Excited-State Molecular Dynamics

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Computational
Biomolecular
Chemistry

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Non-Adiabatic Molecular Dynamics

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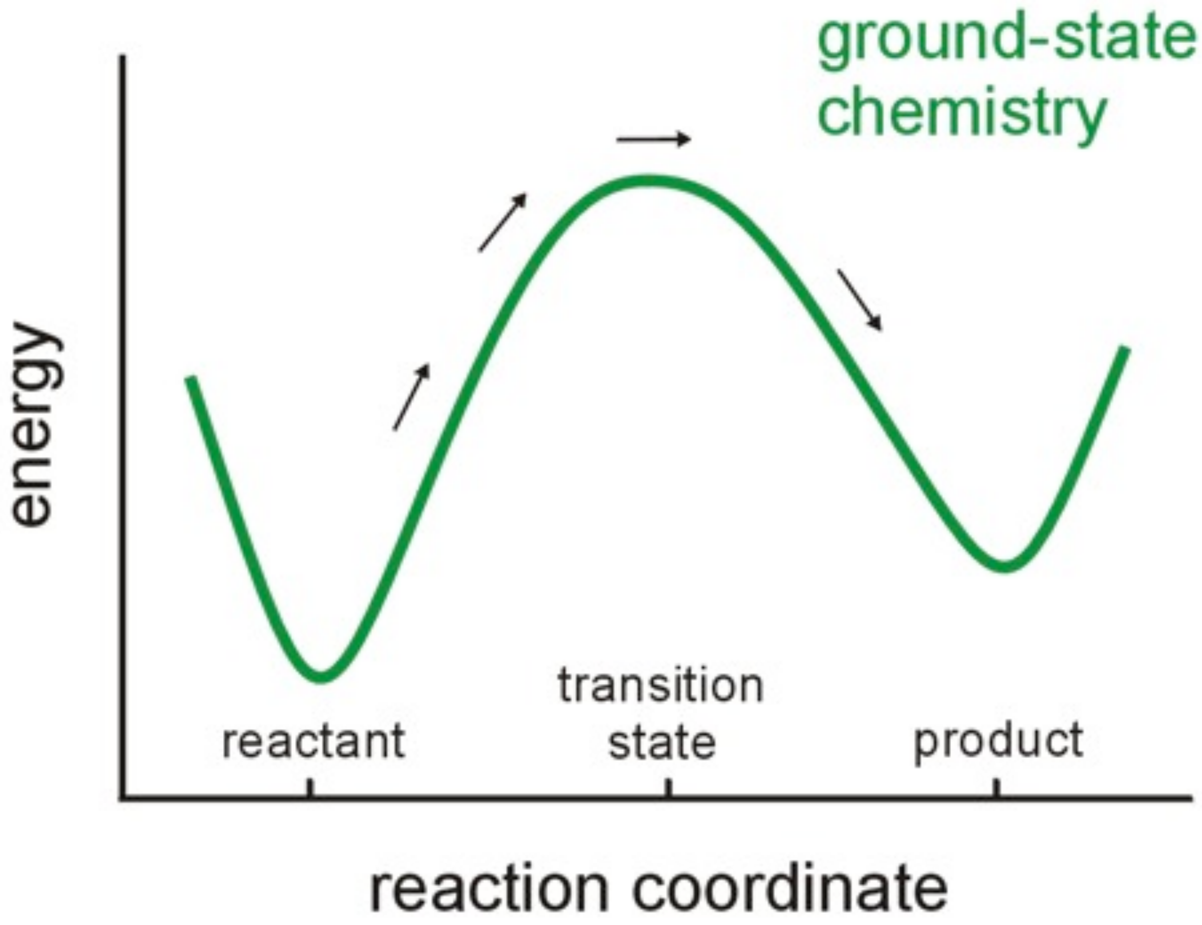
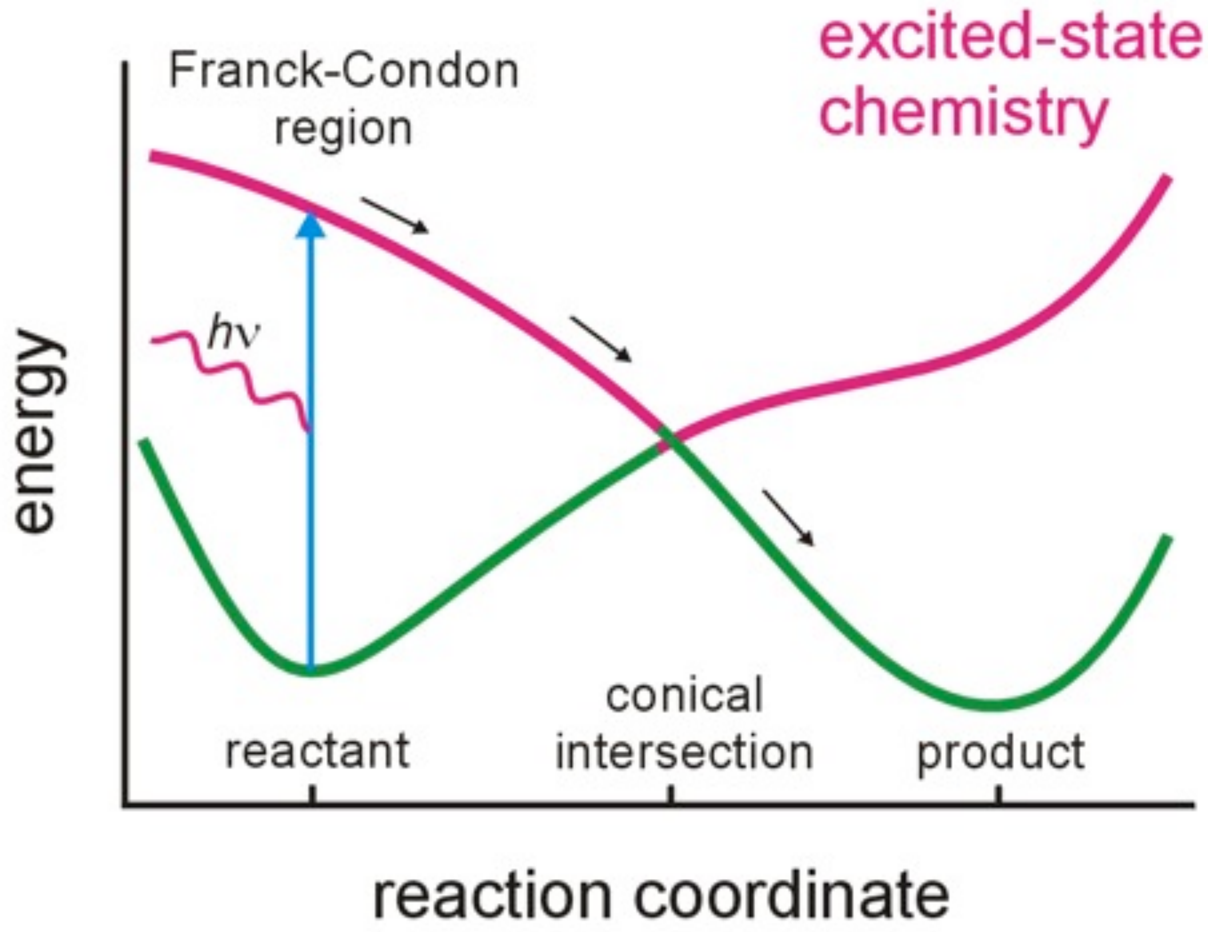
non-adiabatic chemistry

nuclear dynamics in more than one electronic state

transitions between electronic states!

adiabatic & non-adiabatic chemisty





thermodynamic control

statistical mechanics (Eyring)

kinetic control

dynamics

non-adiabatic chemistry

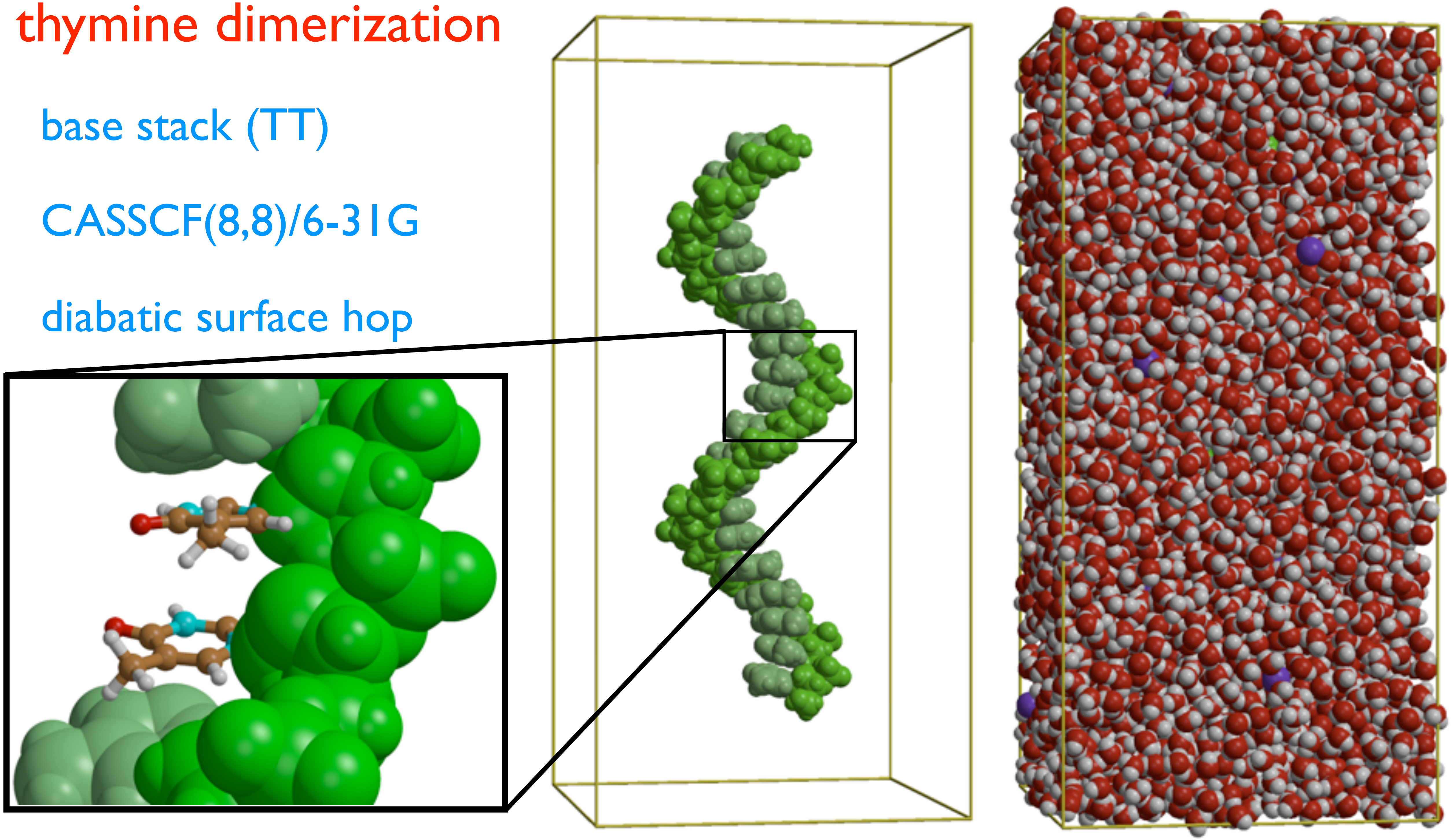
example: radiation damage in DNA

thymine dimerization

base stack (TT)

