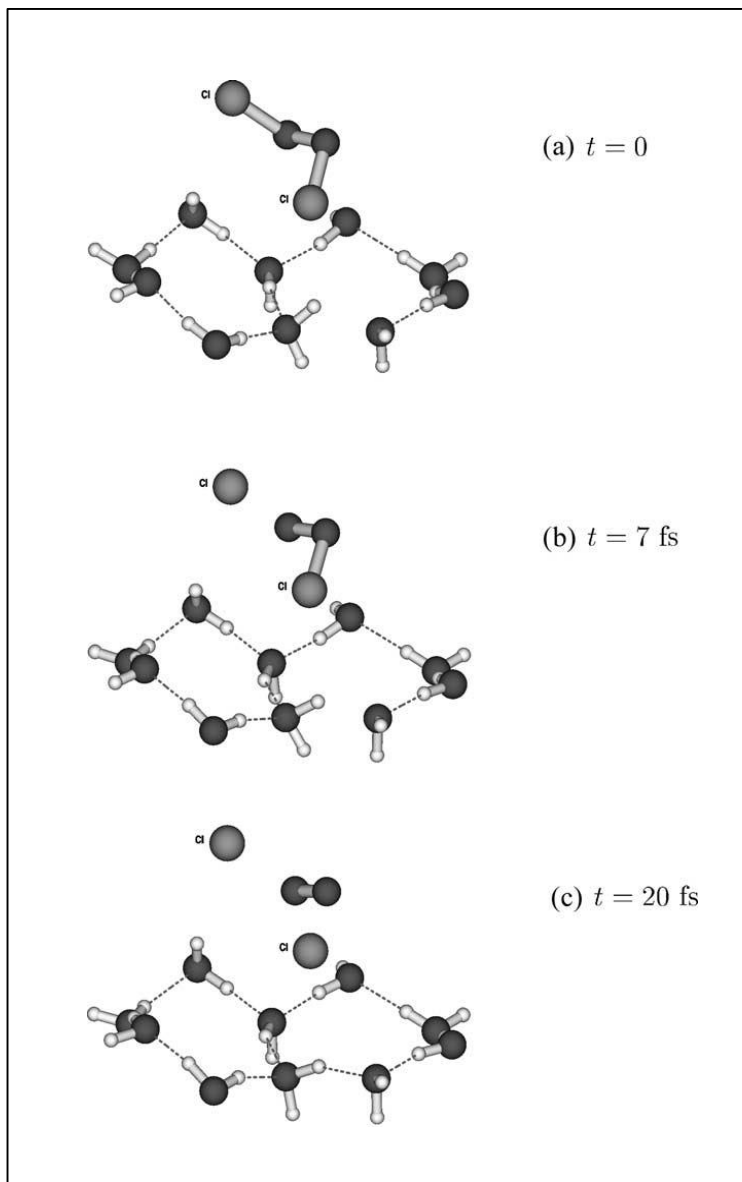
AM1 / Amber, Tully's FSA

Solute solvent interactions

Isolated solute ———
State specific ·············

diabatic

adiabatic

energy

internal coordinate

M. Persico et al., Journal of Molecular Structure (Theochem) 621 (2003) 119–126
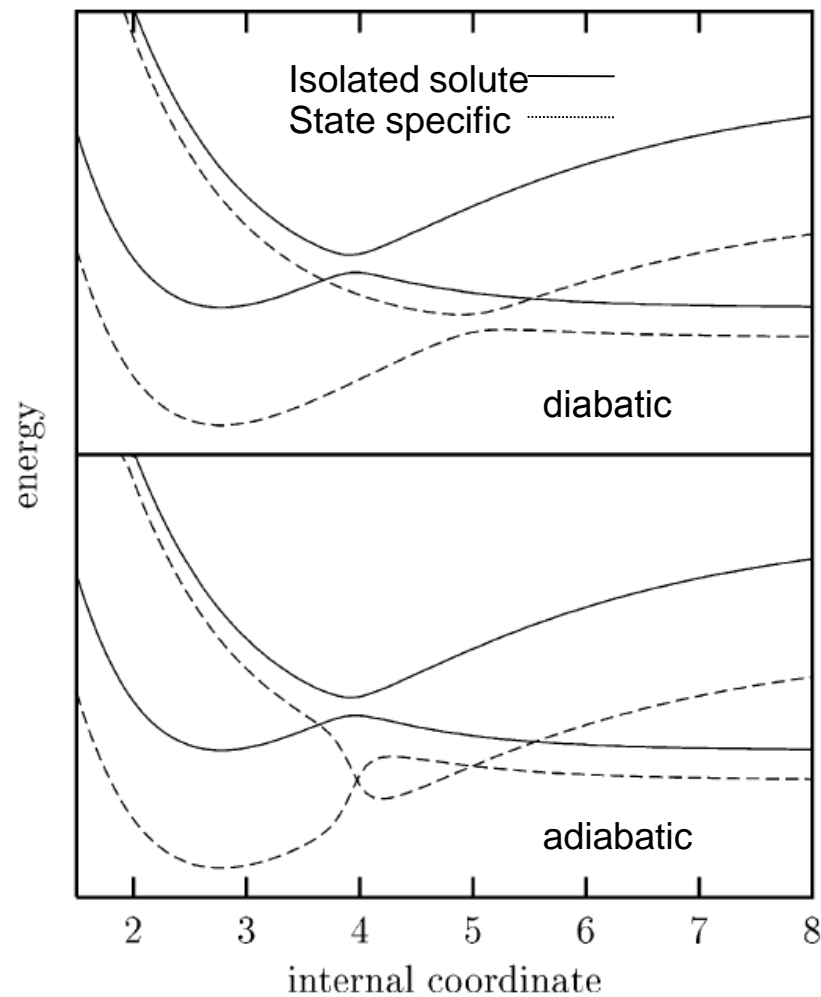
Azobenzene

cis-trans isomerisation in vacuo with AM1 FOMO

CNN inversion

trans

CNNC torsion

hv, T

hv

cis
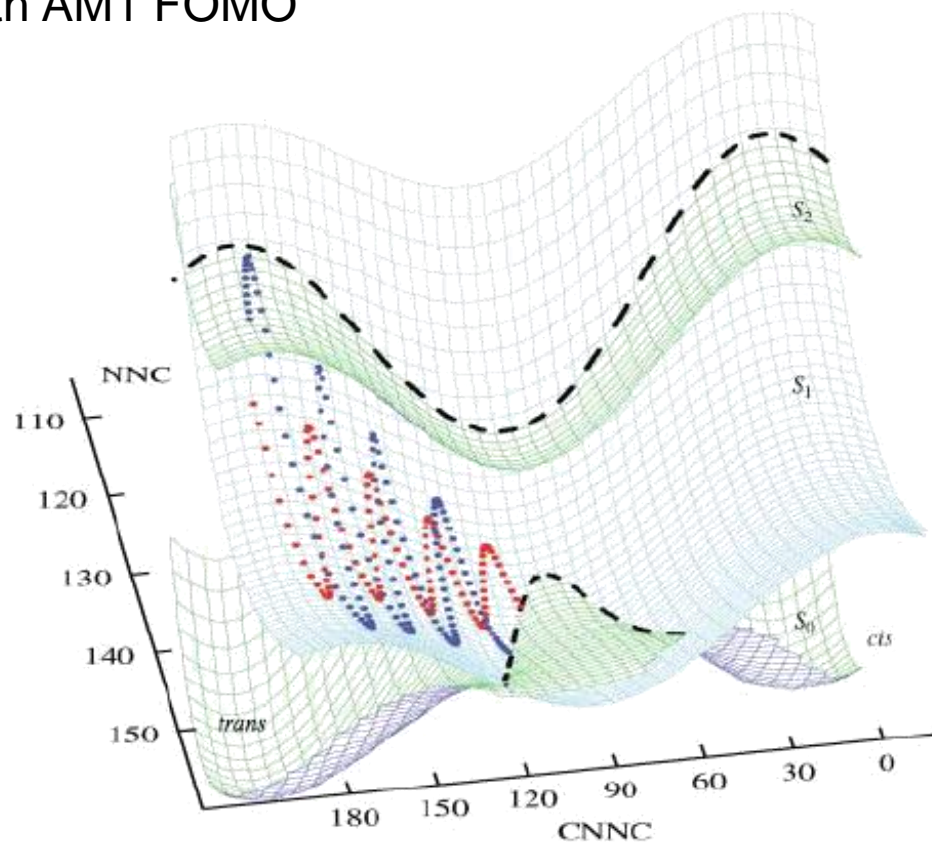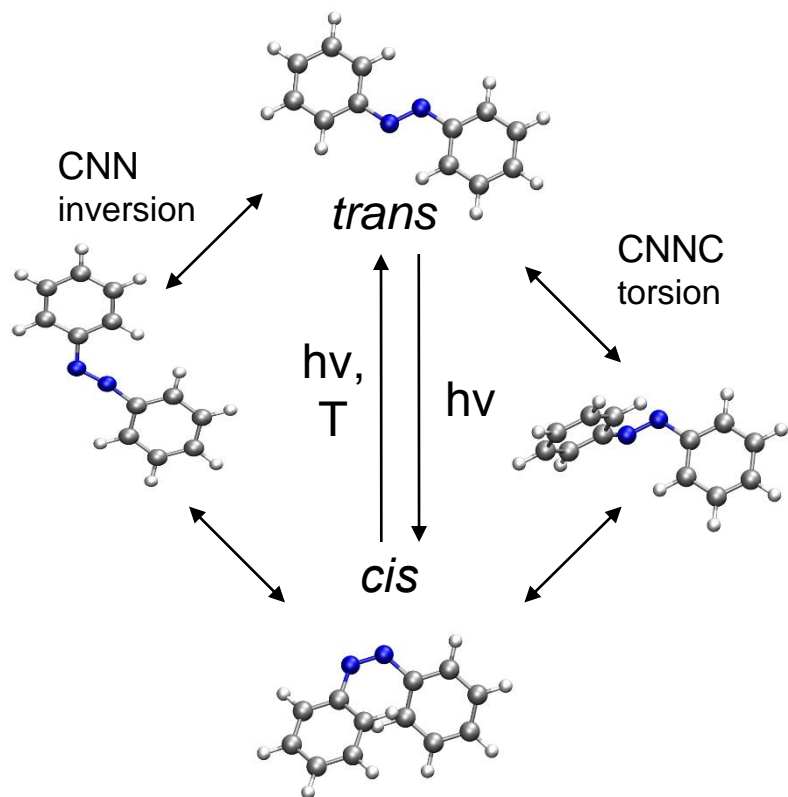
	$n \rightarrow \pi^*$ excitation	$\pi \rightarrow \pi^*$ excitation
$\Phi_{trans \rightarrow cis}$, computed	0.33 ± 0.03	0.15 ± 0.02
$\Phi_{trans \rightarrow cis}$, experimental	0.20–0.36	0.09–0.20
$\Phi_{cis \rightarrow trans}$, computed	0.61 ± 0.03	0.48 ± 0.03
$\Phi_{cis \rightarrow trans}$, experimental	0.40–0.75	0.27–0.44

96

Ciminelli et al. Chem. Eur. J. 2004, 10, 2327

Photoisomerisation of Azobenzene compounds

Azobenzen in Bulk liquid environment, i.e 1 cis/trans Azobenzene solvated by 343 Azobenzenes in cubic 45 Å box, with CPMD / GROMOS, Tully's FSA
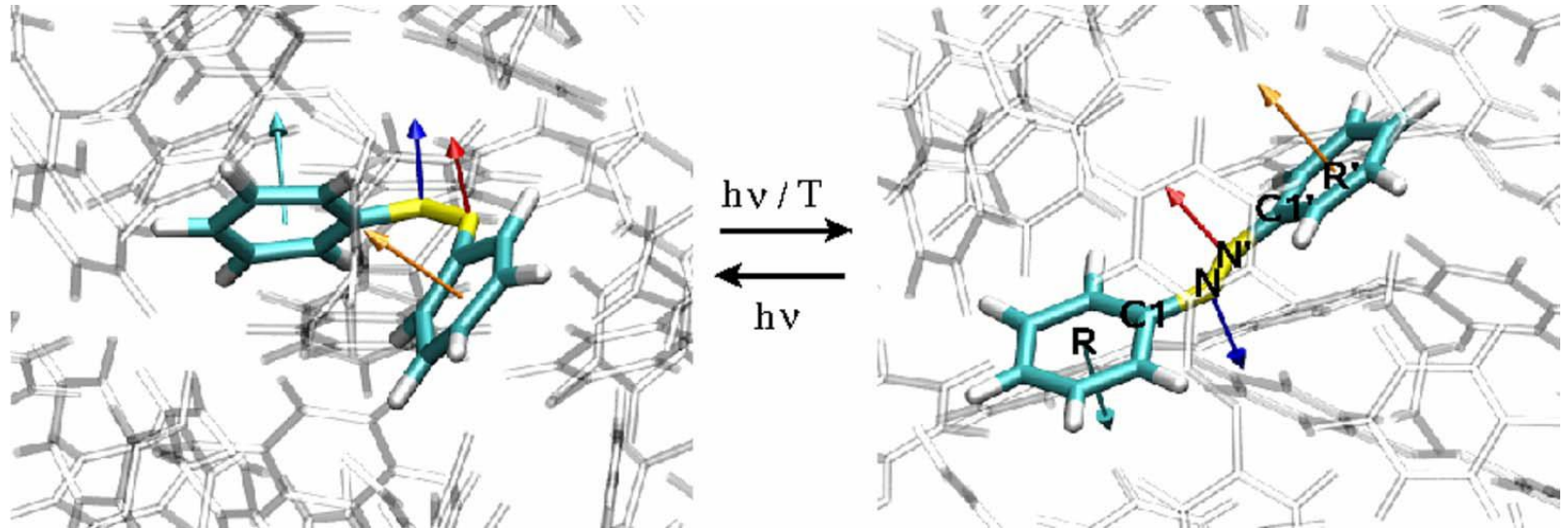
Z-E Isomerisations mostly unaffected in bulk phase

No E-Z Isomerisations

Isomerisation via "Pedal motion" of CNNC Fragment

Böckmann et al, Phys. Rev. E 78, 36101 (2010)

Photoisomerisation of Azobenzene compounds

Supramolecular
azobenzene cyclo-
peptidic derivative
(ABCP)

solvated with
103 Water molcules

MOPAC/Amber

- 557 Atoms

- 30 Atoms in
  QM region

- 171 Trajectories

- 1.5 ps running
  time

cis
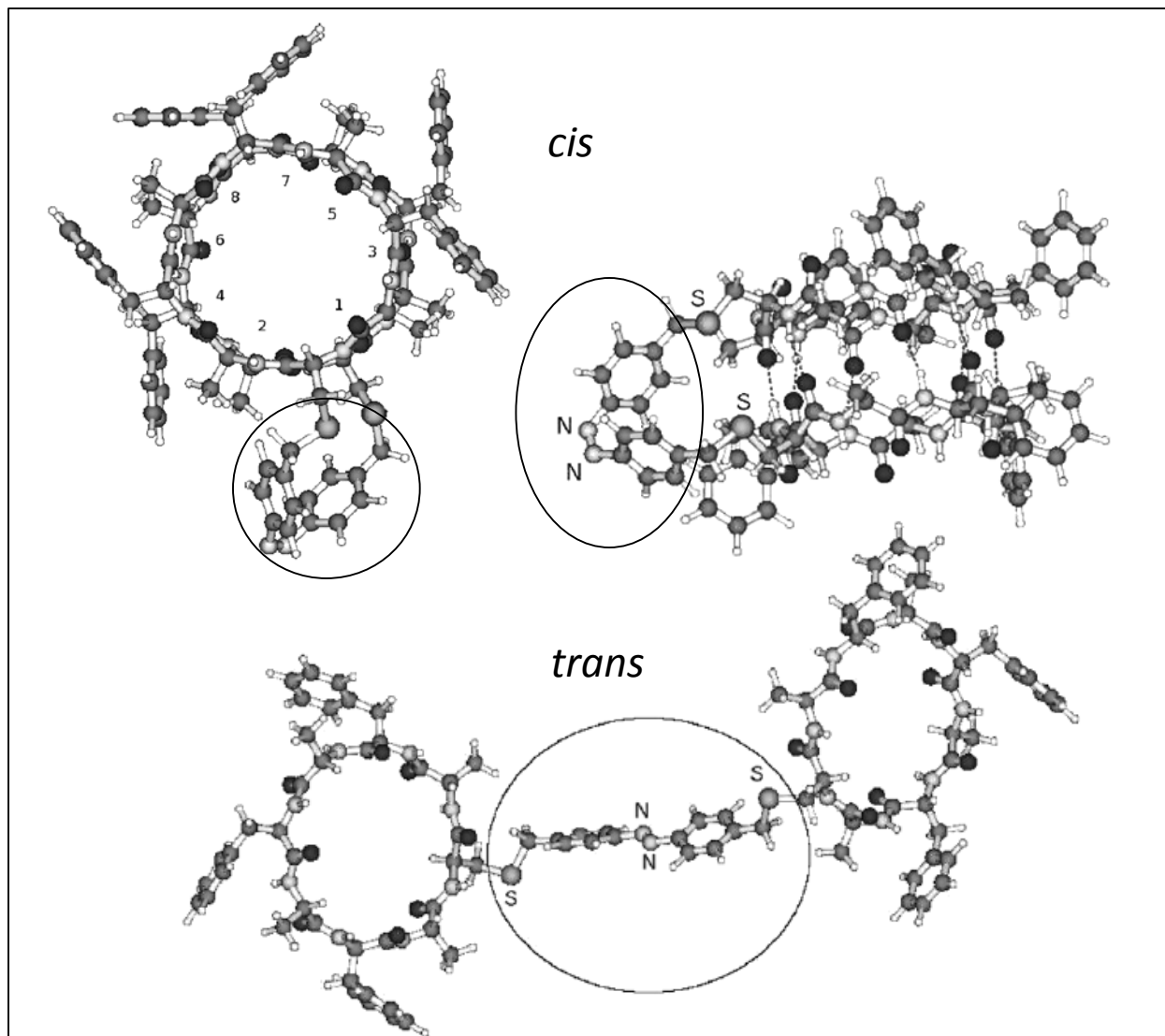
trans

Ciminelli et al., Chem. Phys 349 (2008) 325–333

Photoisomerisation of Azobenzene compounds

Trajectory start point: *cis*-Azobenzene

- *cis*-ABCP isomer is stabilized by hydrogen bonds formed between the two cyclopeptides
- *cis*-*trans* isomerisation
- completed after 200 fs

Ciminelli et al., Chem. Phys 349 (2008) 325–333
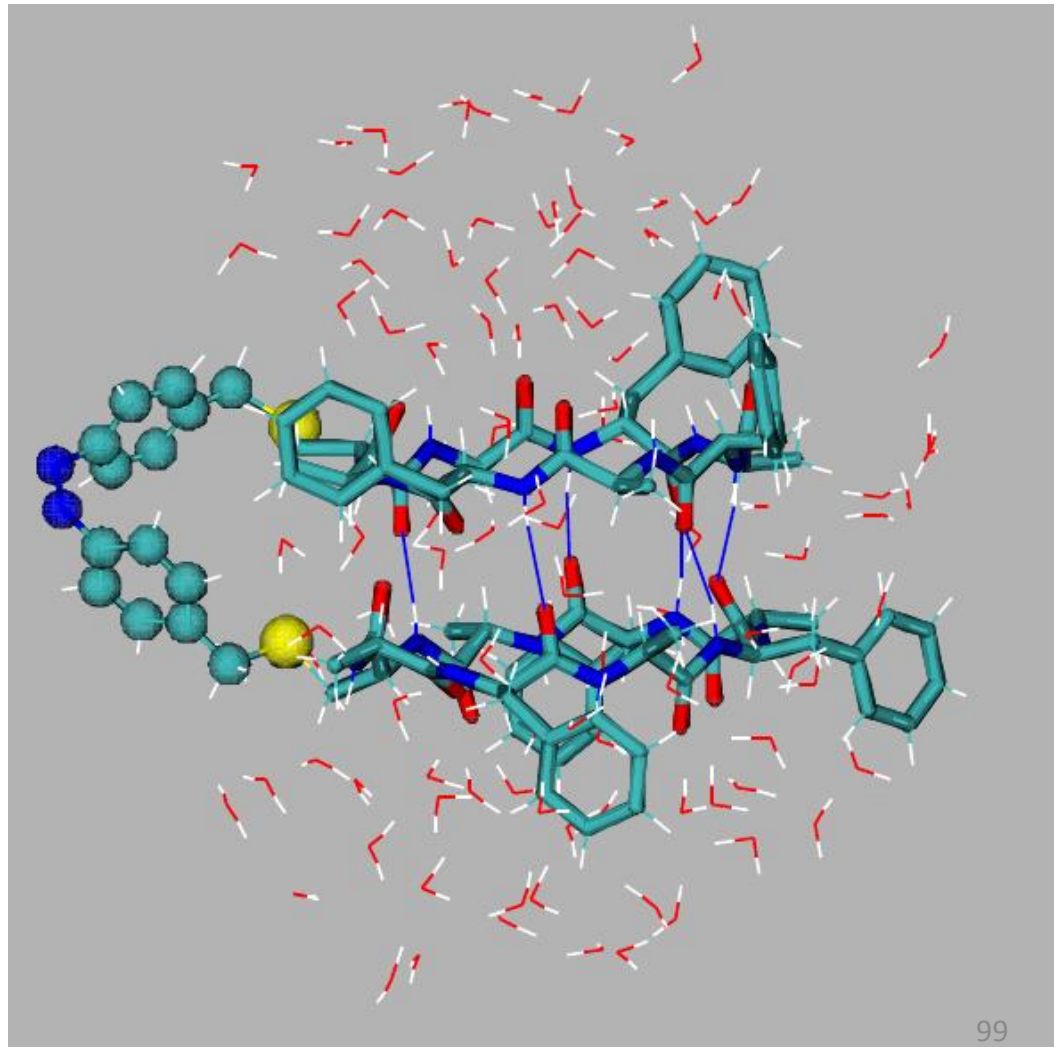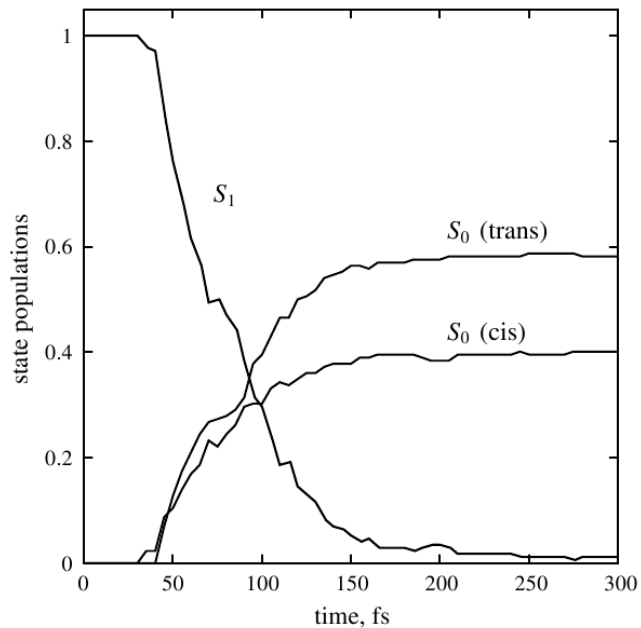
Protein Folding

Controlled protein folding dynamics using cyclic peptides

Peptide Sequence:

Ac-Tty-(Ala-Ala-Ala-Ala-Lys)$_3$-Tty-CONH$_2$ Ac-Aty-(Ala-Ala-Ala-Ala-Lys)$_3$-Aty-CONH$_2$
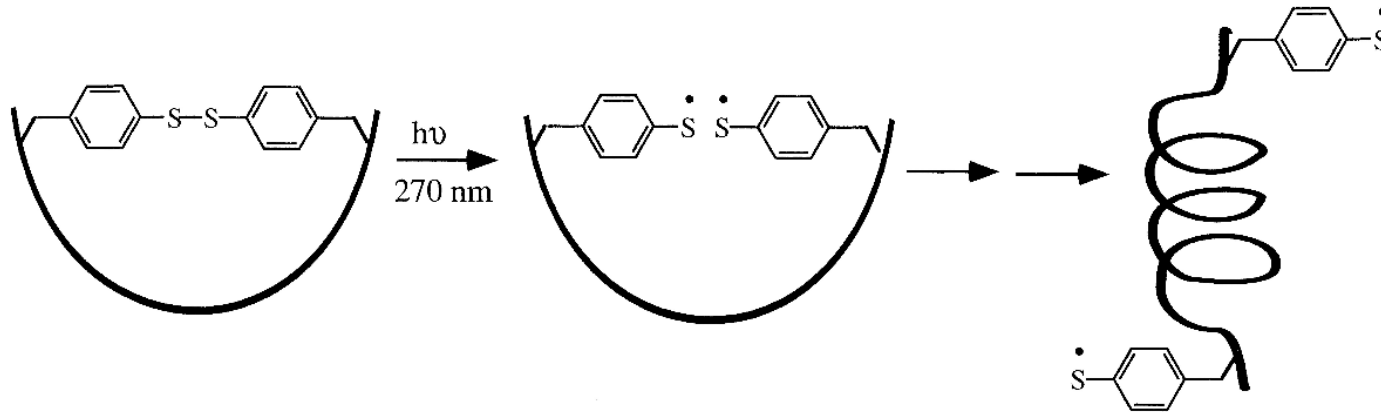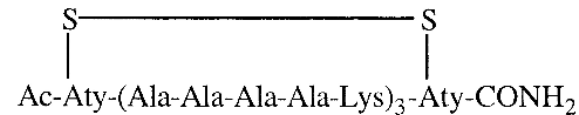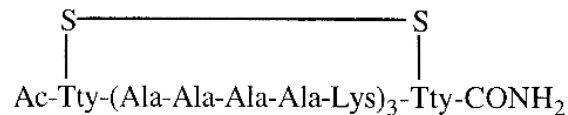
Break S-S bond with light pulse – Problem: recombination too fast!