CASSCF(8,8)/6-31G

diabatic surface hop

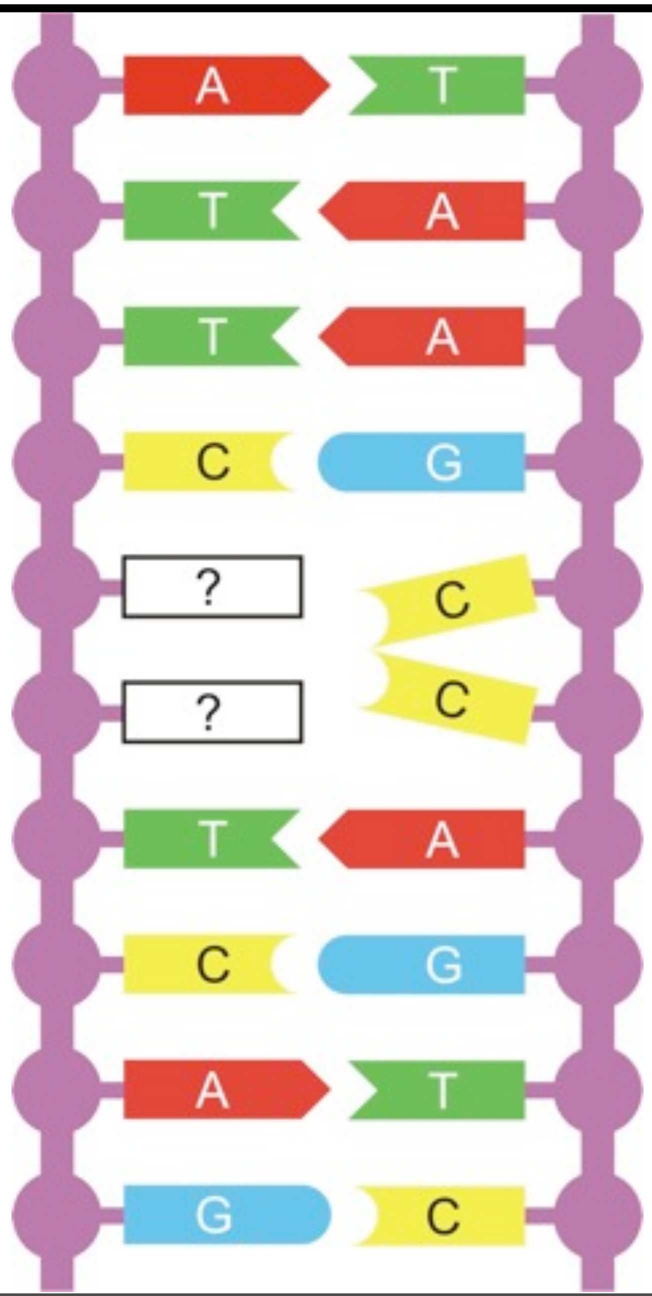


Radiation damage: UV absorption in DNA

thymine dimerization

cell dead?

mutation?



Radiation damage: UV absorption in DNA

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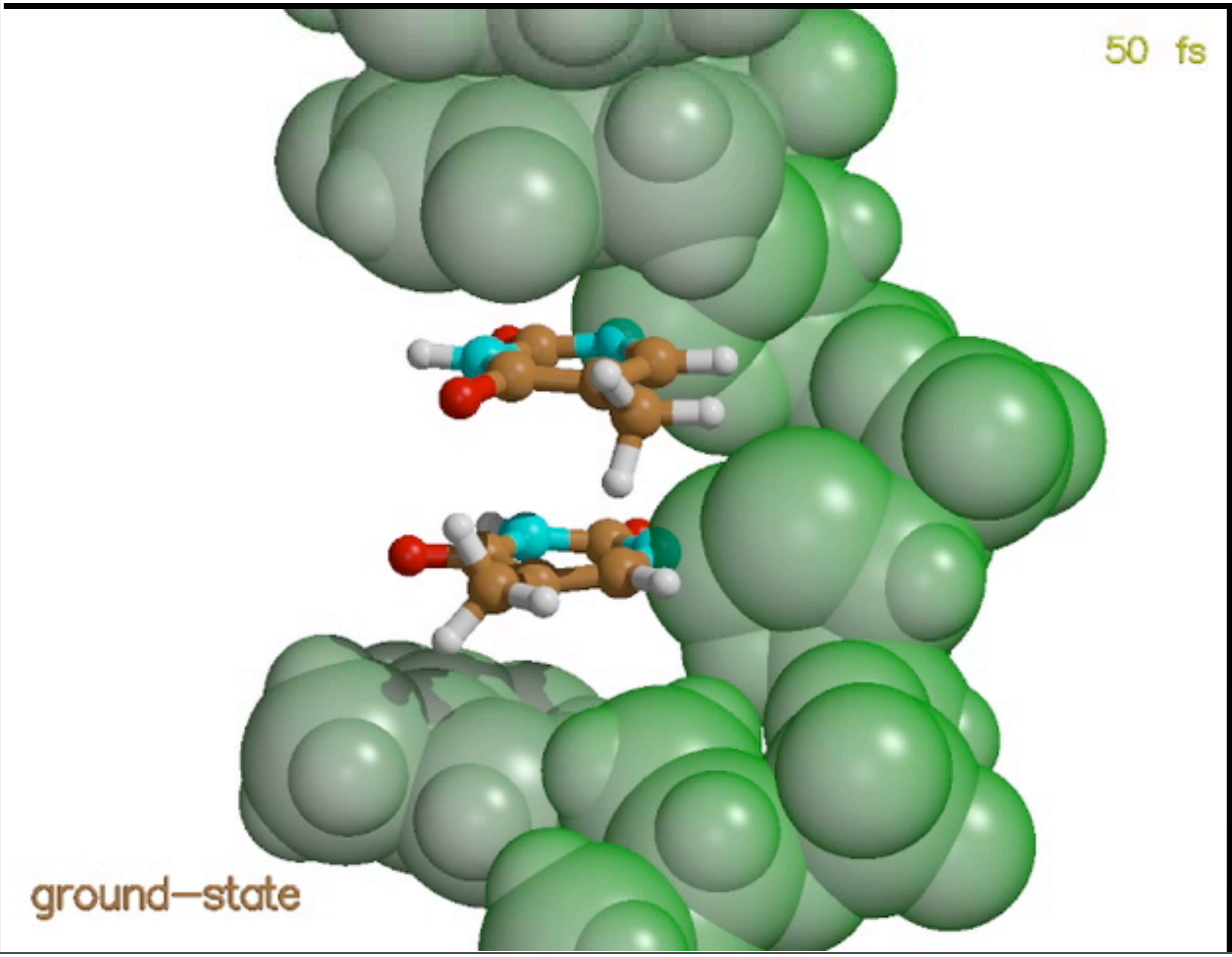

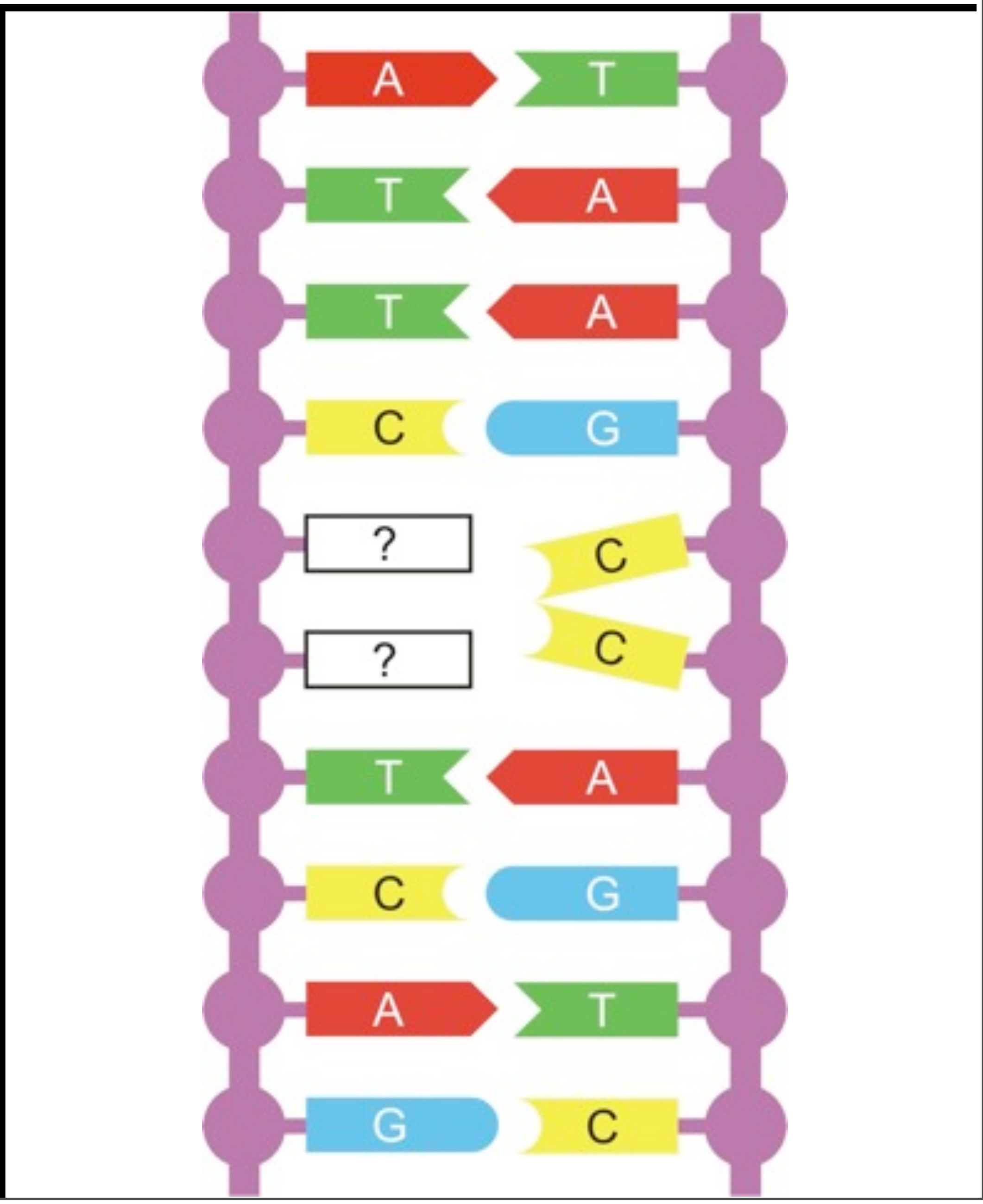

non-adiabatic chemistry

David R. Yarkony:

"Non-adiabatic processes are at the center of any approach to efficiently harvest solar energy"

"Biological systems have developed elegant protein-chromophore systems for harvesting and utilizing visible and higher-energy photons"