Protein Folding

Following protein folding dynamics in real time using cyclic peptides
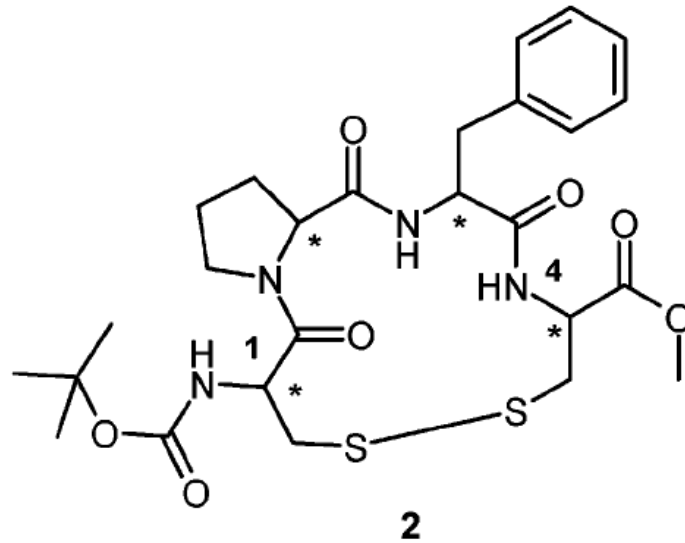
β-turn cyclic tetrapeptide: long lifetime → investigate decay dynamics

Kolano et al, J. Phys. Chem. B 2007, 111, 11297.

Protein Folding

Linked ab initio / classical simulations with CPMD/Gromacs

Recyclisation after S-S Photocleavage in a Peptide:
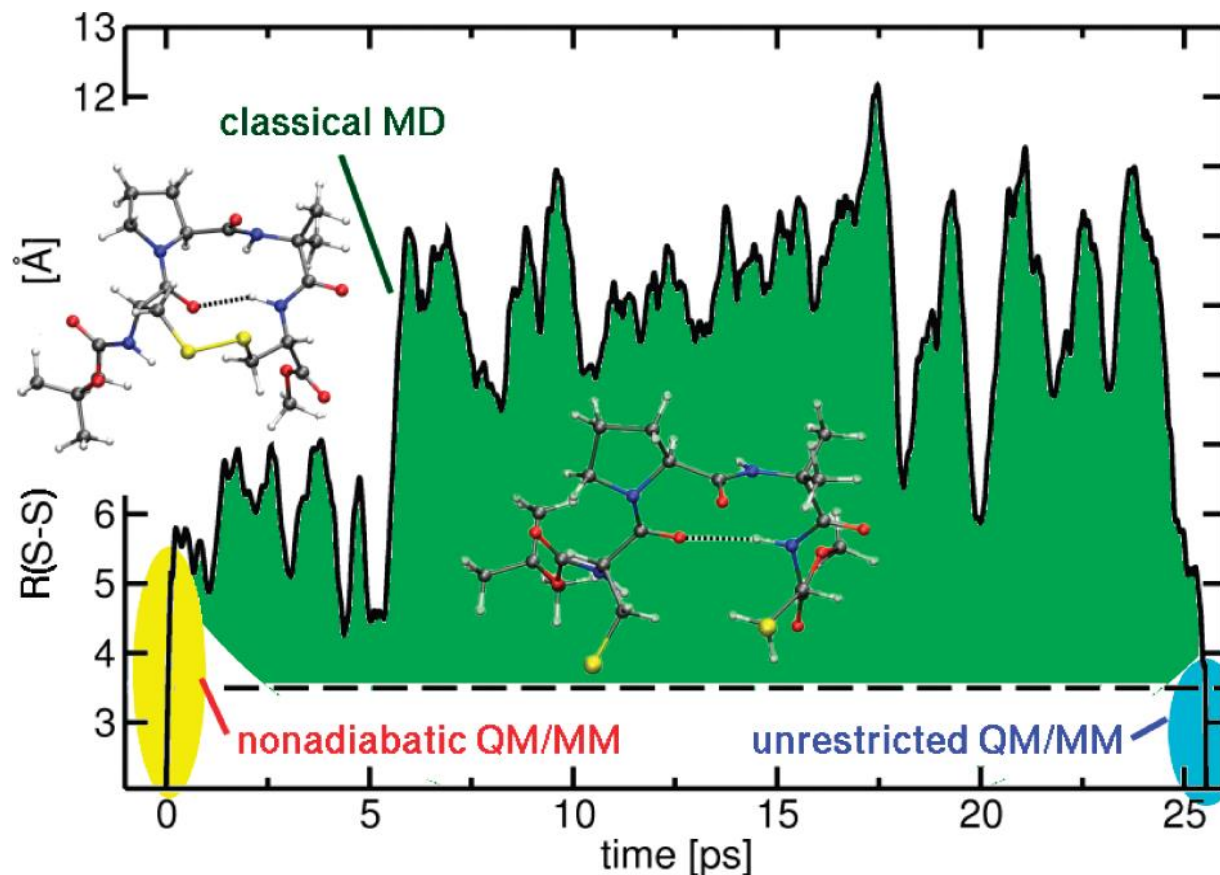
Protein Folding

In Vacuo: fast Dissociation (100%), recombination within ca 50 ps

In CH_3CN: Dissociation 10%, damped oscillatory motion restores bond

Ab initio part (Nonadiabatic dynamics)
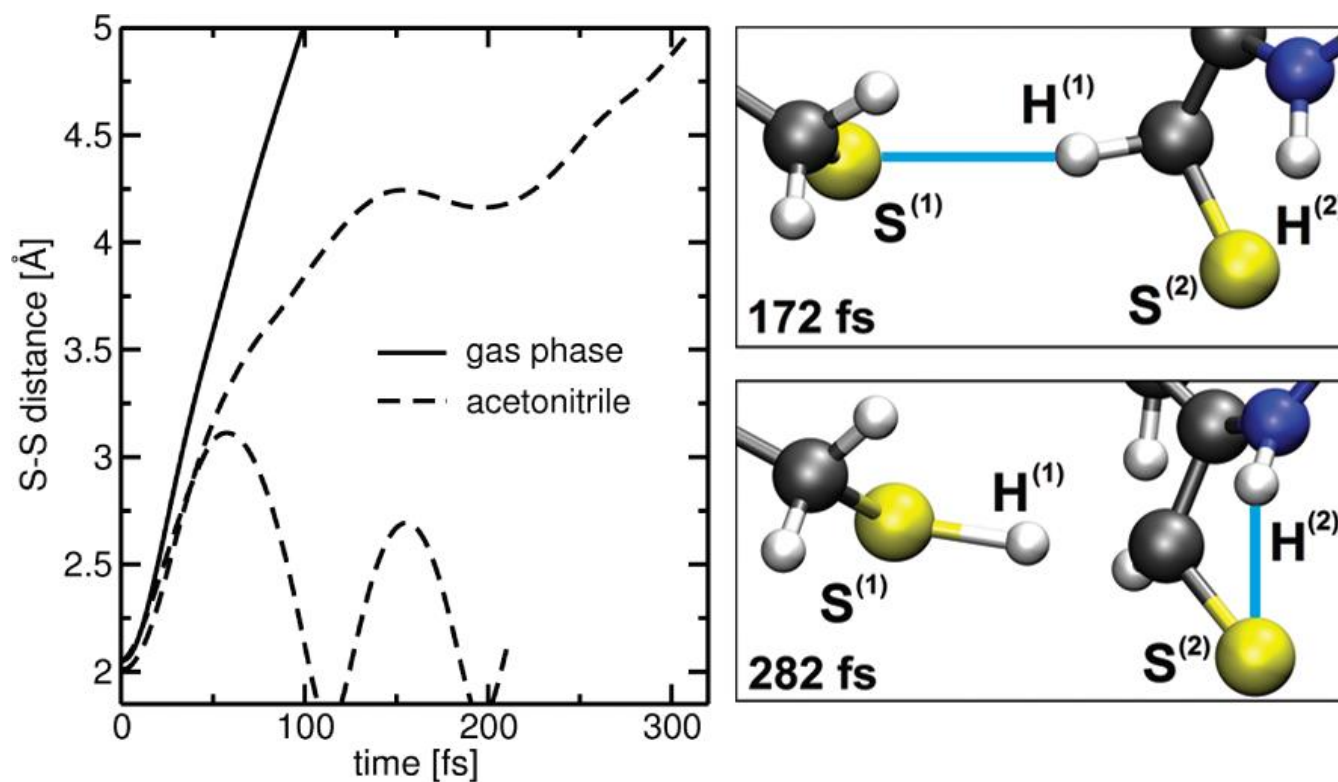
PSII systems

PCCP

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: Phys. Chem. Chem. Phys., 2017, 19, 14924

Atomistic non-adiabatic dynamics of the LH2 complex with a GPU-accelerated *ab initio* exciton model†

Aaron Sisto,[ab] Clem Stross,[c] Marc W. van der Kamp,[cd] Michael O'Connor,[ce] Simon McIntosh-Smith,[e] Graham T. Johnson,[fg] Edward G. Hohenstein,[h] Fred R. Manby,[c] David R. Glowacki[*ce] and Todd J. Martinez[*ab]
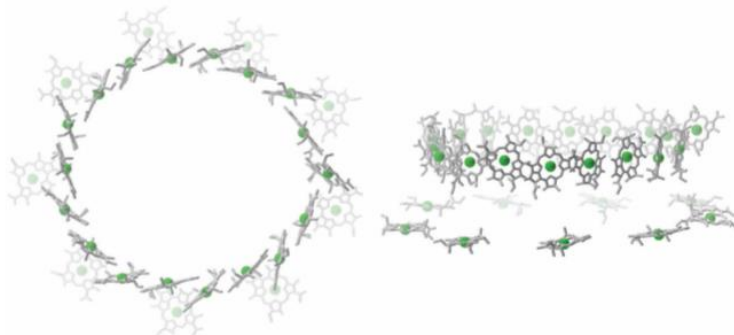
Fig. 1 The 27 Bchla chromophores comprising LH2, from 'top-down' (left panel) and 'side-on' (right panel) views. LH2 consists of two different ring structures: a 9-chromophore B800 ring (named for its spectral absorption maximum at 800 nm), and an 18-chromophore B850 ring (named for its absorption maximum at 850 nm). The 18 chromophores of the B850 ring form 9 adjacent dimer pairs. The phytyl tails of the BChlas, along with the surrounding protein scaffold and carotenoids, have been removed in this figure for the sake of clarity.
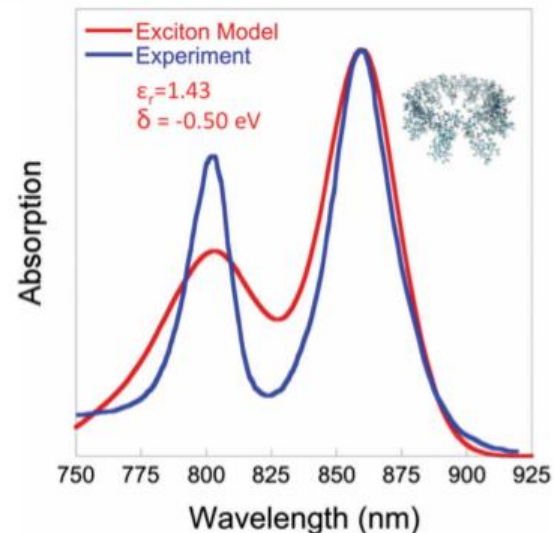
Fig. 2 Absorption spectra of LH2 complex computed using exciton model (red) and from experiments (blue) carried out at 298 K.[86] The best-fit parameters obtained from the exciton model are also shown.

- Diabatic Hamiltonian, site energy, exciton coupling
- QM/MM
- TSH in adiabatic representation
- GPU

Exciton diffusion

Simulation of Singlet Exciton Diffusion in Bulk Organic Materials

Julian J. Kranz and Marcus Elstner*

Institute of Physical Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

ABSTRACT: We present a scheme for nonadiabatic direct dynamics simulation of Frenkel exciton diffusion in bulk molecular systems. The fluctuations of exciton couplings caused by the molecular motion can crucially influence exciton transport in such materials. This effect can be conveniently taken into account by computing the exciton couplings along molecular dynamics trajectories, as shown recently. In this work, we combine Molecular Dynamics simulations with a Frenkel Hamiltonian into a combined quantum-mechanical/molecular mechanics approach in order to allow for a simultaneous propagation of nuclear and electronic degrees of freedom using nonadiabatic dynamics propagation schemes. To reach the necessary time and length scales, we use classical force-fields and the semiempirical time-dependent density functional tight-binding method in combination with a fragmentation of the electronic structure. Fewest-switches surface-hopping, with adaptions to handle trivial crossings, and the Boltzmann-corrected Ehrenfest method are used to follow the excitonic quantum dynamics according to the classical evolution of the nuclei. As an application, we present the simulation of singlet exciton diffusion in crystalline anthracene, which allows us to address strengths and shortcomings of the presented methodology in detail.
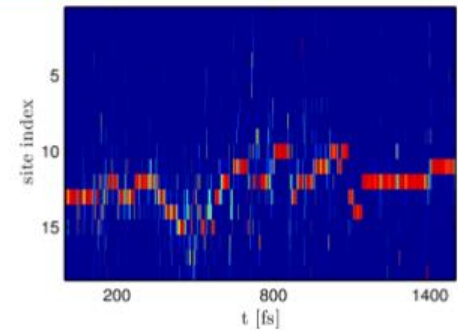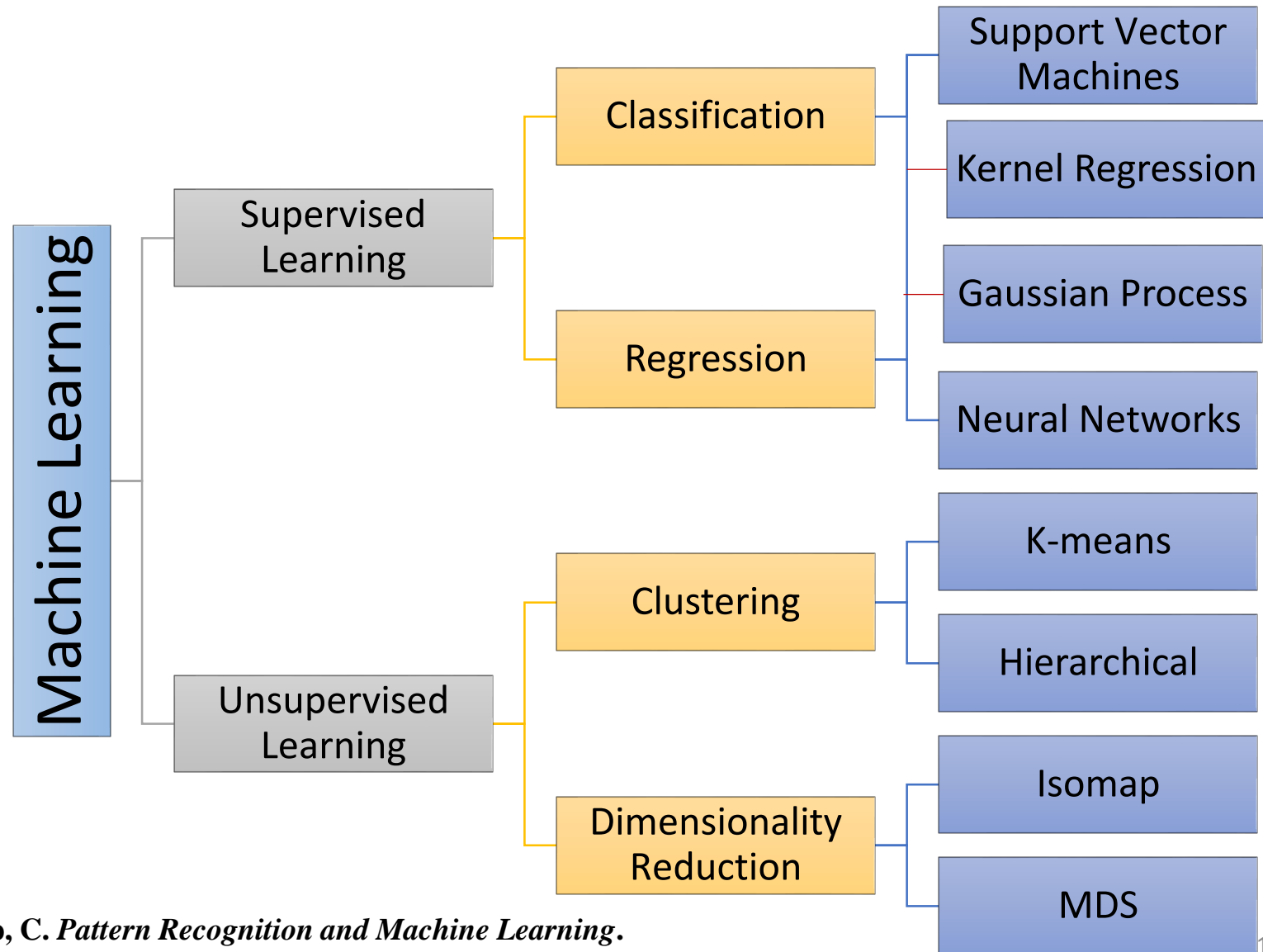
$i\partial_t |\Psi\rangle = H |\Psi\rangle$

Figure 9. Sample surface-hopping trajectory. The exciton remains largely localized on a single molecule, though it is excited to more extended states for short times.

Figure 1. Four sequential molecules in a-(left) and b- (right) direction. The QM regions contained chains of 18 molecules.

- Diabatic Hamiltonian, site energy, exciton coupling
- QM/MM+ TDDFTB
- TSH in adiabatic representation

Part V:
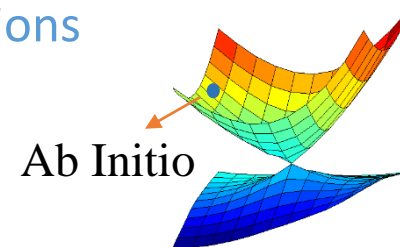# Machine Learning and
Surface Hopping

Machine Learning

Machine Learning
- Supervised Learning
  - Classification
  - Regression
    - Support Vector Machines
    - Kernel Regression
    - Gaussian Process
    - Neural Networks
- Unsupervised Learning
  - Clustering
    - K-means
    - Hierarchical
  - Dimensionality Reduction
    - Isomap
    - MDS

Bishop, C. *Pattern Recognition and Machine Learning.*
Springer-Verlag: New York, 2006.

PES in Nonadiabatic Dynamics

Preconstruction of PES:

◆ Analytical function and Suitable coordinates

◆ A large number of ab initio points

◆ High efficiency after construction

◆ Sometimes reduced models

$E = f(\mathbf{R})$
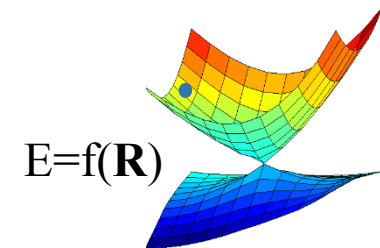
On-the-fly approaches:

◆ Electronic structure calculations guided by trajectory propagation

◆ Many trajectories and many single-point calculations

◆ All nuclear degrees of freedom

◆ A large computational cost

Ab Initio

ML-PES in Nonadiabatic Dynamics

Inclusion of Machine Learning Kernel Ridge Regression Potential Energy Surfaces in On-the-Fly Nonadiabatic Molecular Dynamics Simulation

Deping Hu,[†,‡] Yu Xie,[†] Xusong Li,[†,‡] Lingyue Li,[‡] and Zhenggang Lan*[,†,‡]

Nonadiabatic Excited-State Dynamics with Machine Learning

Pavlo O. Dral,*[,†] Mario Barbatti,*[,‡] and Walter Thiel*[,†]

Deep Learning for Nonadiabatic Excited-State Dynamics

Wen-Kai Chen,[†] Xiang-Yang Liu,[†] Wei-Hai Fang,[†] Pavlo O. Dral,[‡] and Ganglong Cui*[,†]

What do we know from TSH simulation

Population dynamics
Lifetime
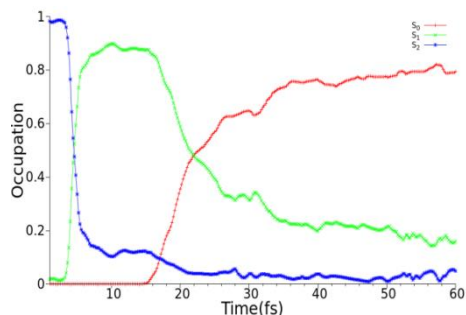
Geometry evolution
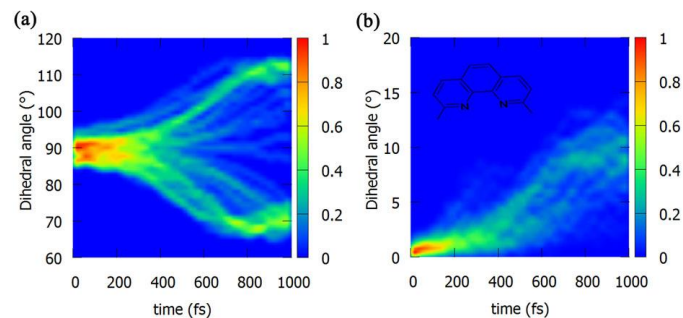
Reaction channels
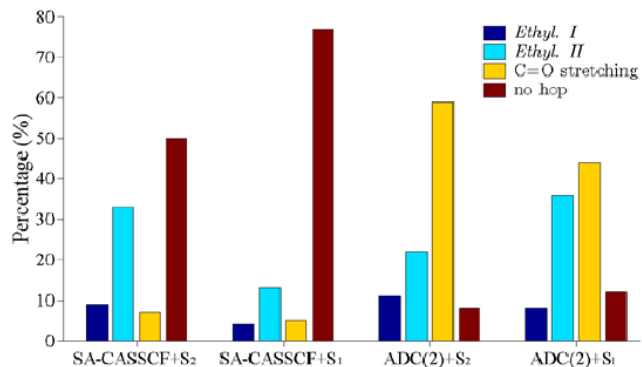
Physical quantities
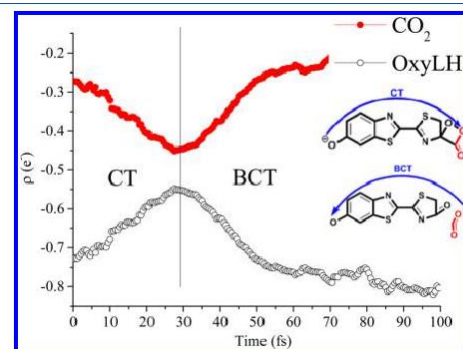
How to analyze geometrical evolution?

Traditional approaches:

- Typical trajectory

> How to define "typical"?

- Distribution of the time-dependent internal coordinates

> How to "pick up" the correct coordinates?

Machine learning approaches:
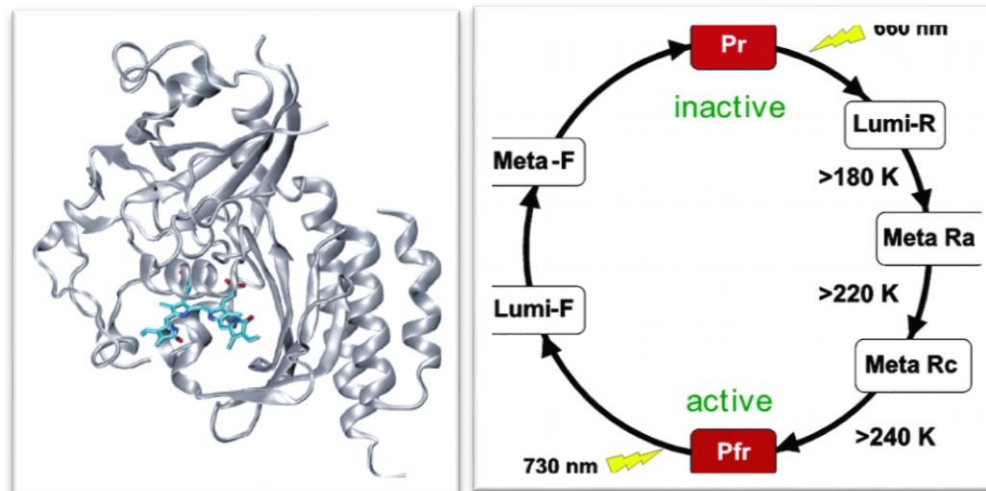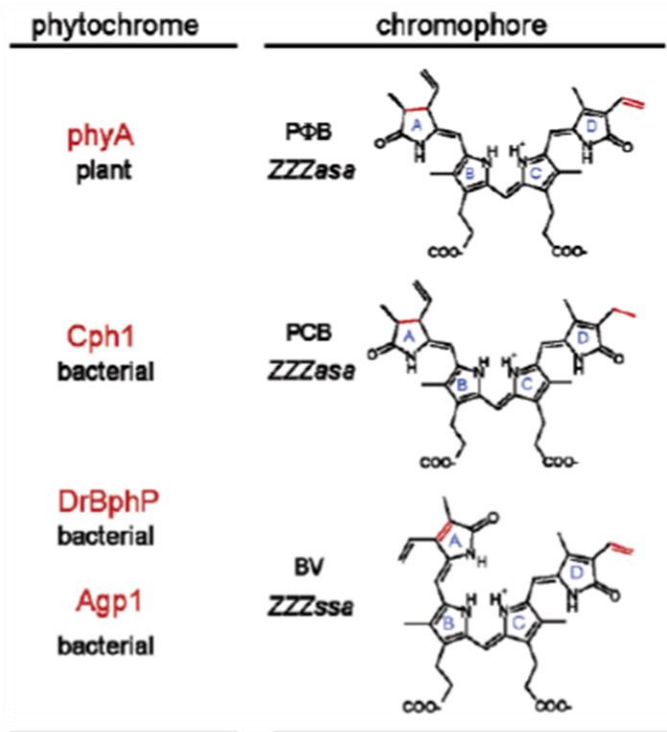
- Big data analysis

- High dimensionality (coordinate space)

ML Dimensionality reductions?