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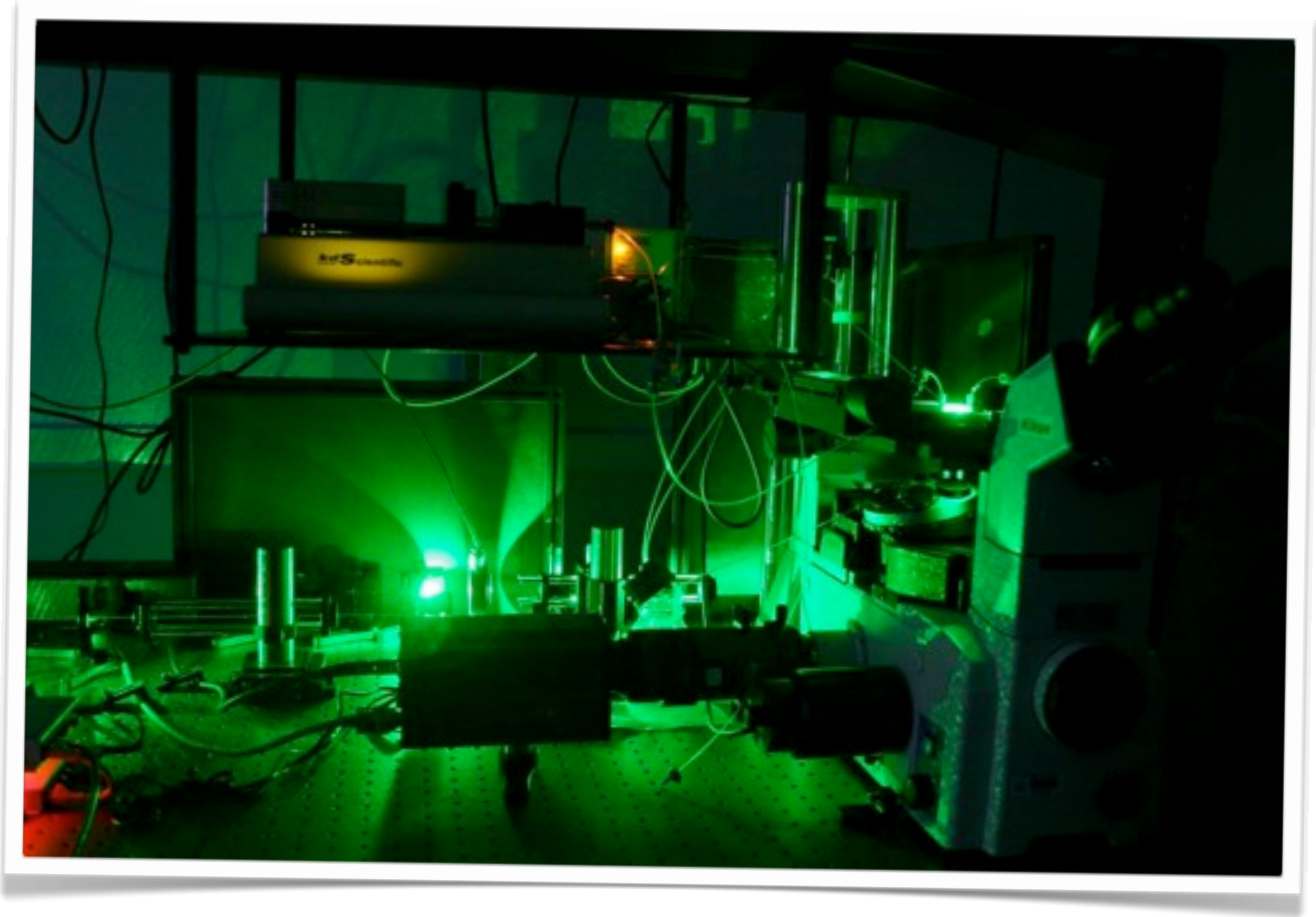
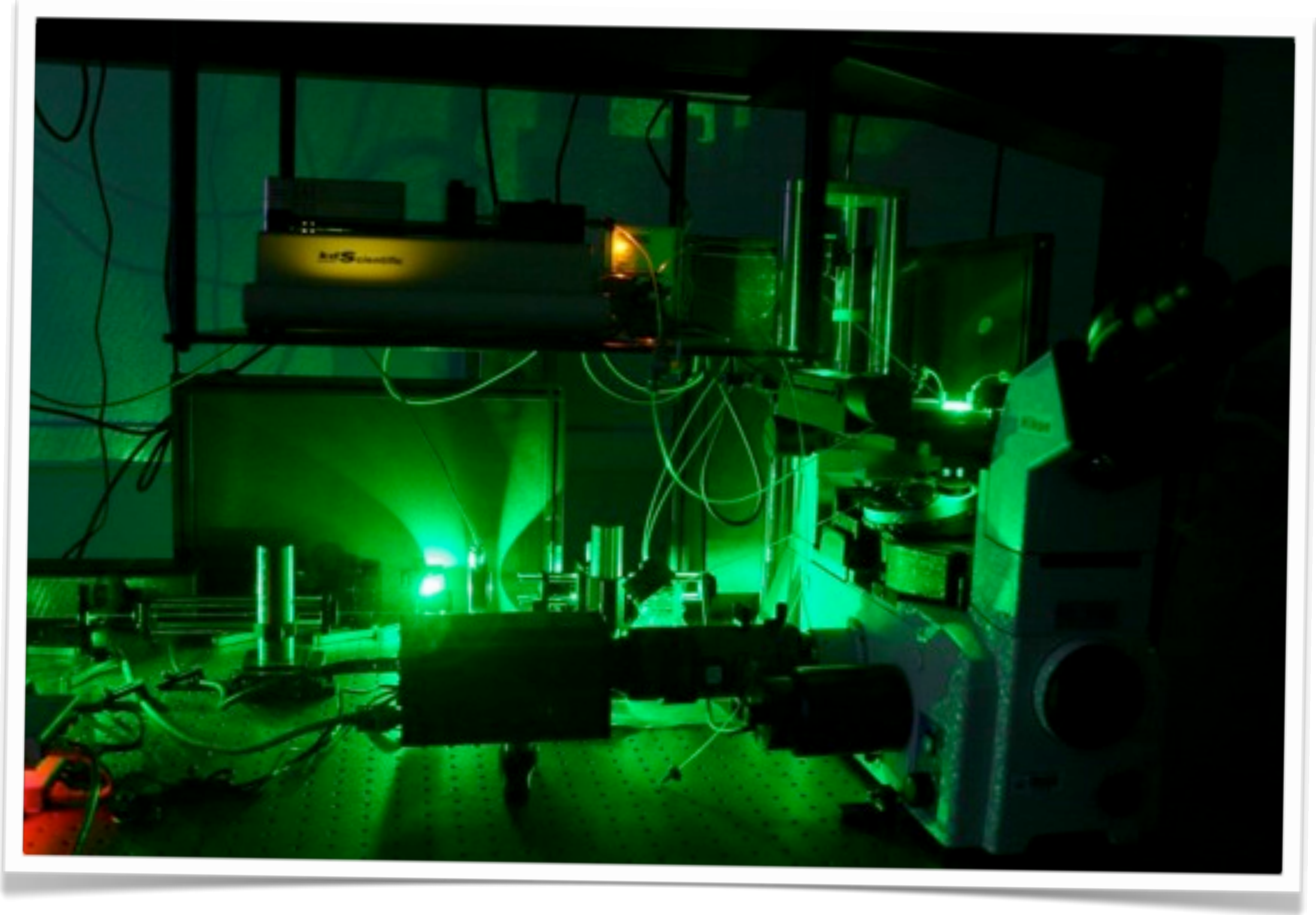
non-adiabatic chemistry

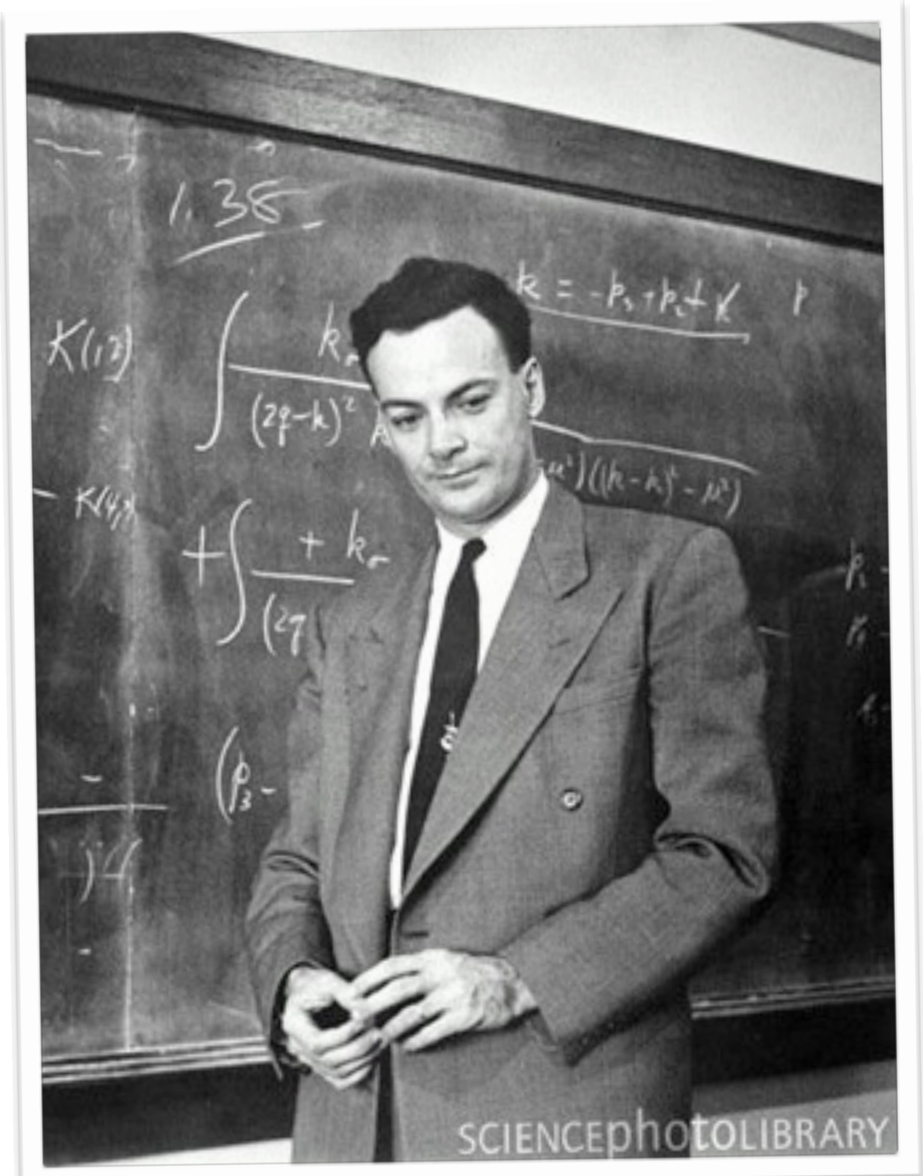
- experiment
  - provides data
  - time-resolved spectroscopy (pump-probe)
    - UV/vis, IR/midIR, x-ray, ...