Machine learning approaches:
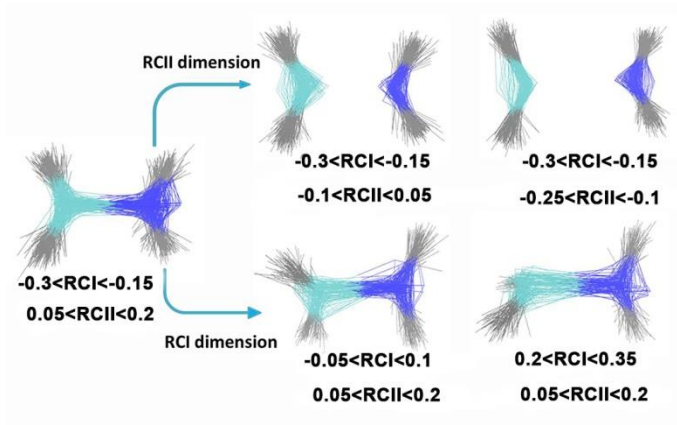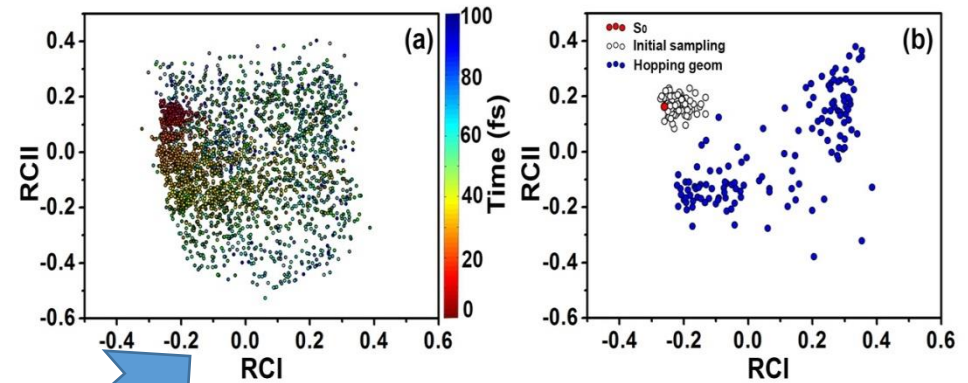
Dimensionality reduction {R$_N$} → {r}

The PΦB model
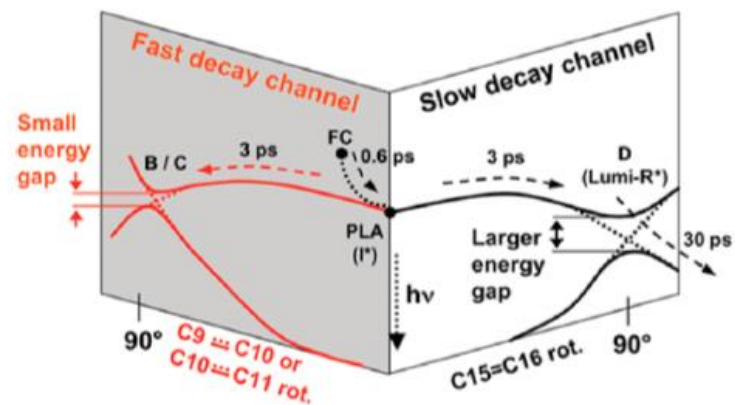
1. *Maria A. M., Daniel H. M., Peter H. Acc. Chem. Res.*, **2007**, *40* (4), pp 258–266
2. Samer G., Hoi L. L., Igor S., Olivucci M. *Chem. Rev.* **2017** *DOI: 10.1021/acs.chemrev.7b00177*

MDS

(a)

(b)

S₀
Initial sampling
Hopping geom

(c)

A

$\tau_{9\_10} \approx 0°$ $\tau_{10\_11} \approx 0°$
-0.3<RCI<-0.1 -0.05<RCII<0.15

B

$\tau_{9\_10} \approx 90°$ $\tau_{10\_11} \approx 0°$
-0.1<RCI<0.1 0<RCII<0.2

C

$\tau_{9\_10} \approx 180°$ $\tau_{10\_11} \approx 0°$
1.2<RCI<1.4 -0.1<RCII<0.1

D

$\tau_{9\_10} \approx 0°$ $\tau_{10\_11} \approx 90°$
-0.25<RCI<-0.05 -0.3<RCII<-0.1

E

$\tau_{9\_10} \approx 0°$ $\tau_{10\_11} \approx 180°$
0.7<RCI<0.9 -1.4<RCII<-1.2
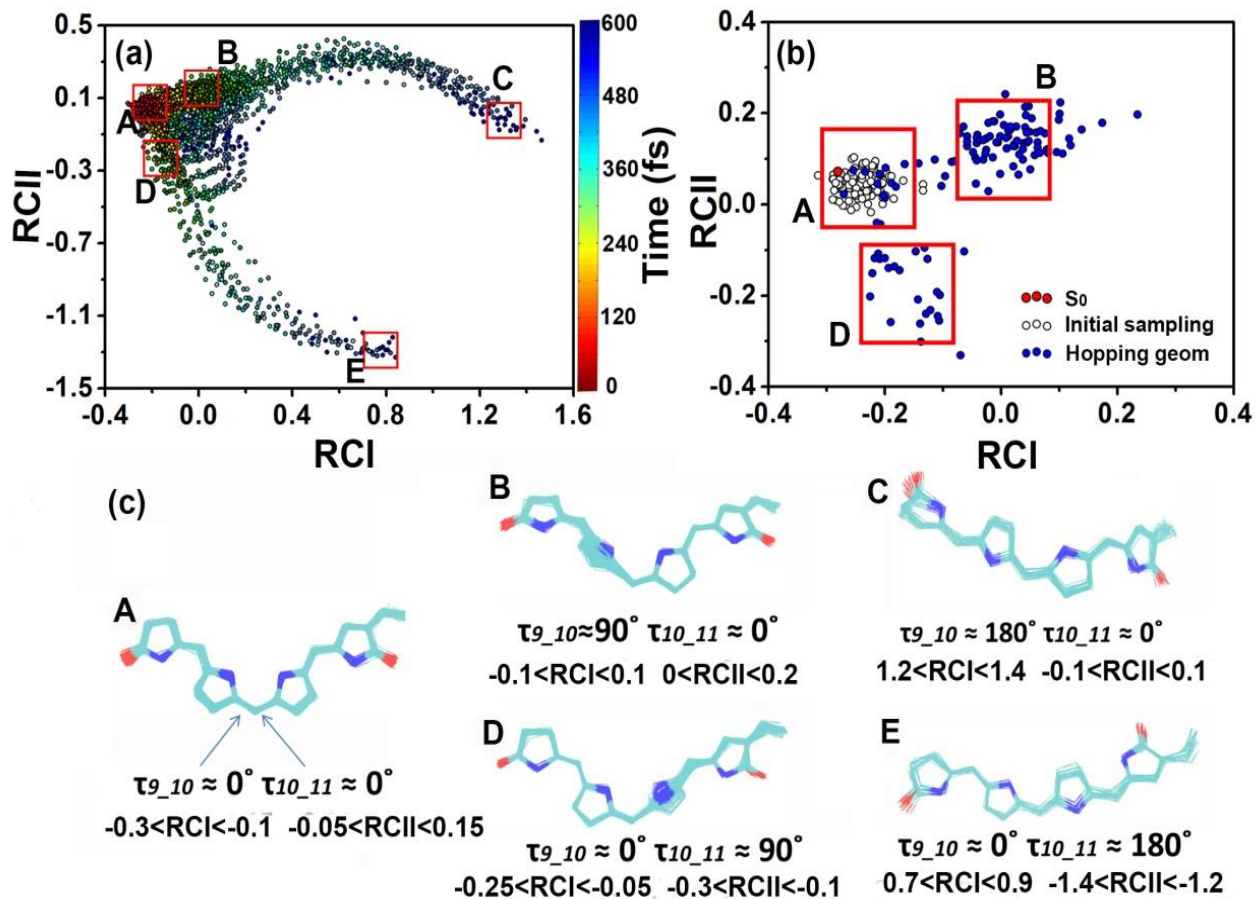
多原子体系非绝热动力学的近似理论方法[*]

兰峥岗[1][**]　　邵久书[2][**]

（1. 中国科学院青岛生物能源与过程研究所　青岛 266101；
2. 北京师范大学化学学院 理论与计算光化学教育部重点实验室　北京 100875）

化学动力学中的非绝热过程及其理论研究

胡德平[①②], 谢宇[①*], 黄静[①②], 杜利凯[①], 郑杰[①②], 兰峥岗[①②*]

Treatment of Nonadiabatic Dynamics by On-The-Fly Trajectory Surface Hopping Dynamics

PENG Jiawei [1,3], XIE Yu [1], HU Deping [1,3], DU Likai [2], LAN Zhenggang [1,3,*]

Part VI:
My Researches

Research highlights

Potential Energy Surfaces

Diabatization

Mixed quantum classical Quasiclassical Semiclassical Dynamics

Quantum Wavepacket and Dissipative Dynamics

Machine Learning

Time-resolved spectroscopy

M. J. Paterson
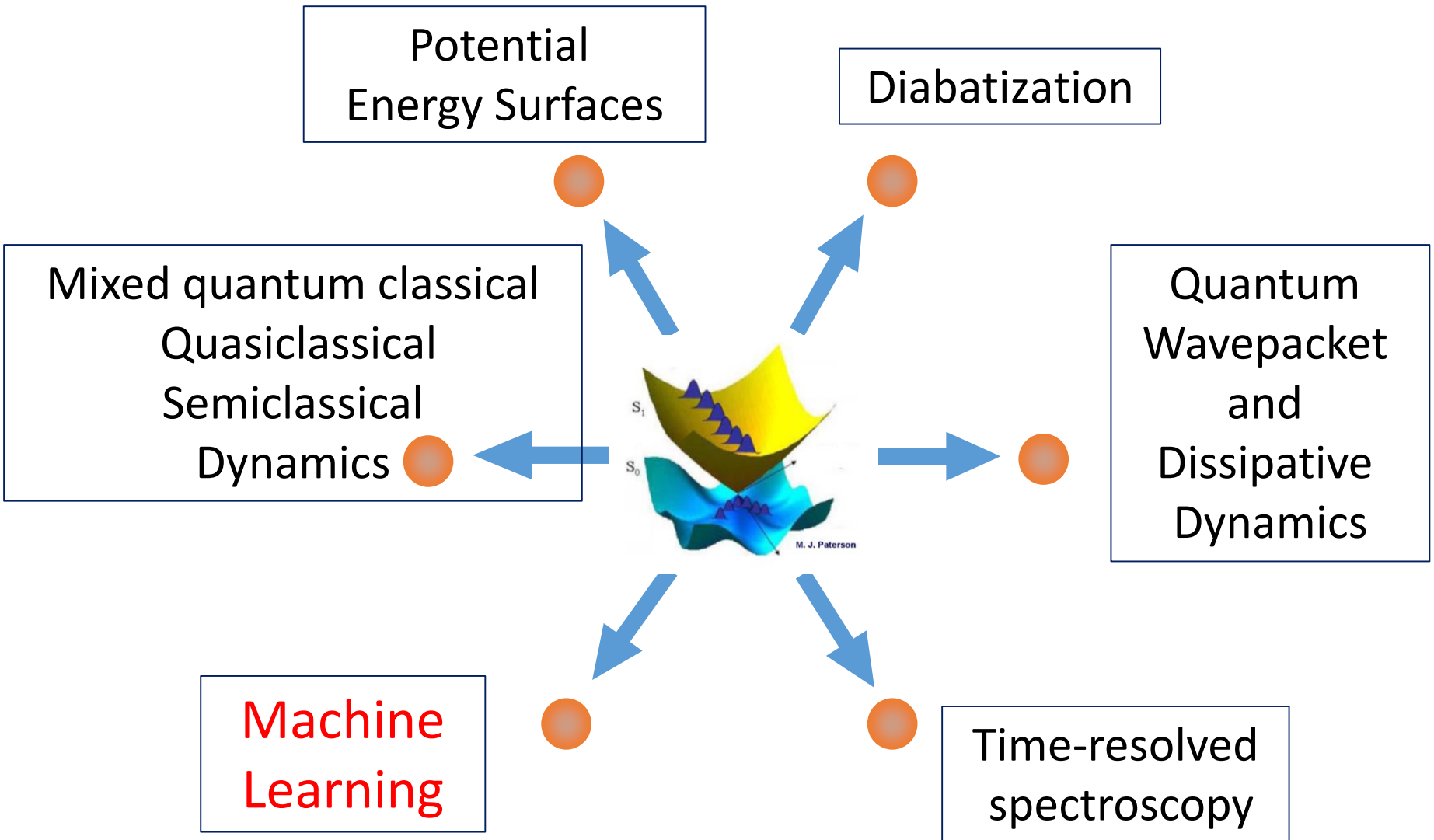
发展TSH方法和程序

面跳跃 直接动力学

方法发展 程序编写

解析和数值 非绝热耦合
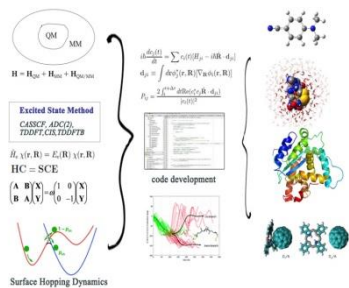
全原子水平模拟 非绝热动力学 JCTC，2015

无监督 机器学习

降维算法

大数据分析
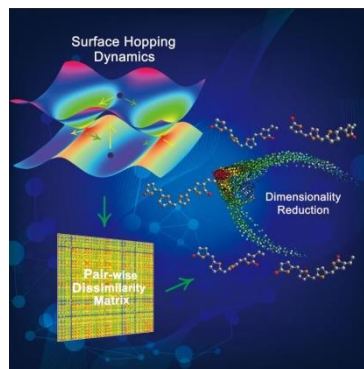
自动寻找主导 运动模式 JCTC，2017
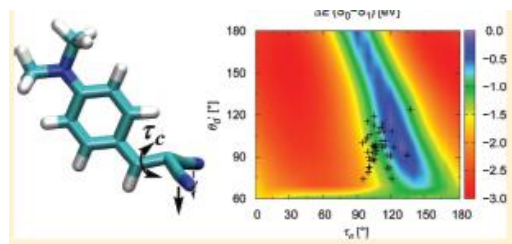
监督 机器学习