non-adiabatic chemistry

- theory
  - provides concepts
    - explain
    - predict





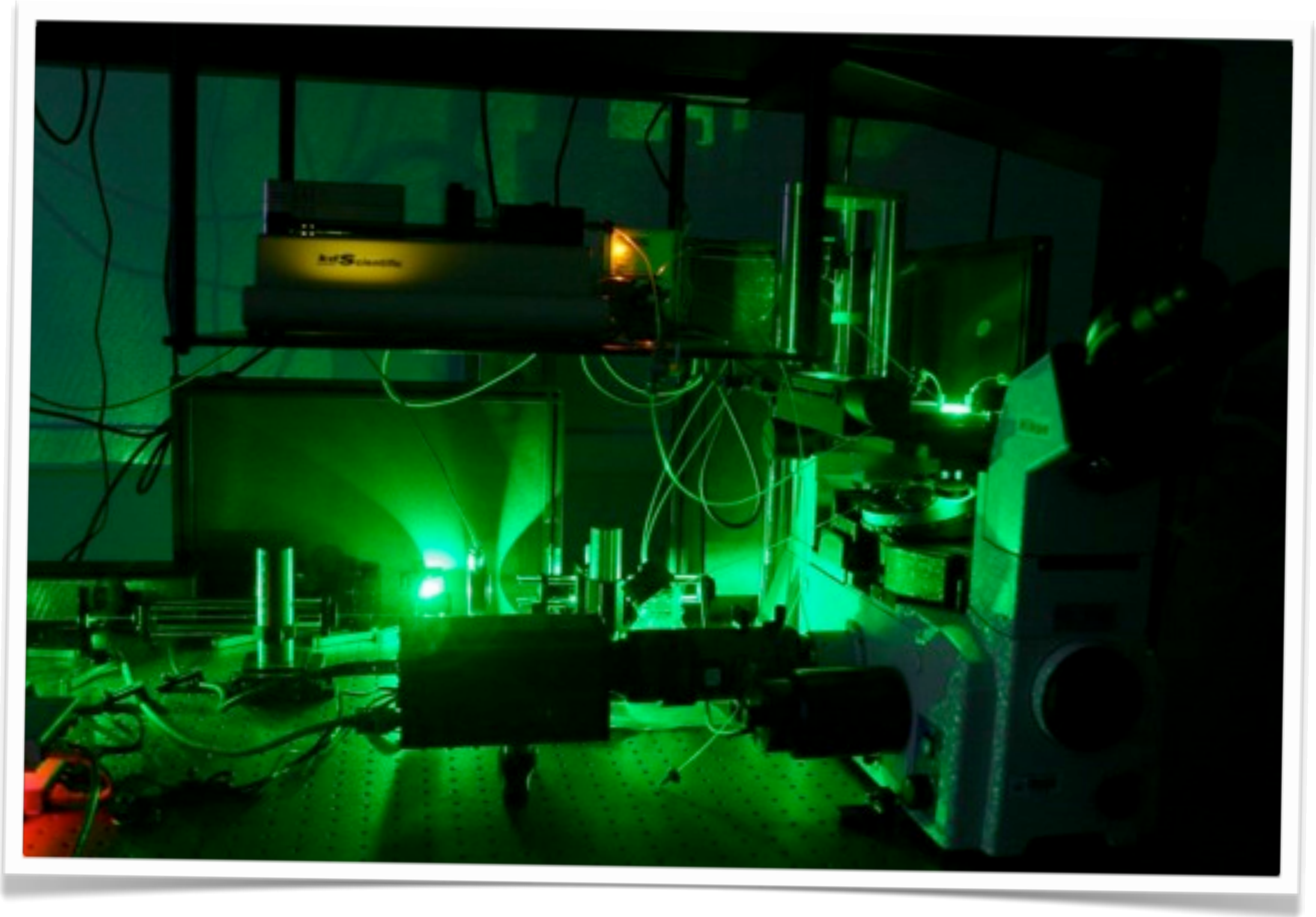
non-adiabatic chemistry

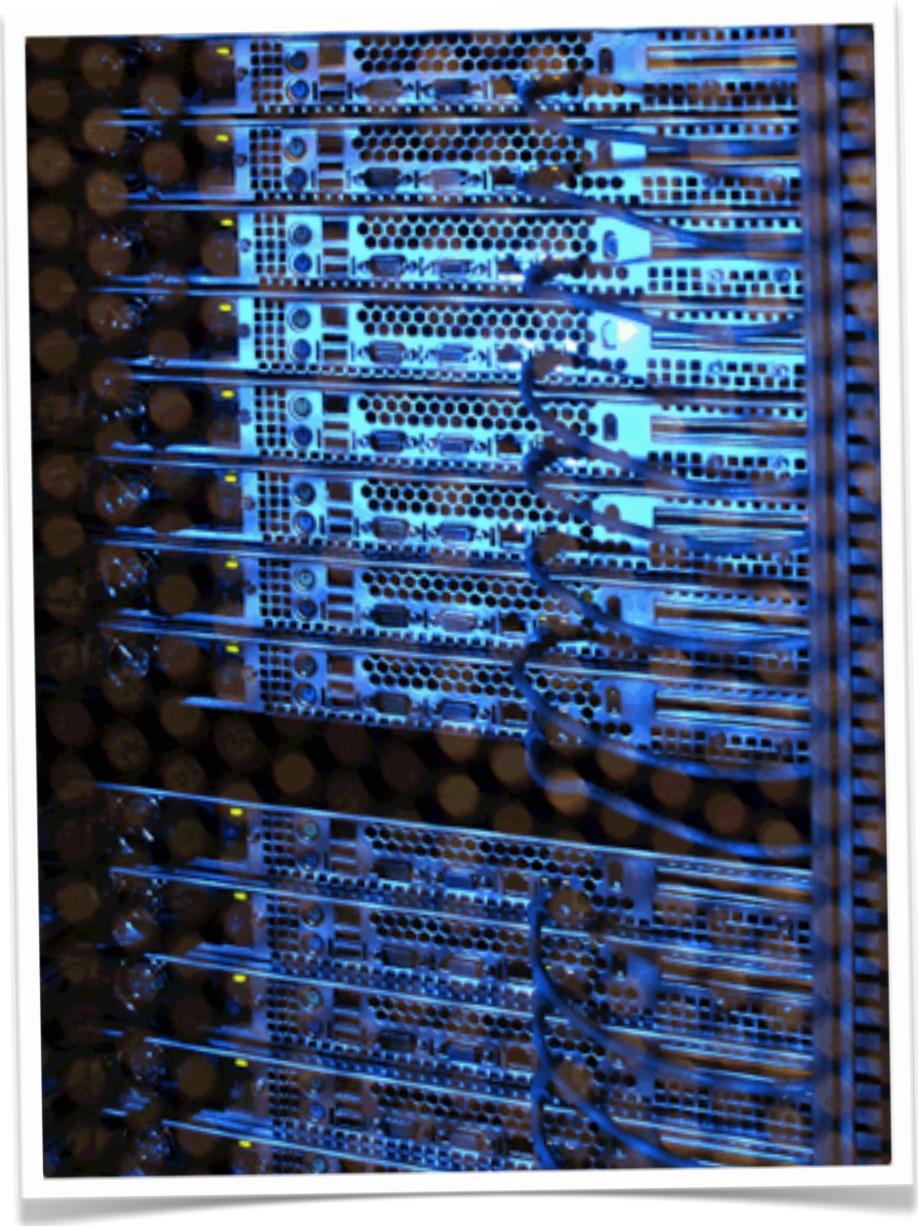
computation & simulation

provides data (predictions)

like experiment (in my view)

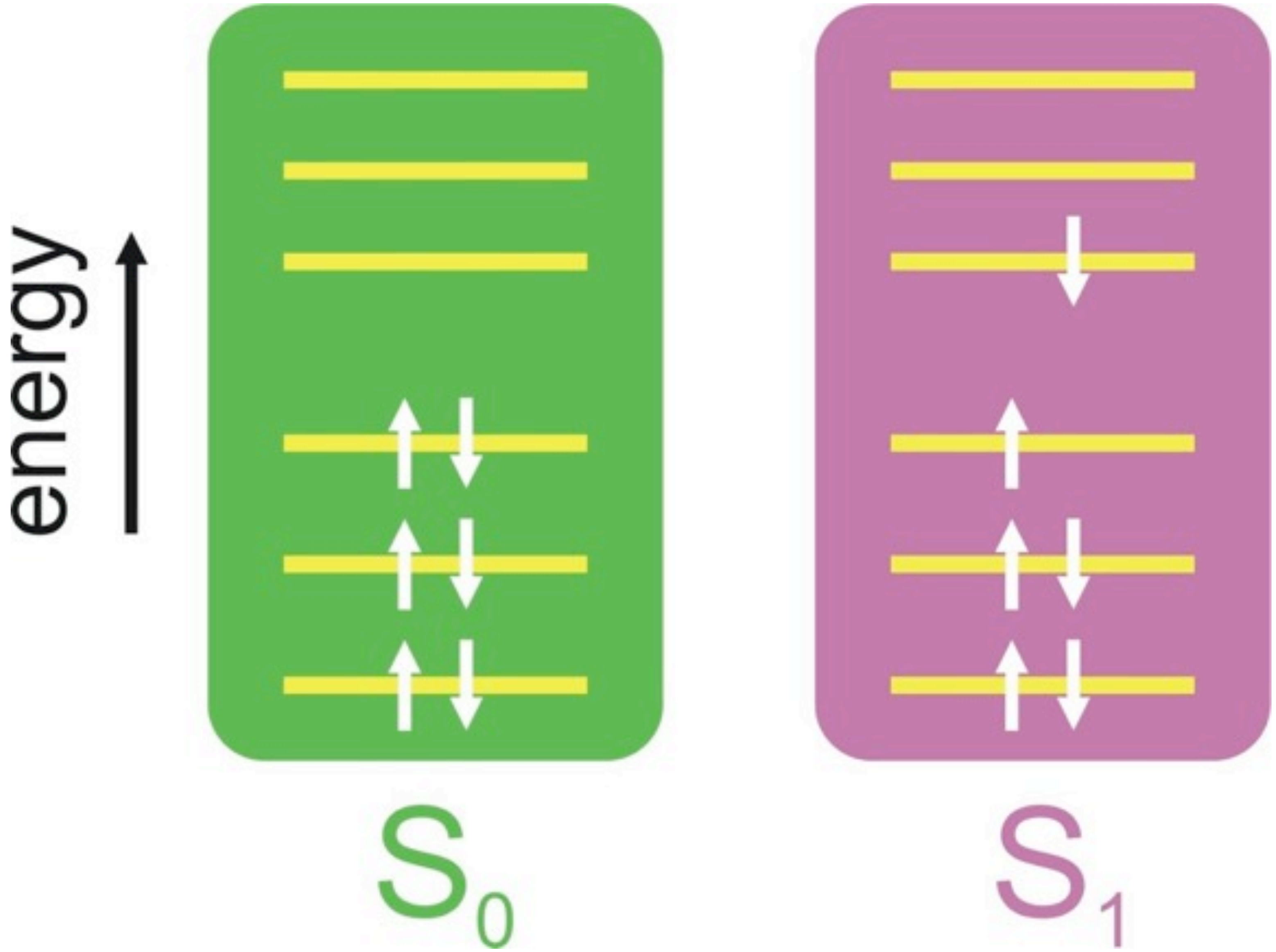
fills gaps in time & length scale





preview excited state quantum chemistry

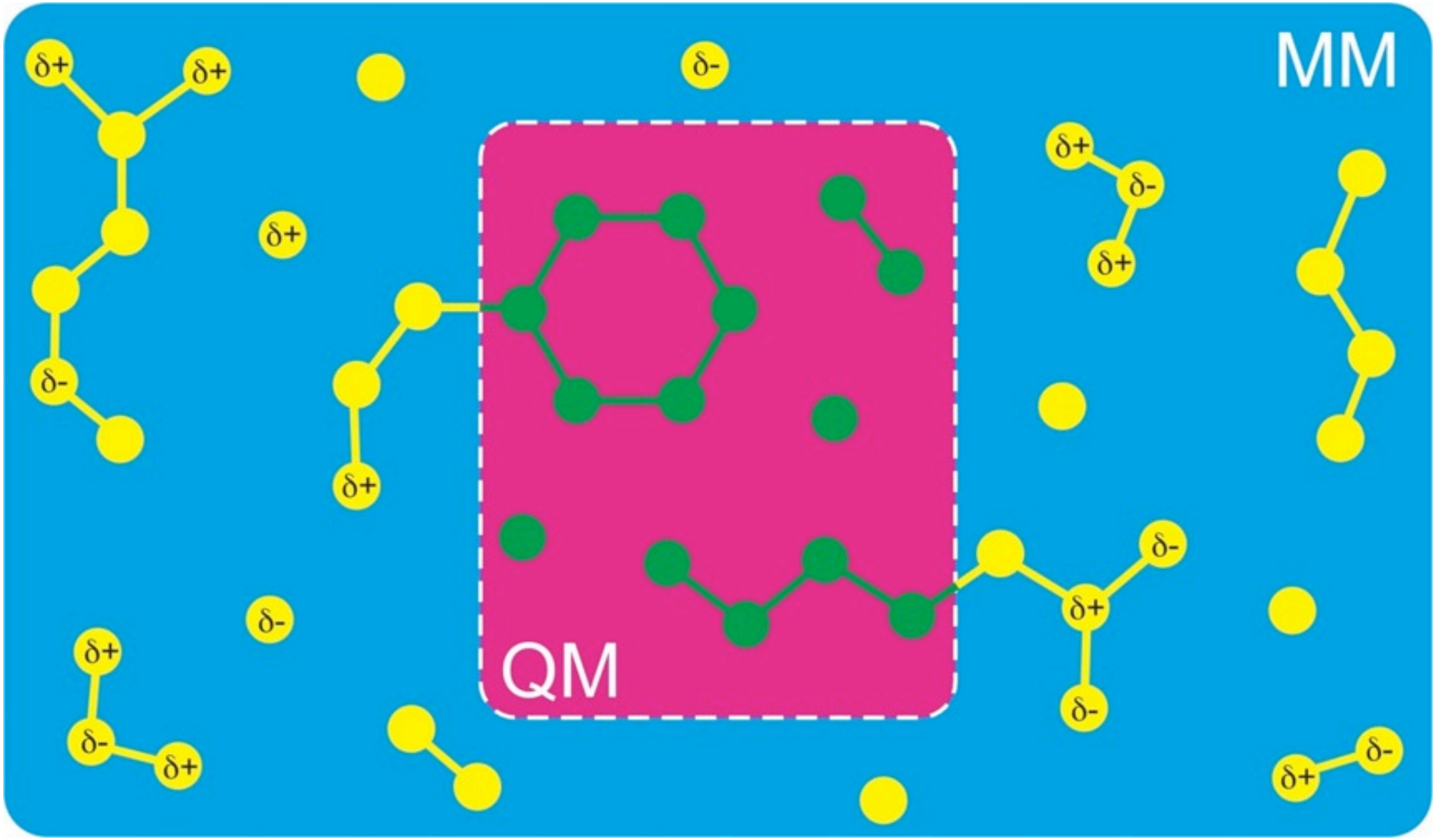
- electronic excitation
- multi-configuration methods
  - CASSCF, CASPT2, ...
  - limited to small systems (up to 40 atoms)



preview QM/MM (see also Bernd)