核函数回归

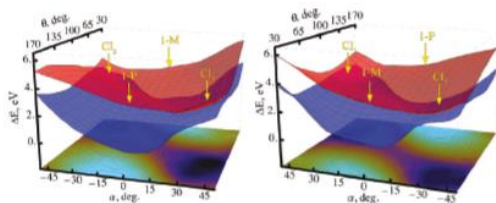采样与势能面拟合
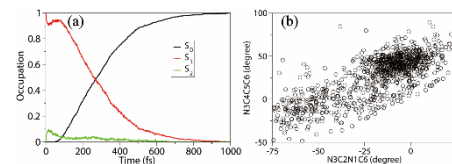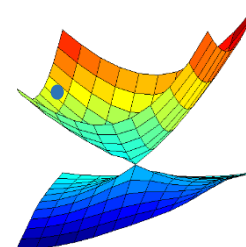
加速非绝热 动力学模拟 JPCL, 2018

光物理与光化学

◆ DNA体系
  光稳定性
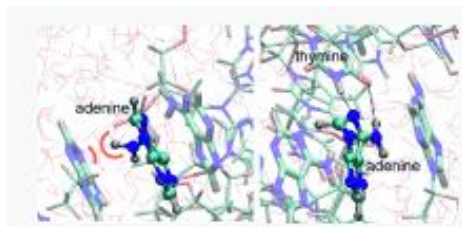
- *Angew. Chem. Int. Edit*. 2011; *PNAS* 2008
- *Top Curr. Chem*. 2015
- *PCCP*. 2017, 2013, 2012, 2007
- *CPC* 2011, 2009
- *JPCB,* 2009, JCP, 2012

◆ 探针分子

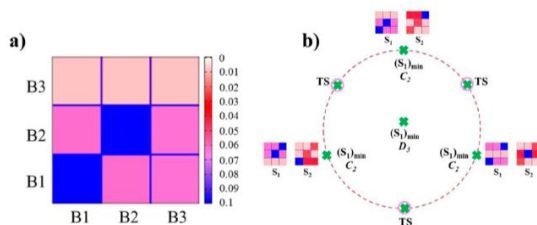- *JPCL* 2011
- *JCTC* 2011, 2015, 2017
- *JPCA* 2012, 2017

◆ 生物体系
  的光化学

- *JACS* 2012
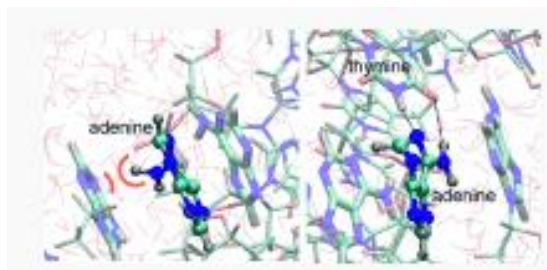- *JPCL* 2015
- *PCCP* 2013, 2012
- *JPCA/B/C* 2013, 2012

◆ 光伏体系的
  光反应

- *JACS 2016,*
- *Nano Lett. 2016, 2018*
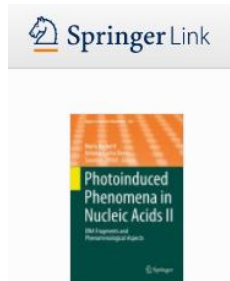- *PCCP 2016,*
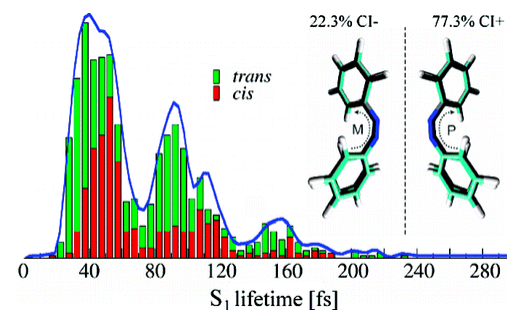- *JPCA/B/C 2018，2017，2016, 2015,*

光物理与光化学

◆ DNA体系光稳定性

Angew. Chem. Int. Edit.
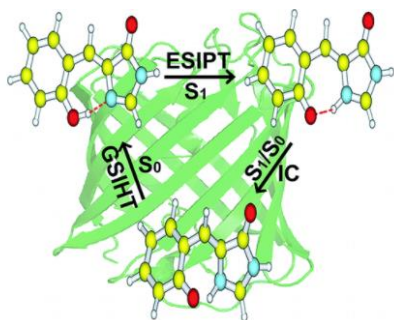2011, 50, 6864 –6867

◆ DNA光物理和光化学

Top Curr. Chem.
2015, 356，89–122

◆ 光异构化
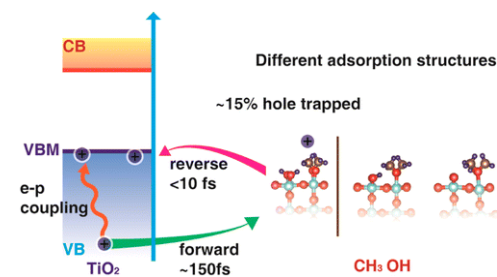

JPCL 2011, 2, 1506–1509

◆ 荧光蛋白体系光化学

JACS 2012, 134, 1662–1672
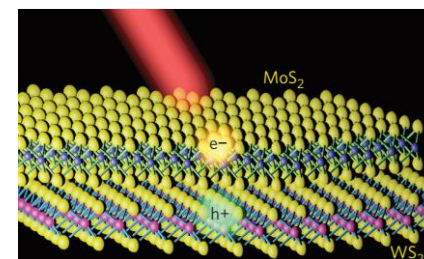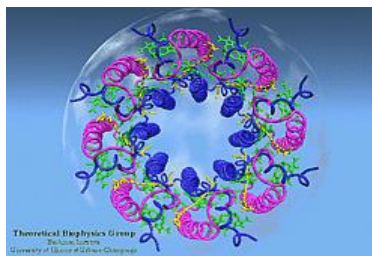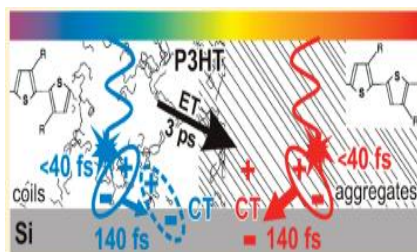
◆ 生物和化学发光

JPCL 2015, 6, 540-548

◆ 光催化

JACS 2016, 138, 13740–13749
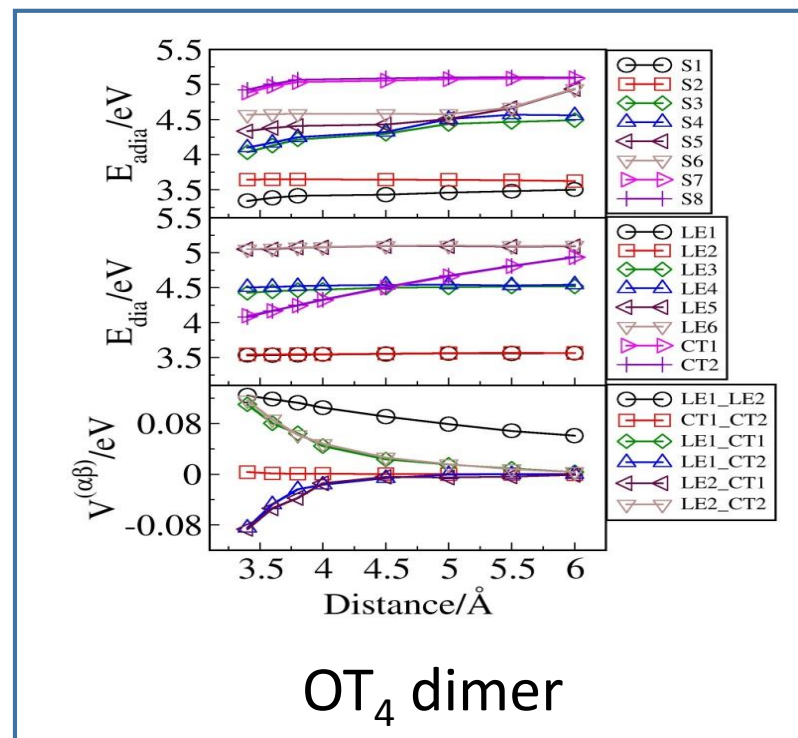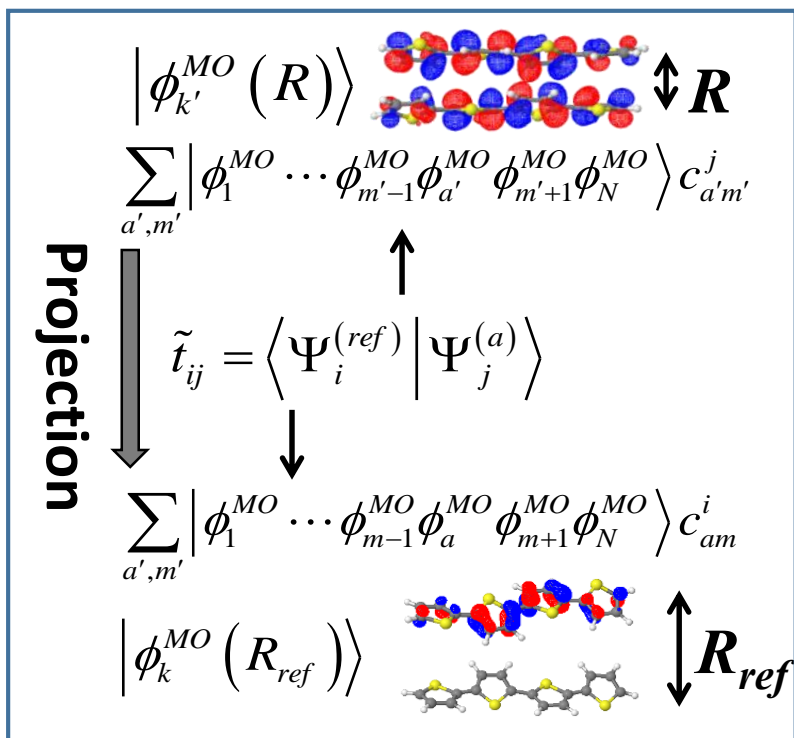
Exciton Dynamics

Diabatization

- **Wavefunction Projection**

  for molecular systems

  for extended systems

- **Fock-Matrix Block**

  Diagonalization

Nonadiabatic Dynamics

- **ML-MCTDH**

- **Quasi-Classical Dynamics based**

  on Mapping Hamiltonian

Diabatization

Wavefunction Projection for Molecular Systems

$$\left| \phi_{k'}^{MO}(R) \right\rangle \quad \updownarrow R$$

$$\sum_{a',m'} \left| \phi_1^{MO} \cdots \phi_{m'-1}^{MO} \phi_{a'}^{MO} \phi_{m'+1}^{MO} \phi_N^{MO} \right\rangle c_{a'm'}^{j}$$

Projection

$$\tilde{t}_{ij} = \left\langle \Psi_i^{(ref)} \middle| \Psi_j^{(a)} \right\rangle$$

$$\sum_{a',m'} \left| \phi_1^{MO} \cdots \phi_{m-1}^{MO} \phi_a^{MO} \phi_{m+1}^{MO} \phi_N^{MO} \right\rangle c_{am}^{i}$$

$$\left| \phi_k^{MO}(R_{ref}) \right\rangle \quad \updownarrow R_{ref}$$

OT$_4$ dimer

- **Generate the local-excited/charge-transfer (LE and CT) states and their couplings**
- **Suitable for molecular systems**

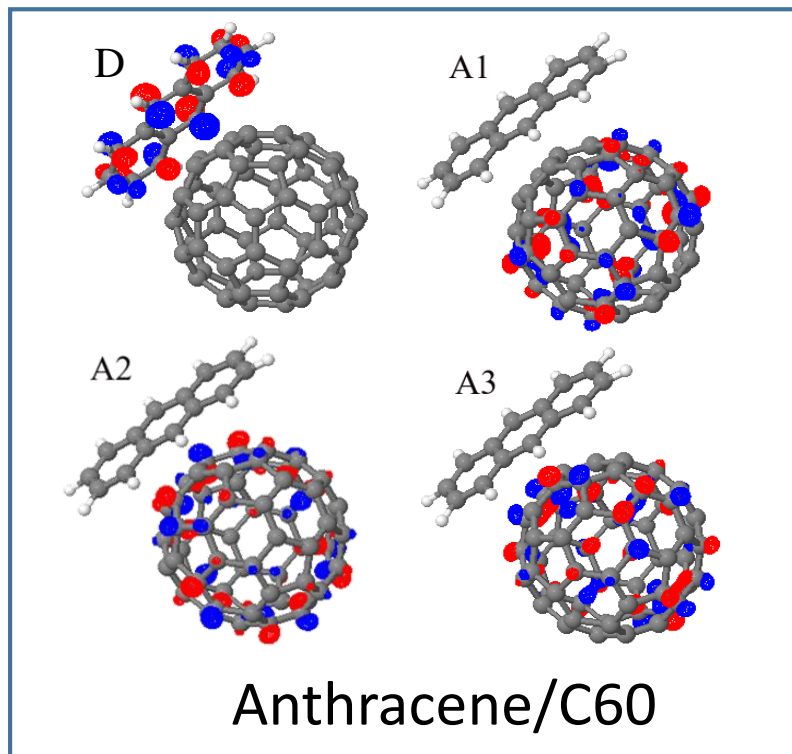Y. Xie, S. Jiang, J. Zheng and Z. Lan, *J. Phys. Chem. A* **121** (50), 9567-9578 (2017).