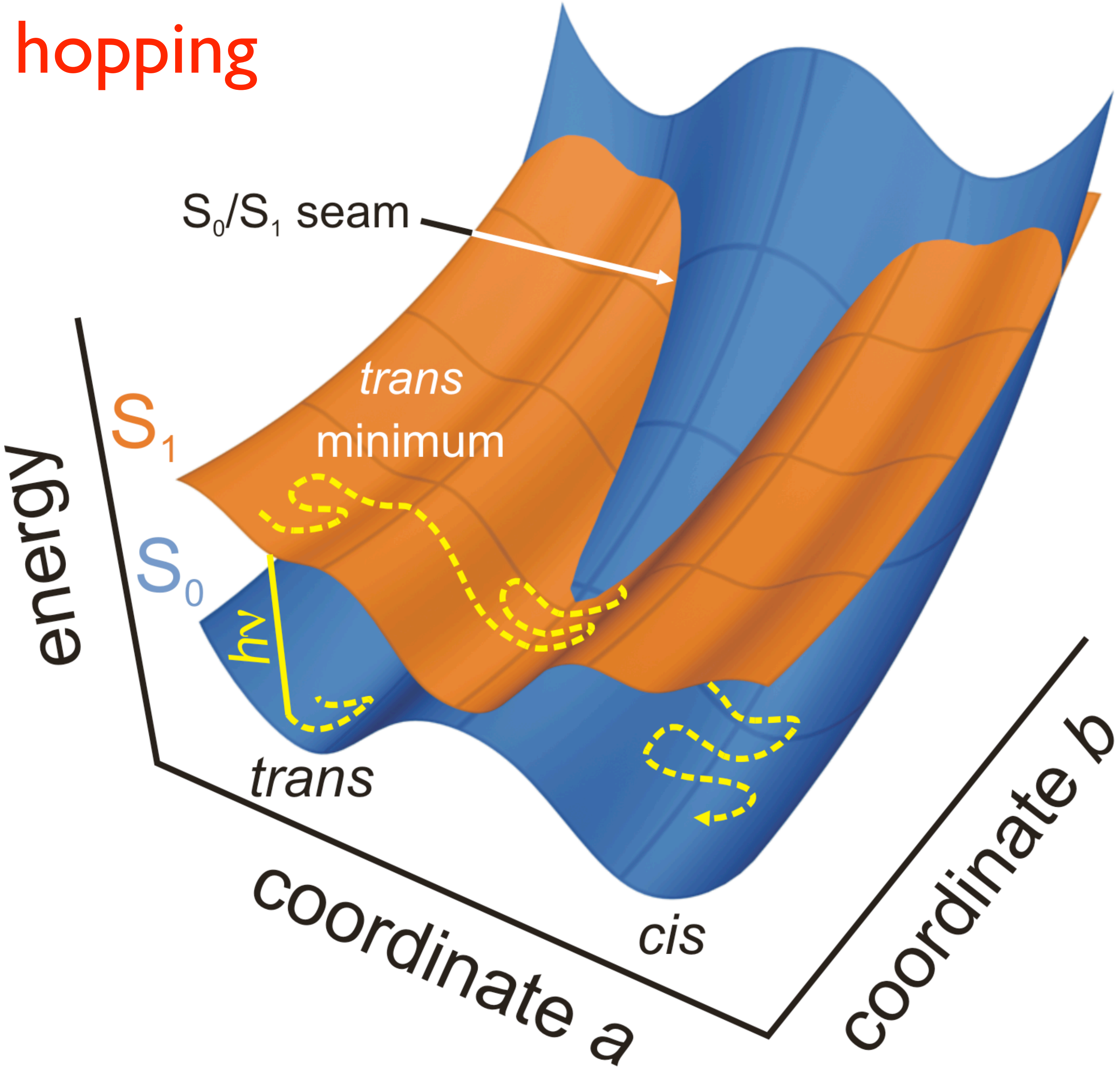
hybrid quantum mechanics/molecular mechanics

on the fly QM/MM MD simulations



sneak III (non-adiabatic dynamics)

- seam between potential energy surfaces (S_1 and S_0)
  - conical intersection
- radiationless transitions to ground state (S_0)
  - surface hopping



computational photochemistry

goals

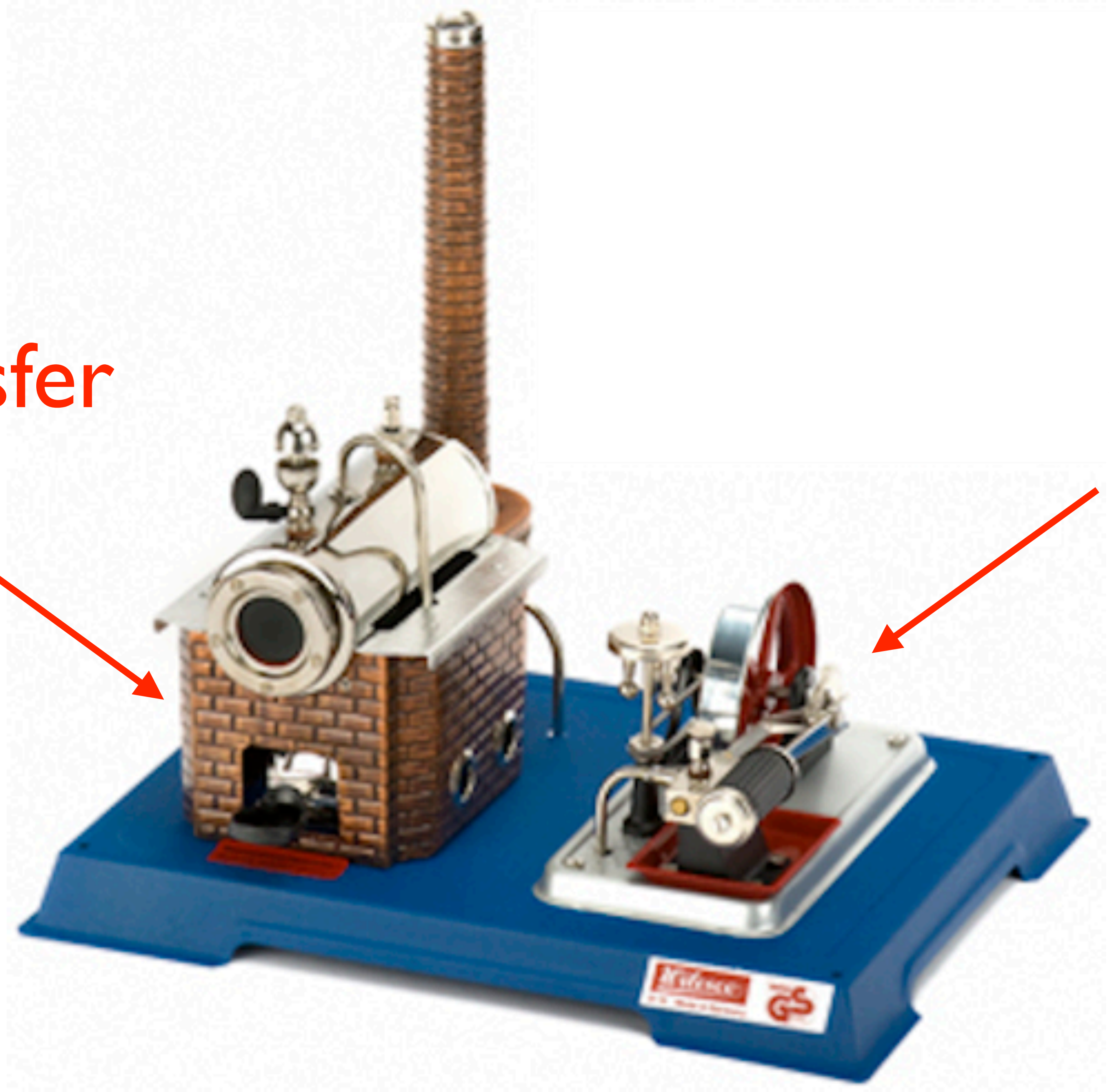
- mechanistic details
- interpretation of measurements
- control photoreactivity