Diabatization

Fock-Matrix Block Diagonalization

$$\left| \tilde{\varphi}_n \right\rangle = \sum_j \left(S^{-1/2} \right)_{jn} \left| \varphi_j \right\rangle$$

$$\tilde{\mathbf{F}} = \mathbf{S}^{1/2} \mathbf{F} \mathbf{S}^{1/2} \qquad \tilde{\mathbf{F}} = \begin{pmatrix} \tilde{\mathbf{F}}_{dd} & \tilde{\mathbf{F}}_{da} \\ \tilde{\mathbf{F}}_{ad} & \tilde{\mathbf{F}}_{aa} \end{pmatrix}$$

$$\bar{\mathbf{F}}_{\alpha\alpha} = \mathbf{D}_\alpha^\dagger \tilde{\mathbf{F}}_{\alpha\alpha} \mathbf{D}_\alpha \qquad \bar{\mathbf{F}}_{\alpha\beta} = \mathbf{D}_\alpha^\dagger \tilde{\mathbf{F}}_{\alpha\beta} \mathbf{D}_\beta$$

$$\bar{\mathbf{F}} = \begin{pmatrix} \bar{\mathbf{F}}_{dd} & \bar{\mathbf{F}}_{da} \\ \bar{\mathbf{F}}_{ad} & \bar{\mathbf{F}}_{aa} \end{pmatrix} = \begin{pmatrix} \varepsilon_{1,d} & 0 & \cdots & & & \\ 0 & \varepsilon_{2,d} & \cdots & & \bar{\mathbf{F}}_{da} & \\ \vdots & \vdots & \ddots & & & \\ & & & \varepsilon_{1,a} & 0 & \cdots \\ & \bar{\mathbf{F}}_{ad} & & 0 & \varepsilon_{2,a} & \cdots \\ & & & \vdots & \vdots & \ddots \end{pmatrix}$$

Anthracene/C60

- **Generate the localized orbitals and their couplings**
- **Suitable for molecular systems**

Y. Xie, J. Zheng and Z. Lan, *J. Chem. Phys.* **142** (8), 084706 (2015).

MCTDH and ML-MCTDH

$$\Psi\left(Q_1,\cdots,Q_f,t\right)=\sum_{j_1=1}^{N_1}\cdots\sum_{j_f=1}^{N_f}C_{j_1\cdots j_f}\left(t\right)\prod_{\kappa=1}^{f}\chi_{j_\kappa}^{(\kappa)}\left(Q_\kappa\right)$$

$$i\frac{\partial}{\partial t}C_J=\sum_L H_{JL}C_L$$
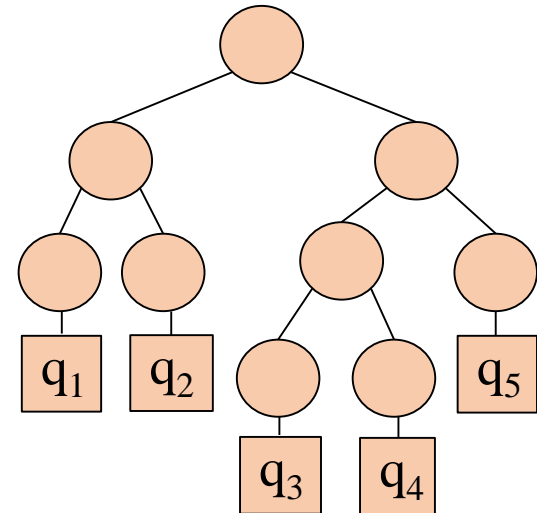
$$f_{max}\sim 9$$

ML-MCTDH

$$\varphi_m^{z-1,}\left(Q_{\kappa_{l-1}}^{z-1},t\right)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_{p_{\kappa_l}}=1}^{n_{\kappa_l}}A_{j_1\cdots j_{p_{\kappa_l}}}^{z}\left(t\right)\prod_{\kappa_l=1}^{p_{\kappa_l}}\varphi_{j_{\kappa_l}}^{z,\kappa_l}\left(Q_{\kappa_l}^z,t\right)$$
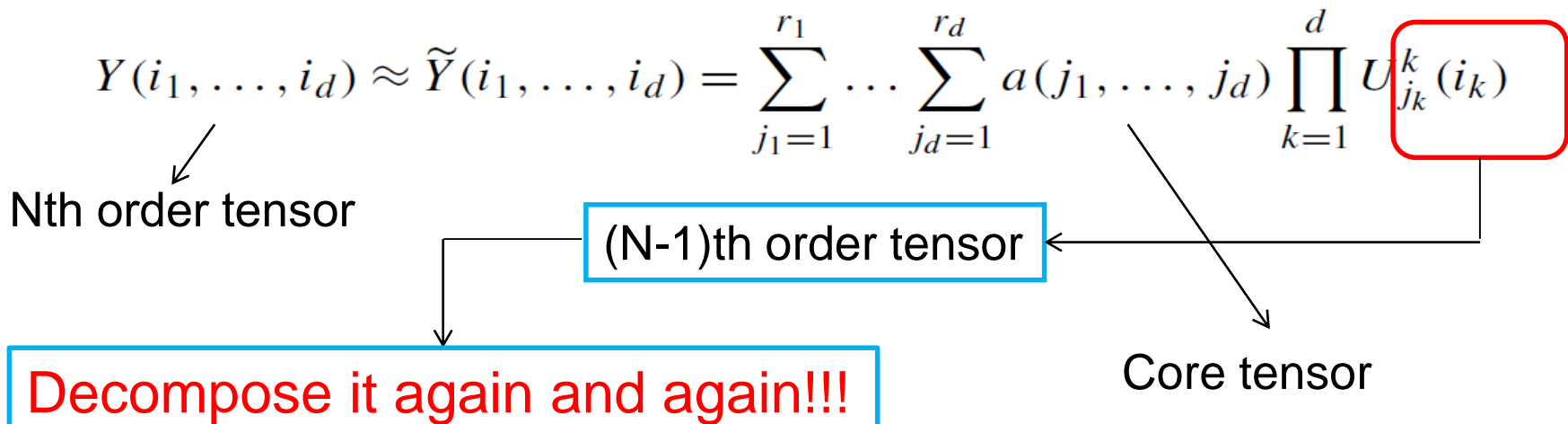
$$i\dot{A}_J^l=\sum_L\left\langle\Phi_J^l\left|H\right|\Phi_L^l\right\rangle A_L^l$$

$$i\dot{\varphi}_n^{z,\kappa_l}=\left(1-\hat{P}_{\kappa_l}^z\right)\sum\left(\rho^{z,\kappa_l}\right)_{nj}^{-1}\left\langle H\right\rangle_{jm}^{z,\kappa_l}\varphi_m^{z,\kappa_l}$$

$$f_{max}\sim 1500$$

MCTDH

$$\Psi\left(Q_1,\cdots,Q_f,t\right)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_f}A_{j_1\cdots j_f}\left(t\right)\prod_{\kappa=1}^{f}\varphi_{j_\kappa}^{(\kappa)}\left(Q_\kappa,t\right)$$

$$i\dot{A}_J=\sum_L\left\langle\Phi_J\left|H\right|\Phi_L\right\rangle A_L$$

$$i\dot{\boldsymbol{\varphi}}^{(\kappa)}=\left(1-P^{(\kappa)}\right)\left(\boldsymbol{\rho}^{(\kappa)}\right)^{-1}\left\langle H\right\rangle^{(\kappa)}\boldsymbol{\varphi}^{(\kappa)}$$

$$f_{max}\sim 60$$

Tensor decomposition and ML-MCTDH

$$Y(i_1, \ldots, i_d) \approx \widetilde{Y}(i_1, \ldots, i_d) = \sum_{j_1=1}^{r_1} \cdots \sum_{j_d=1}^{r_d} a(j_1, \ldots, j_d) \prod_{k=1}^{d} U_{j_k}^{k}(i_k)$$

Nth order tensor

(N-1)th order tensor

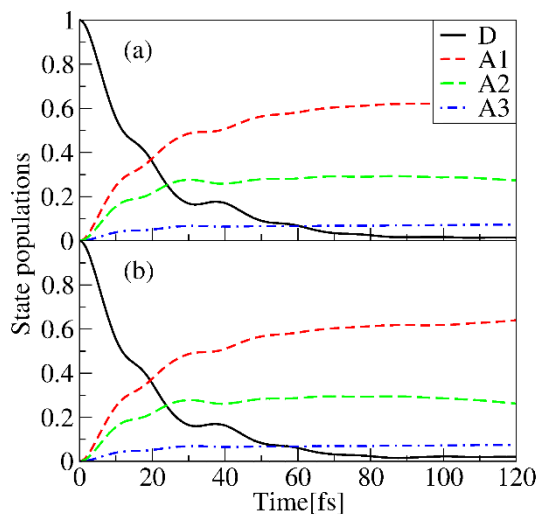Decompose it again and again!!!

Core tensor

- **The decomposition structure is not unique.**
- **The good one works 10 times faster than the bad one.**

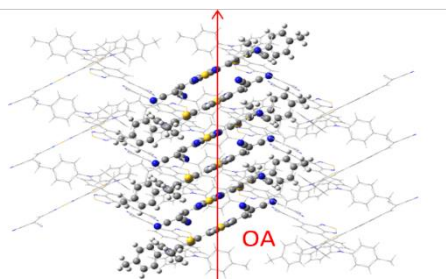Arnold, A.; Jahnke, T., Bit 2014, 54 (2), 305-341.
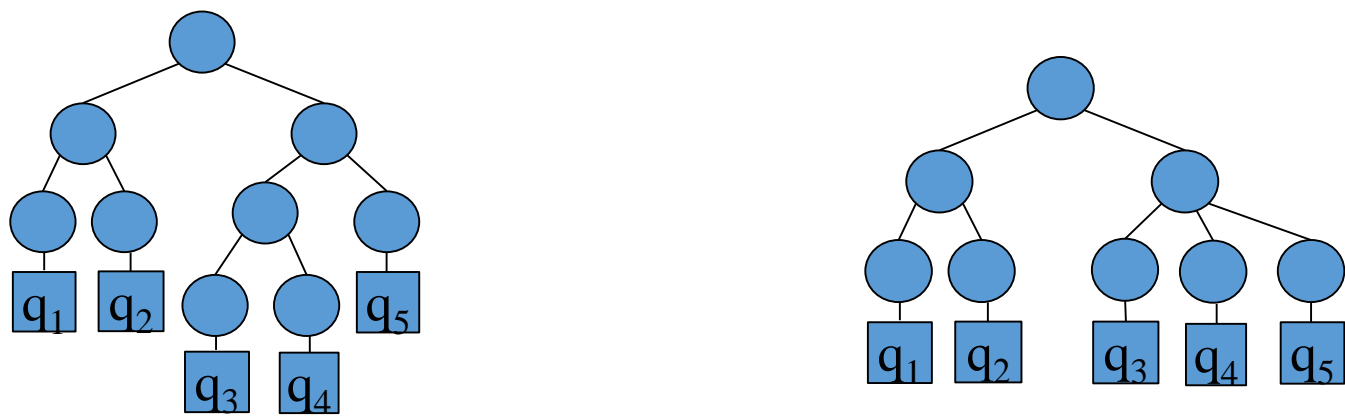
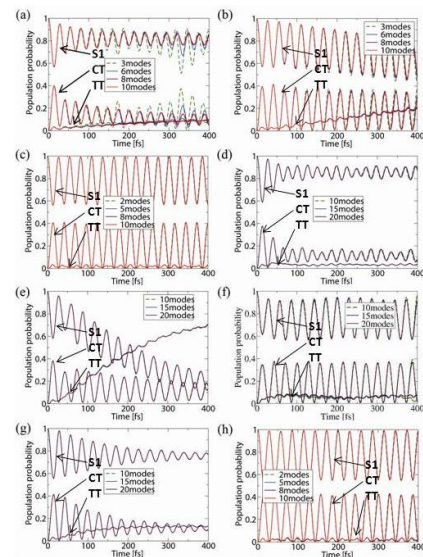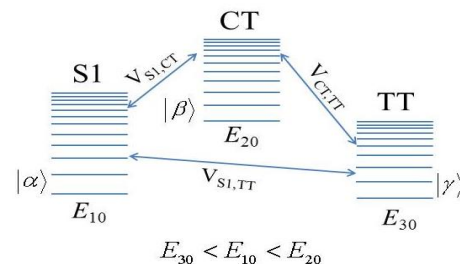# Understanding Exciton Dynamics using ML-MCTDH

Charge Transfer
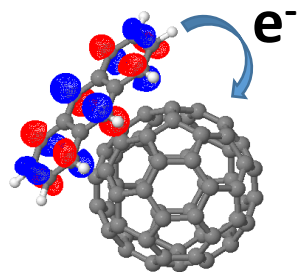
Energy Transfer
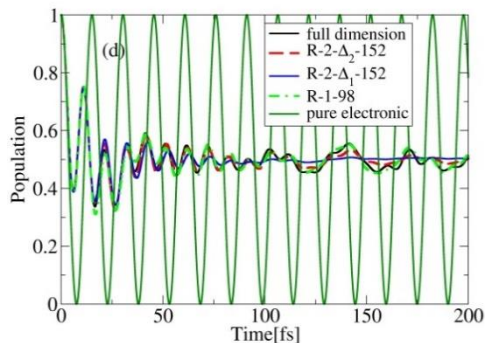
Singlet Fission

Y. Xie, J. Zheng and Z. Lan, *J. Chem. Phys.* **142** (8), 084706 (2015).

J. Zheng, Y. Xie, S. Jiang and Z. Lan, *J. Phys. Chem. C* **120** (3), 1375-1389 (2016).

S. Jiang, J. Zheng, Y. Yi, Y. Xie, F. Yuan and Z. Lan, *J. Phys. Chem. C* **121** (49), 27263-27273 (2017).

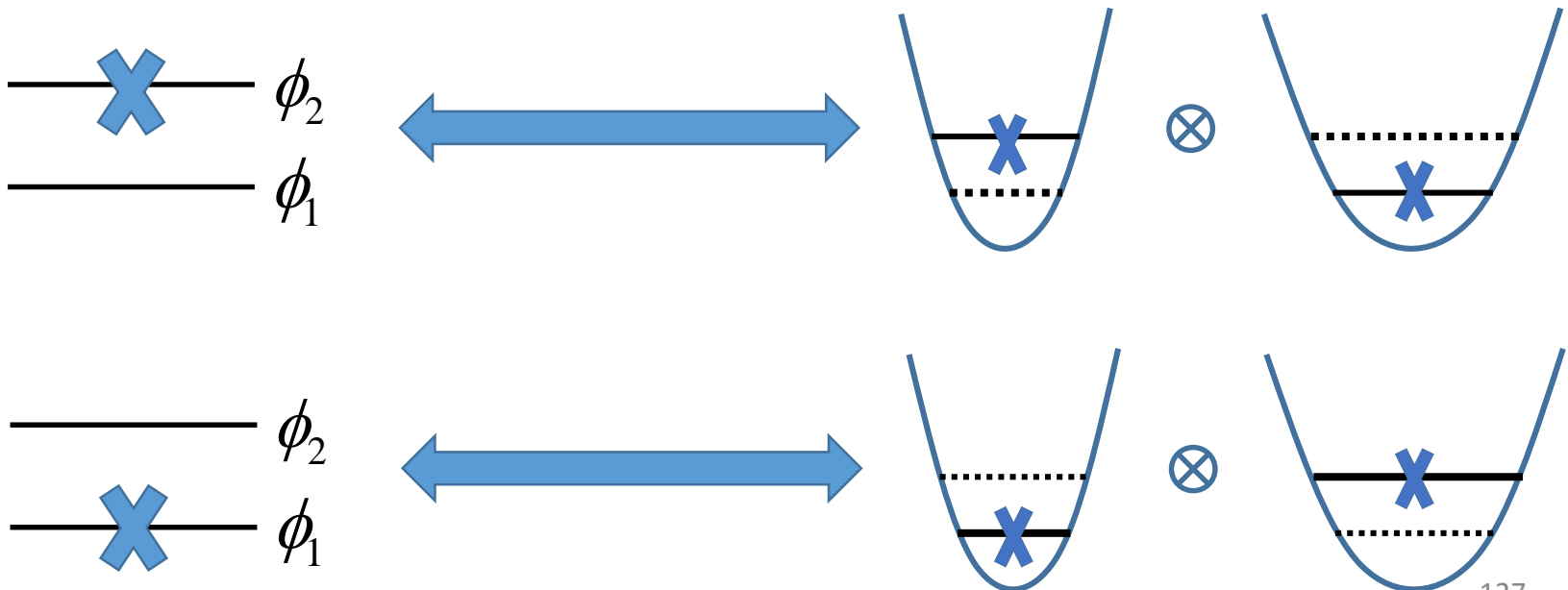S. Jiang, Y. Xie and Z. Lan, *Chem. Phys.* **Accepted** (2018).

Mapping Hamiltonian

$$|\phi_n\rangle\langle\phi_m| \mapsto a_n^+ a_m,$$

$$|\phi_n\rangle \mapsto |0_1 \cdots 1_n \cdots 0_N\rangle.$$

$$\hat{H} = \sum_{n,m} \hat{h}_{nm} |\phi_n\rangle\langle\phi_m|$$

$$\hat{x}_n = \left(\hat{a}_n^+ + \hat{a}_n\right)/\sqrt{2}$$

$$\hat{p}_n = i\left(\hat{a}_n^+ - \hat{a}_n\right)/\sqrt{2}$$

$$\hat{H} = \sum_n \frac{1}{2}\left(\hat{x}_n^{\;2} + \hat{p}_n^{\;2} - 1\right)\hat{h}_{nn}$$
$$+ \frac{1}{2}\sum_{n \neq m}\left(\hat{x}_n \hat{x}_m + \hat{p}_n \hat{p}_m\right)\hat{h}_{nm}$$

- H. D. Meyer and W. H. Miller, J. Chem. Phys. 70 (7), 3214-3223 (1979).
- G. Stock and M. Thoss, Phys. Rev. Lett. 78 (4), 578-581 (1997).

Dynamical Methods based on mapping

Semiclassical Initial Value Representation (SC-IVR)

$$S_{2,1}(t) = \int d\mathbf{x}_1 \, d\mathbf{X}_1 \int d\mathbf{p}_1 \, d\mathbf{P}_1 \left[\frac{\partial(\mathbf{x}_t, \mathbf{X}_t)}{\partial(\mathbf{p}_1, \mathbf{P}_1)} / (2\pi i\hbar)^{F+N} \right]^{1/2} \chi_2^*(\mathbf{X}_t) \Phi_{k_2}^*(\mathbf{x}_t) \Phi_{k_1}(\mathbf{x}_1) \chi_1(\mathbf{X}_1) \, e^{iS_t(\mathbf{x}_1, \mathbf{p}_1, \mathbf{X}_1, \mathbf{P}_1)/\hbar}$$

Quantum-Classical Liouville Dynamics in the Mapping Basis

$$\frac{d}{dt} B_m(x, X, t) = -\{H_m, B_m(t)\}_{x,X} + \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \left(\frac{\partial}{\partial r_{\lambda'}} \frac{\partial}{\partial r_\lambda} + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) \frac{\partial}{\partial P} B_m(t) \equiv i\mathcal{L}_m B_m(t)$$

Quasi-Classical Dynamics (QC)

$$H = \sum_n \frac{1}{2}\left(x_n^2 + p_n^2 - \gamma\right) h_{nn} + \frac{1}{2}\sum_{n\neq m}\left(x_n x_m + p_n p_m\right) h_{nm}, \gamma < 1$$

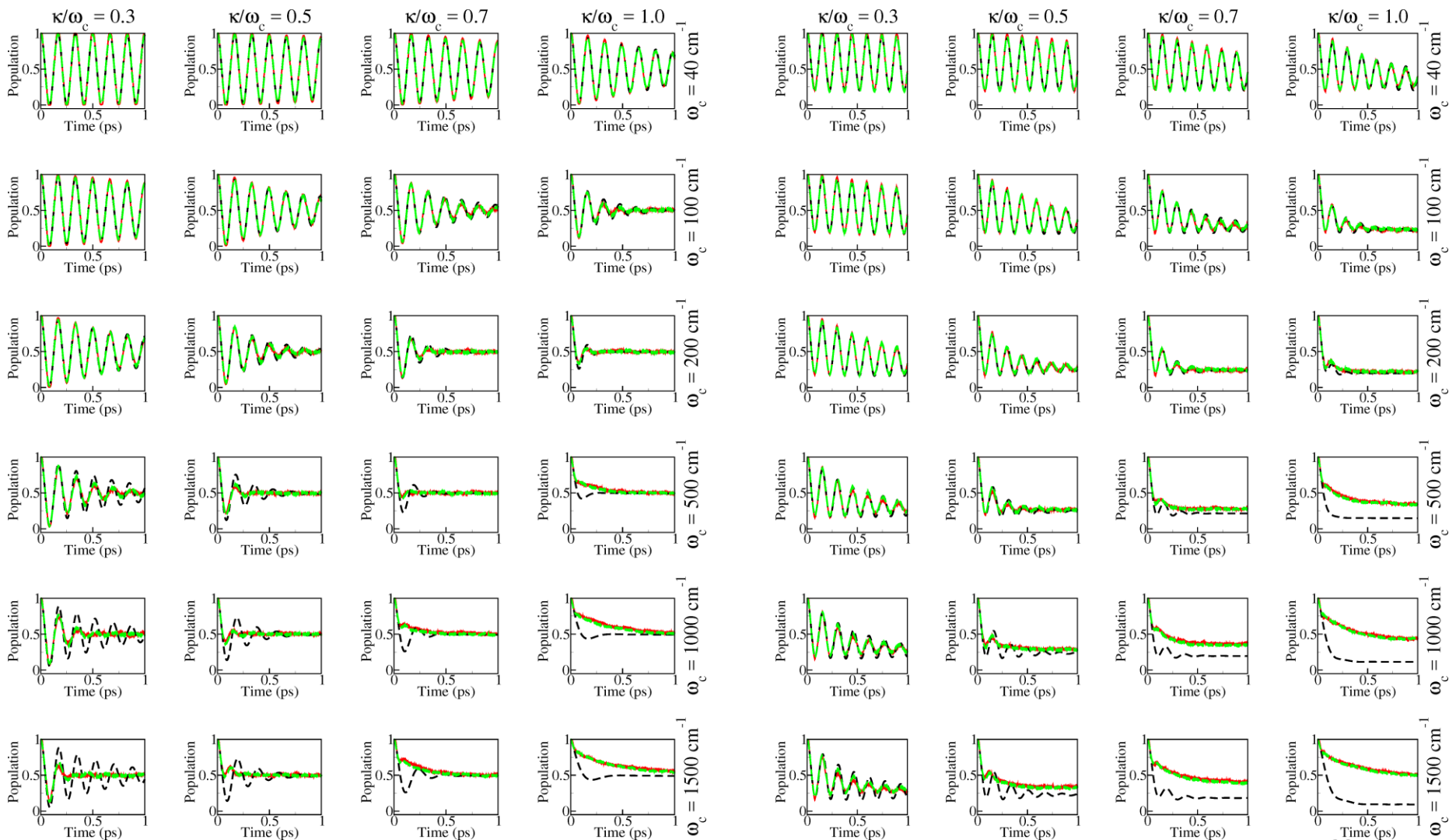Symmetrical Quasi-Classical Dynamics (SQC)

$$P_{N_2 \leftarrow N_1}^{SQC} = \int_{N_1 - 1/2}^{N_1 + 1/2} dn_1 \int_{N_2 - 1/2}^{N_2 + 1/2} dn_2 \left(2\pi \left| \frac{\partial n_2}{\partial q_1} \right| \right)^{-1}$$

- B. Li and W. H. Miller, J. Chem. Phys. 137 (15), 154107 (2012).
- H. Kim, A. Nassimi and R. Kapral, J. Chem. Phys. 129 (8), 084102 (2008).
- H. D. Meyer and W. H. Miller, J. Chem. Phys. 71 (5), 2156-2169 (1979).
- S. J. Cotton and W. H. Miller, J. Phys. Chem. A 117 (32), 7190-7194 (2013).

Site-exciton model

ΔE = 0

ΔE = 100 cm⁻¹

Dynamics methods

Quantum Dynamics
Quantum wavepacket
MCTDH, ML-MCTDH

Quantum dissipative dynamics
Redfiled
HEOM

Bohmian dynamics

Gaussian Wavepacket
Multiply spawning
Multiconfiguational Ehrenfest

Time-dependent DMRG

Quantum Classical Liouville Equation

Surface Hopping
Tully fewest switches
Landau-Zener and Zhu-Nakamura
Exact factorization (Gross)
Pechukas' force
Others.

Ehrenfest

Phase-space branching …

Semiclassical Monte-Carlo

Mapping Hamiltonian
Semiclassical IVR
Quasiclassical Dynamcis
Symmetrical quasi-classical dynamics

A New Starting …

Guangzhou in China

City view of Guangzhou

South China Normal University

New Postdoc and
Research Assistant Positions
are open !!!

Acknowledgement

Funding:
NSCF
CAS

Acknowledgement

Thank You!