biological systems

NATURA
ARTIS
MAGISTRA

Our ultimate goal

arteficial molecular machines

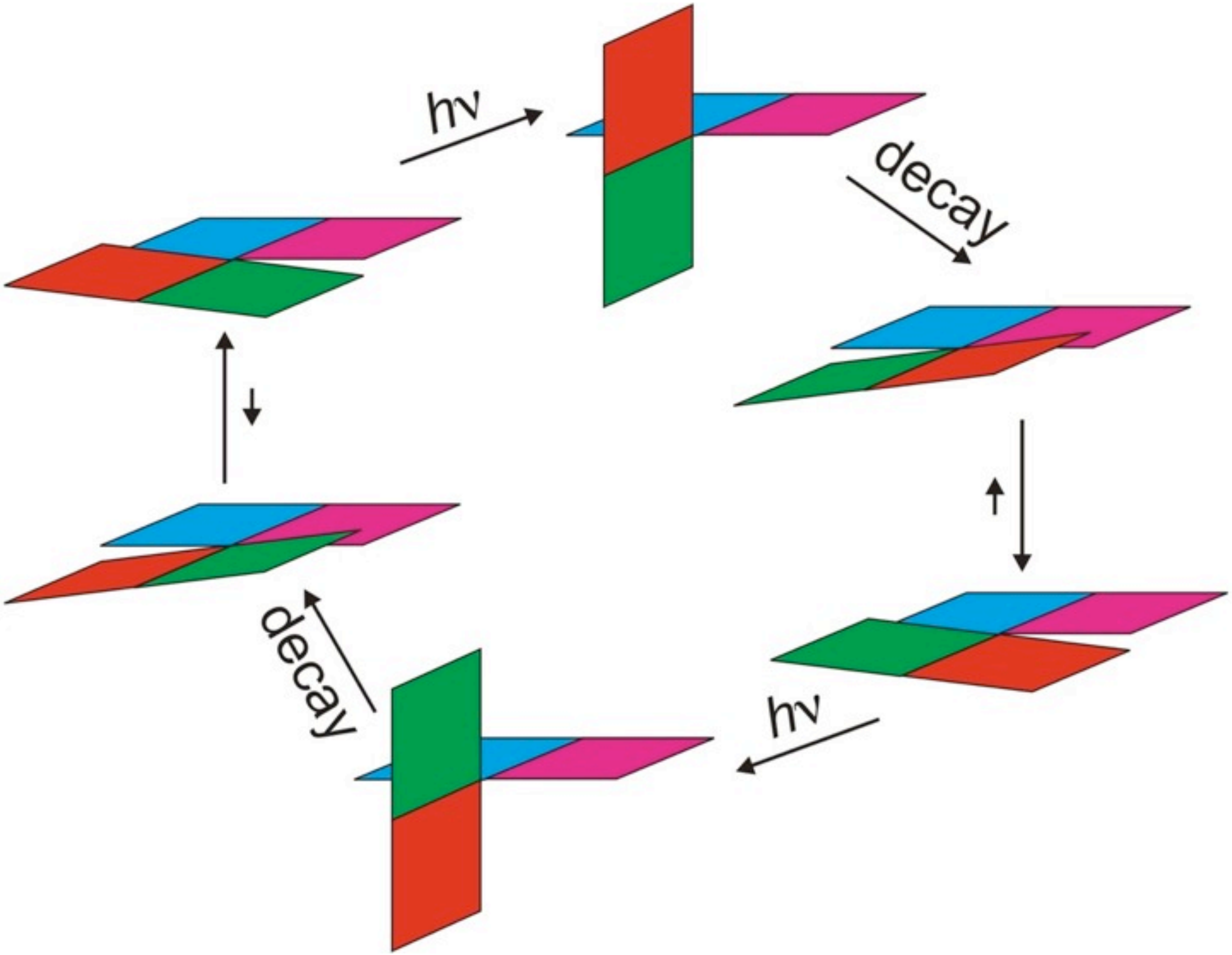


energy transfer

isomerization

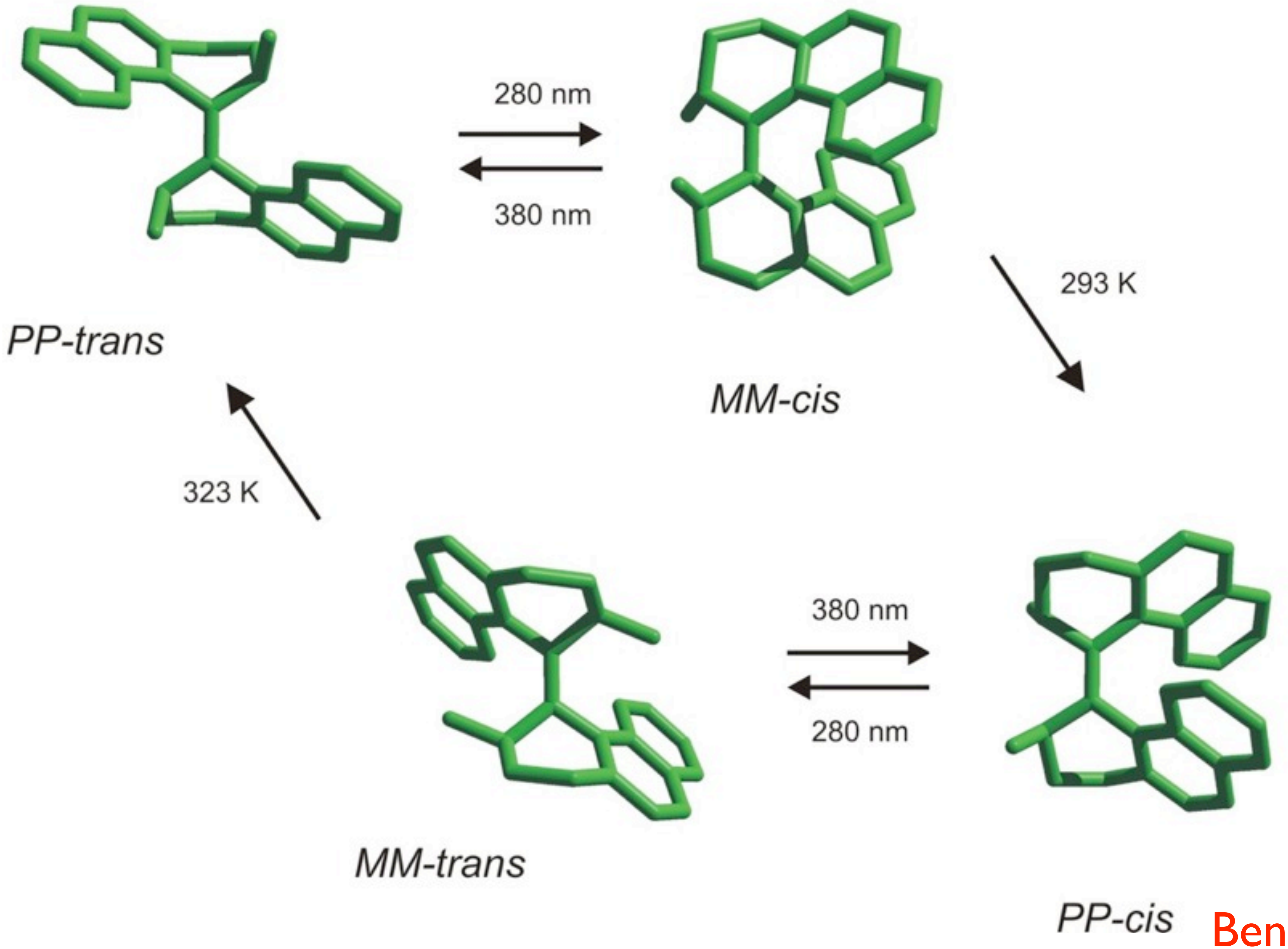
Light driven molecular motors

design principle



Light driven molecular motors

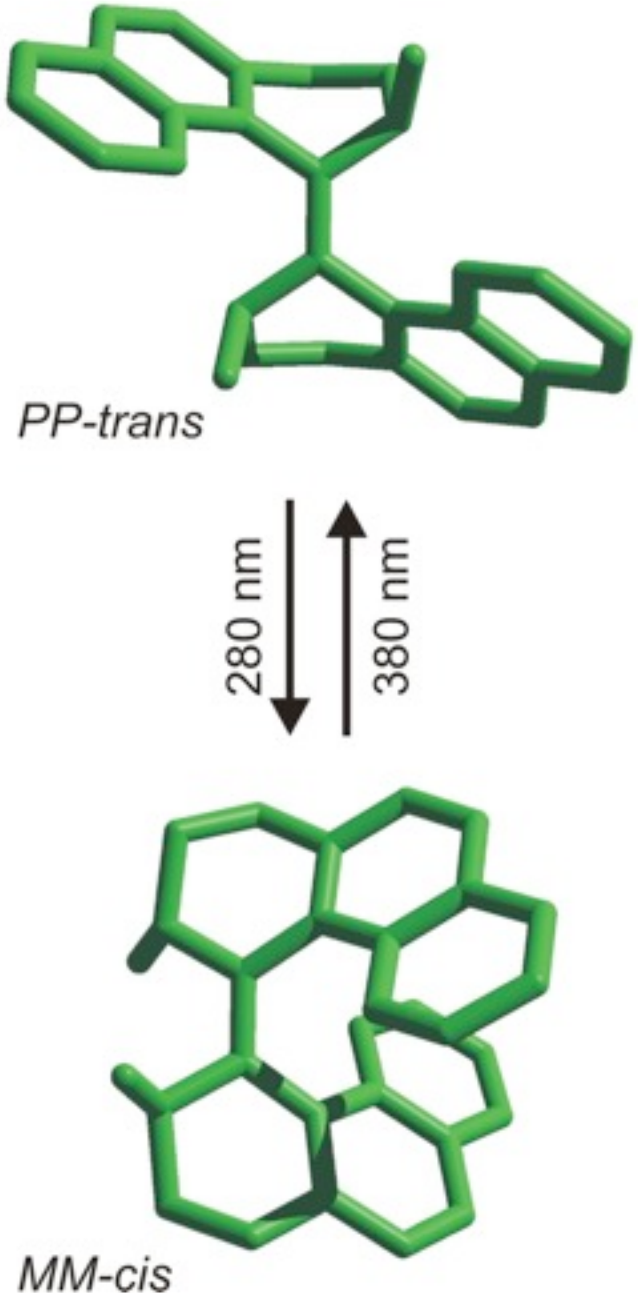
chiral over-croweded alkenes



Ben Feringa

Observe while it happens: molecular motors

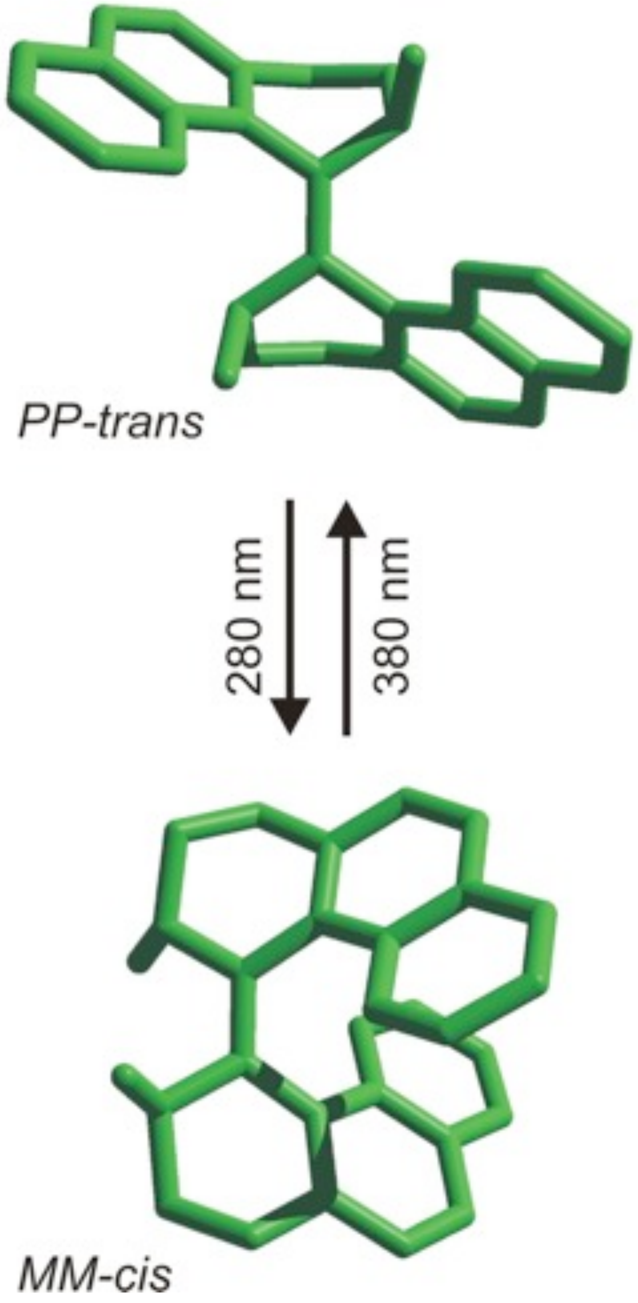
catching the photo-isomerizations in the act

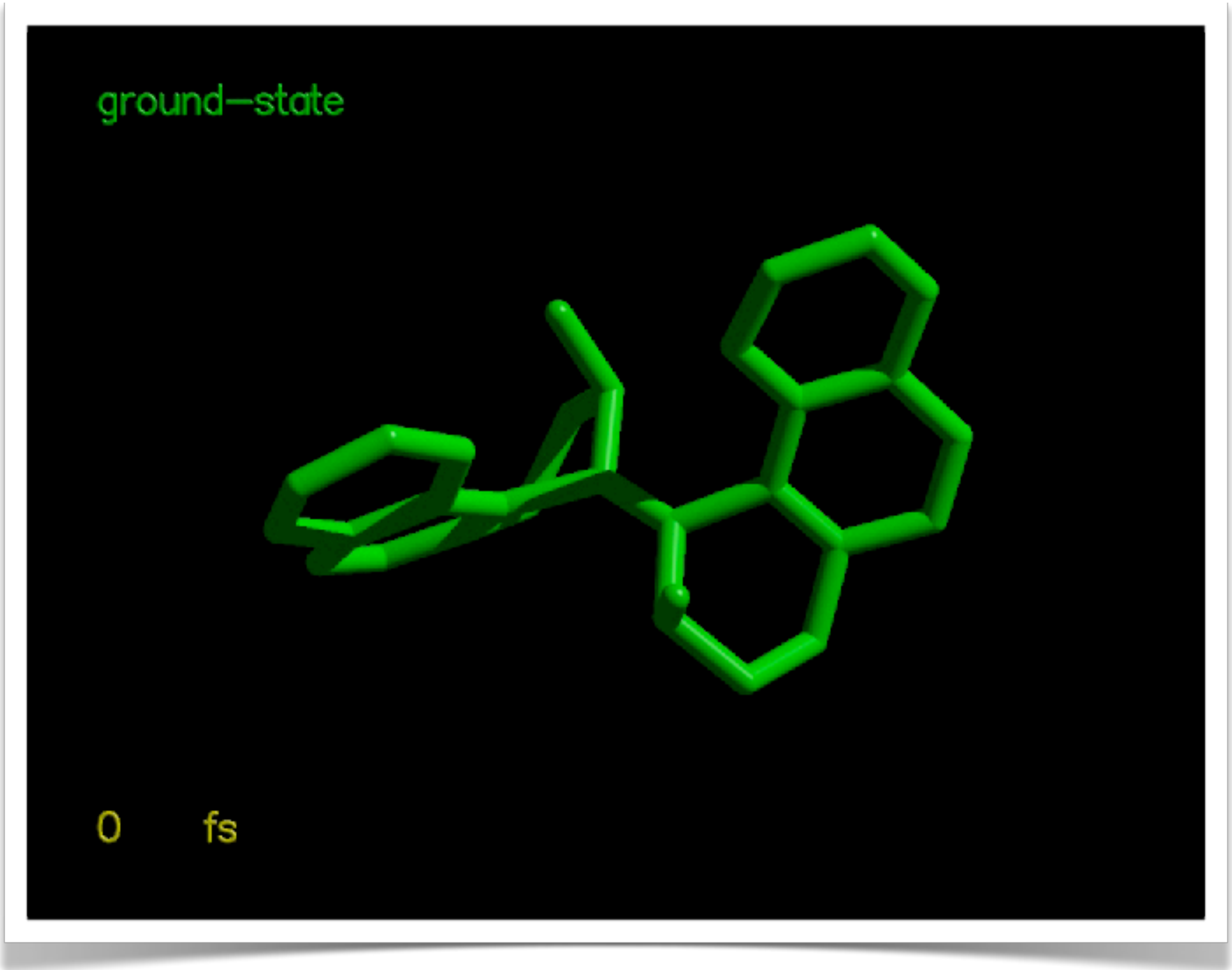


improve isomerization quantum yield (towards 100%)

Observe while it happens: molecular motors

catching the photo-isomerizations in the act

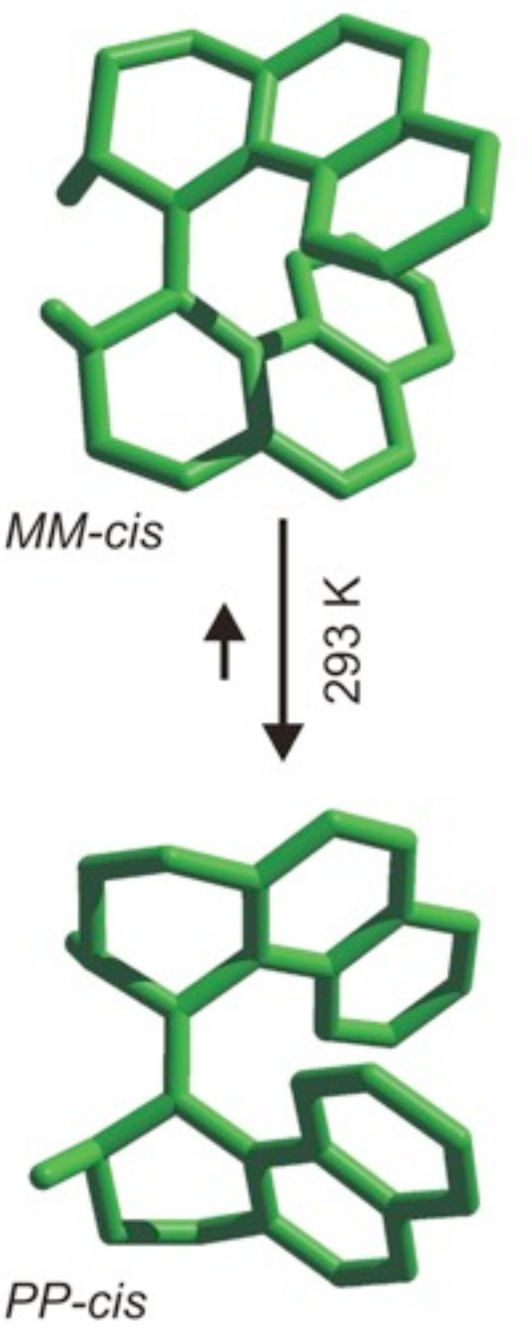




improve isomerization quantum yield (towards 100%)

Observe while it happens: molecular motors

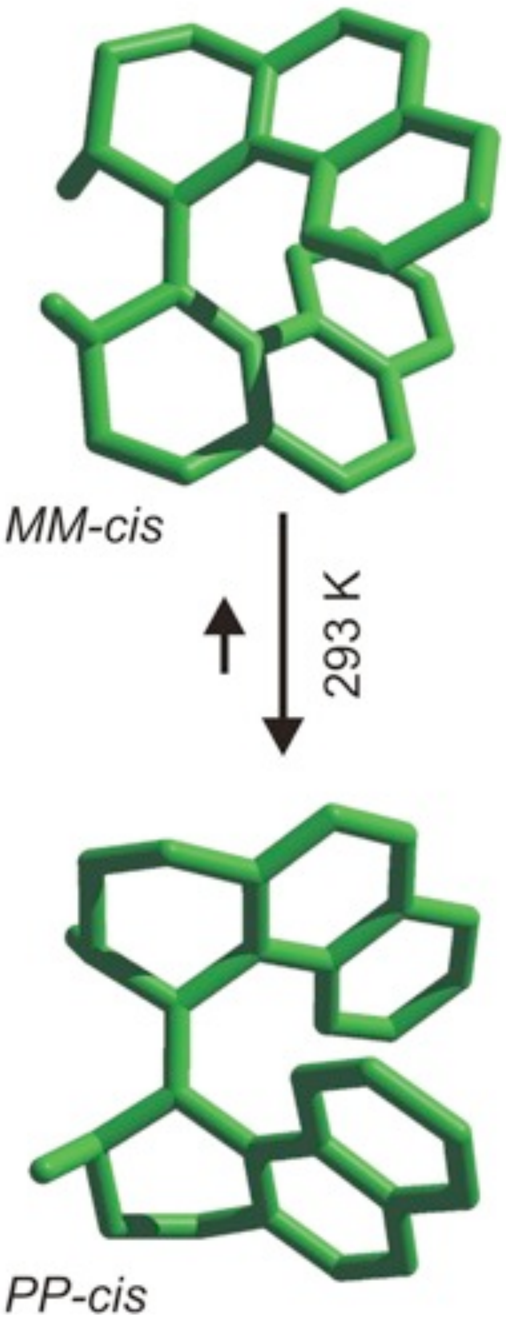
starting dynamics from S_0 transition states

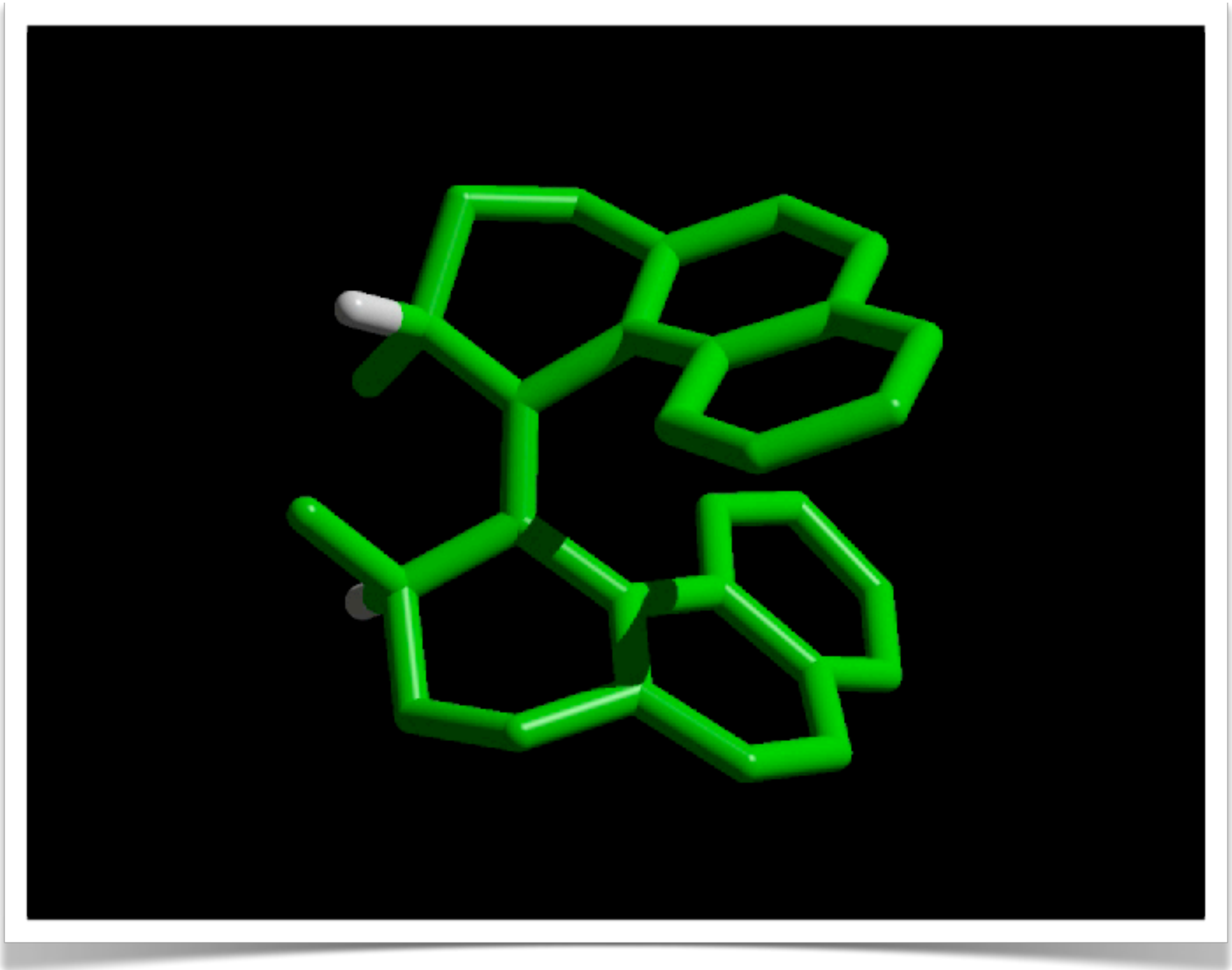


improve overall rate (into picosecond regime)

Observe while it happens: molecular motors

starting dynamics from S_0 transition states





improve overall rate (into picosecond regime)

Get inspired by nature

e.g. photo-isomerization in photoactive yellow protein

learn & mimic the effect of the protein environment

Get inspired by nature

e.g. photo-isomerization in photoactive yellow protein

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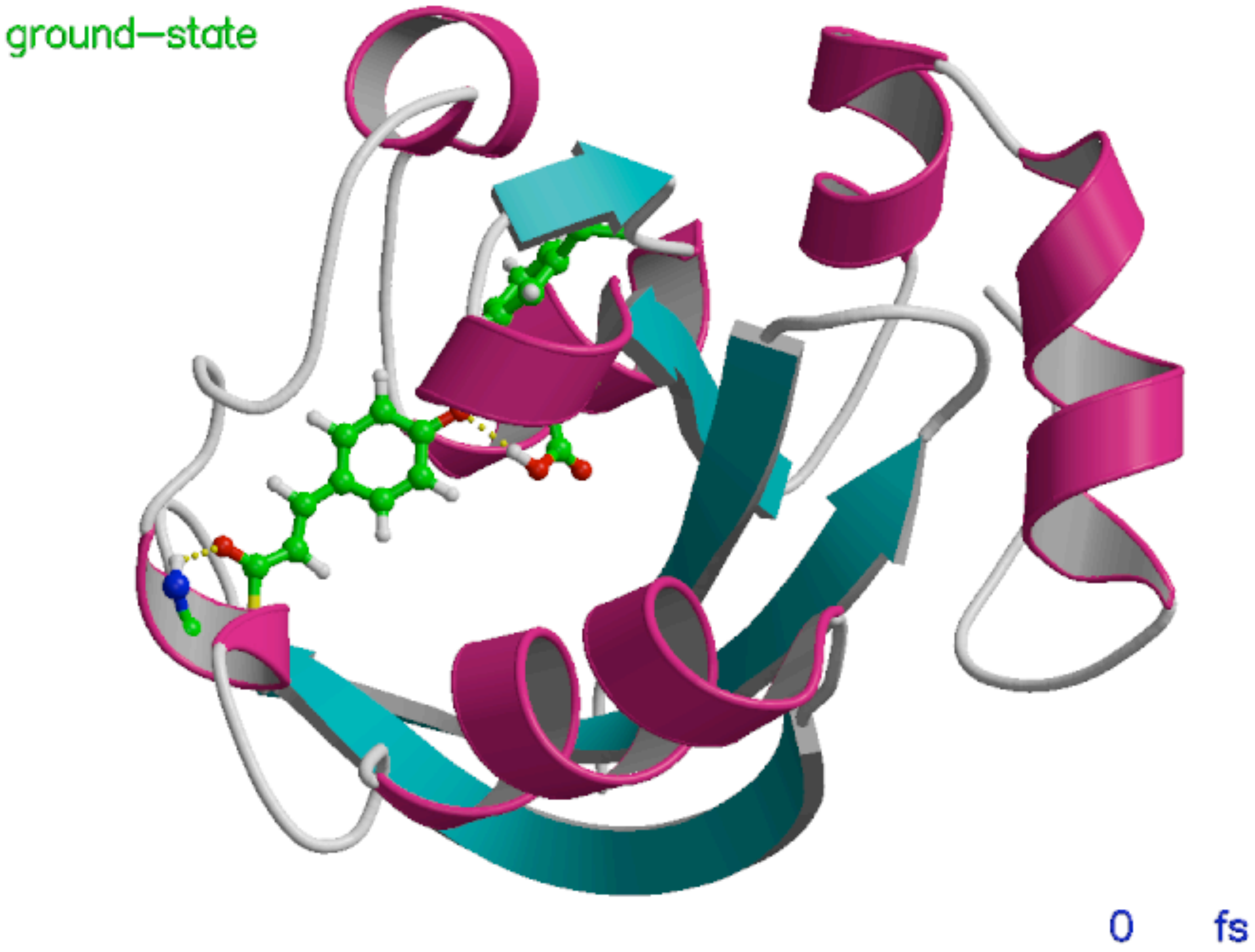
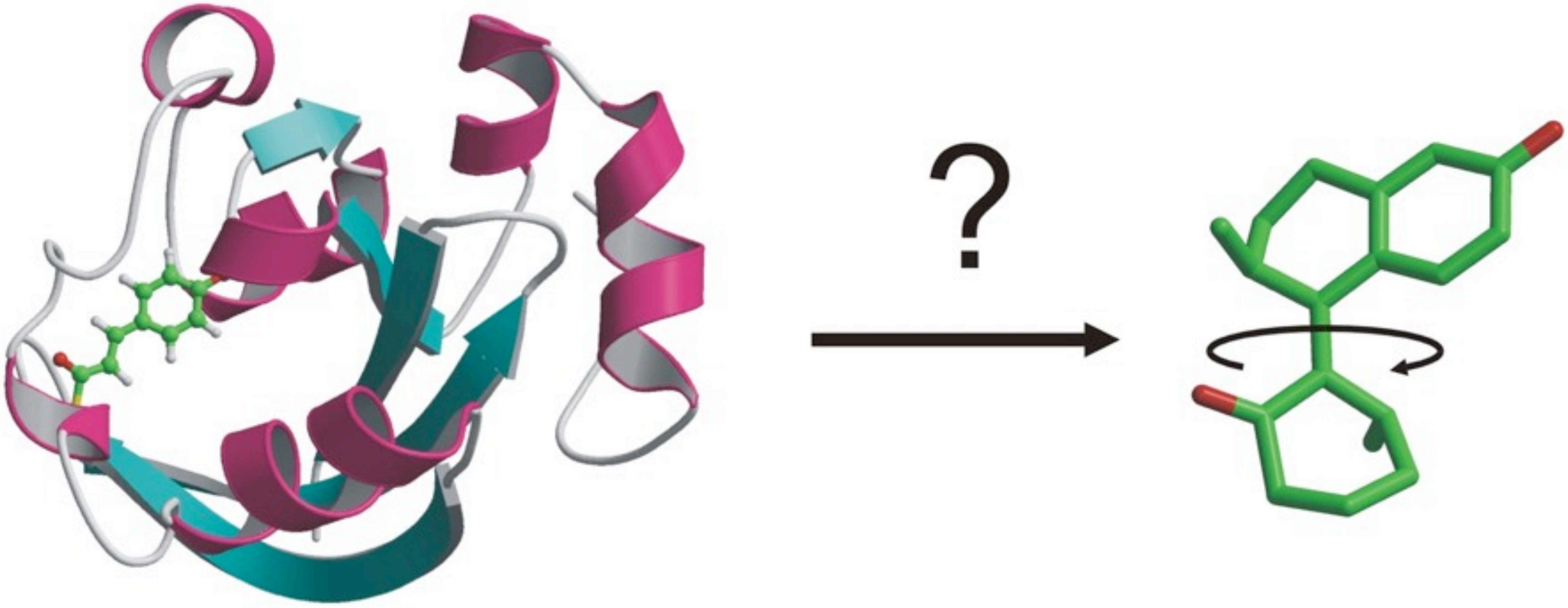


Get inspired by nature

photo-isomerization in photoactive yellow protein

learn & mimic the effect of the protein environment



however....

still too complex, even in our simulations

Menu

Starters Theory

- Born-Oppenheimer approximation
- conical intersections

Mains Non-adiabatic simulations

- surface hopping
- potential energy surfaces

Desert recent application

- role of non-adiabatic dynamics in Excitation Energy Transfer (EET)

all dishes served with examples!!!

Born-Oppenheimer Approximation

- central to chemistry
- separation slow (nuclear) and fast (electronic) motion
  - light electrons: QM (HF, DFT, ...), classical (MM)
  - heavy nuclei: QM (wavepacket/grid), classical (MD)
- crux: nuclei move on single electronic PES
  - large energy gap between electronic states
- derivation of Born-Oppenheimer
  - terms couple nuclear motion on different electronic PES
- break down of Born-Oppenheimer approximation
  - small energy gap between electronic states
    - near surface crossings (degeneracies)
    - radiationless transition
- adiabatic and diabatic electronic states

Born-Oppenheimer Approximation

molecular Schrödinger equation

$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi \qquad H\Psi = E\Psi$$

molecular Hamilton operator

$$H = T_N + T_e + U(\mathbf{r},\mathbf{R})$$

with

$$T_N = -\frac{1}{2}\sum_{i}^{N_N}\frac{\hbar^2}{M_i}\nabla^2_{\mathbf{R}}$$

$$T_e = -\frac{\hbar^2}{2m_e}\sum_{i}^{n_e}\nabla^2_{\mathbf{r}}$$

$$U(\mathbf{r},\mathbf{R}) = \frac{e^2}{4\pi\epsilon_0}\left(\sum_{I}^{N_N}\sum_{J>I}^{N_N}\frac{Z_I Z_J}{|\mathbf{R}_A-\mathbf{R}_B|} - \sum_{I}^{N_N}\sum_{k}^{n_e}\frac{Z_I}{|\mathbf{r}_k-\mathbf{R}_B|} + \sum_{j}^{n_e}\sum_{k>j}^{n_e}\frac{1}{|\mathbf{r}_k-\mathbf{r}_j|}\right)$$

Born-Oppenheimer Approximation

molecular Hamilton operator

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R})$$

step 1: clamped nuclei

separation of fast and slow degrees of freedom

$$T_N = 0$$

always possible, not an approximation!

wrong choice: strong coupling between ‘fast’ and ‘slow’ motions

consider only electronic degrees of freedom

$$H^e = T_e + U(\mathbf{r}, \mathbf{R})$$

electronic Schrödinger equation in field of fixed nuclei

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

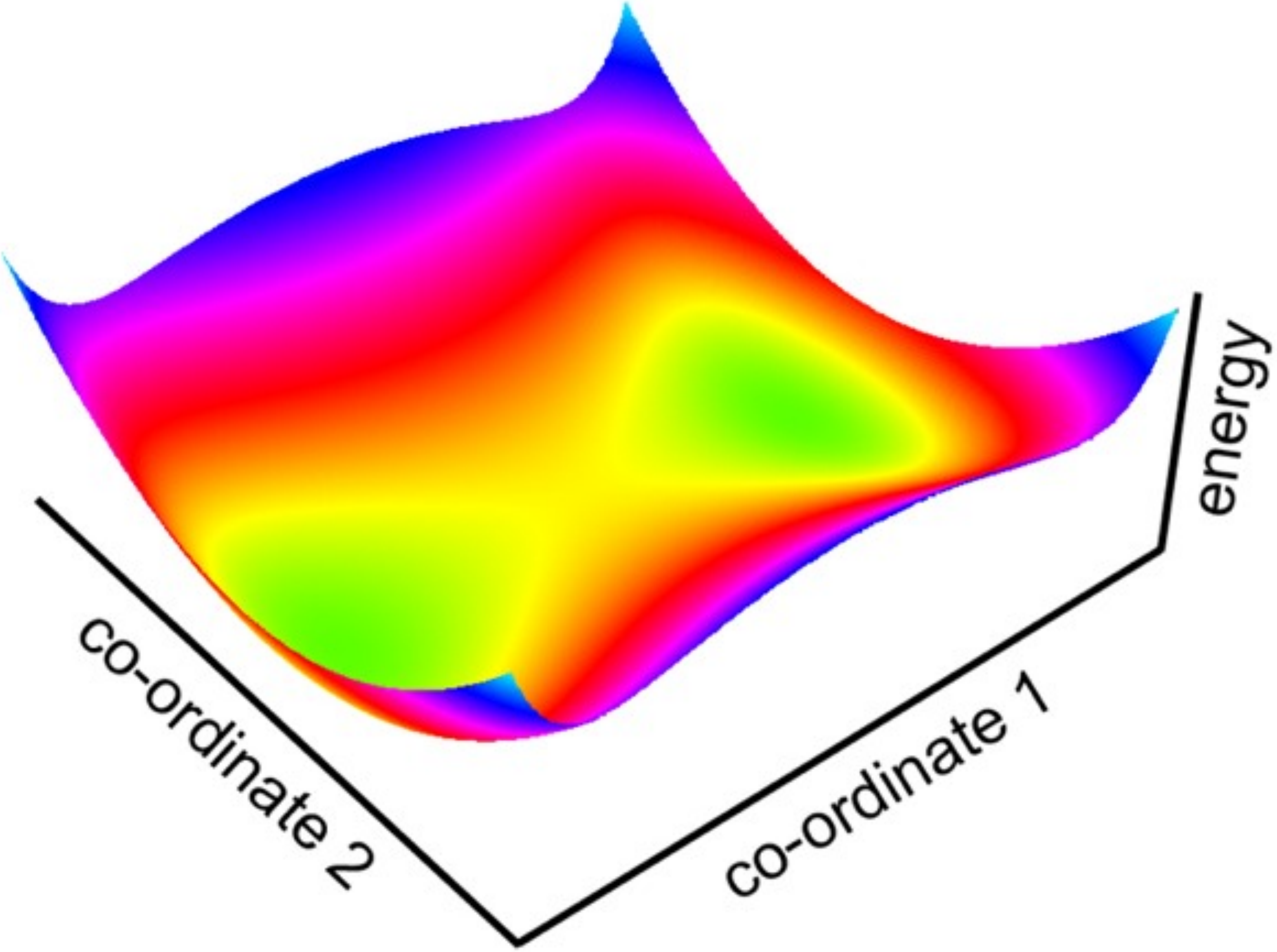
$i \geq 1$: CI, SA-CASSCF, MRCI

Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

electronic potential energy surface (PES)



Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

diagonalize electronic Hamiltonian

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

solution form orthogonal basis (or can be made so)

adiabatic electronic states

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i(\mathbf{r};\mathbf{R})^* \psi_j(\mathbf{r};\mathbf{R}) d\mathbf{r} = \delta_{ij}$$

Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

diagonalize electronic Hamiltonian

$$H^e\psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

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$$\langle\psi_i|\psi_j\rangle = \int_{-\infty}^{\infty}\psi_i(\mathbf{r};\mathbf{R})^*\psi_j(\mathbf{r};\mathbf{R})d\mathbf{r} = \delta_{ij}$$

Born representation: expansion in electronic basis

expansion coefficients are nuclear wavefunctions

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_j \chi_j(\mathbf{R})\psi_j(\mathbf{r};\mathbf{R}),$$

no approximations so far!

Born-Oppenheimer Approximation

molecular wavefunction in Born representation

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_j \chi_j(\mathbf{R})\psi_j(\mathbf{r};\mathbf{R}),$$

$$H^e\psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

molecular hamiltonian

$$H = T_N + T_e + U(\mathbf{r},\mathbf{R}) = T_N + H^e(\mathbf{R})$$

substitute and multiply from left by $\langle\psi_i|$ and integrate

$$\sum_j \langle\psi_i|H|\psi_j\rangle\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\sum_j\langle\psi_i|\psi_j\rangle\chi_j(\mathbf{R})$$

Born-Oppenheimer Approximation

substitute and multiply from left by $\langle\psi_i|$ and integrate

$$\sum_j \langle\psi_i|H|\psi_j\rangle\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\sum_j \langle\psi_i|\psi_j\rangle\chi_j(\mathbf{R})$$

using short-hand notation

$$\begin{aligned} H_{ij}(\mathbf{R}) &= \langle\psi_i(\mathbf{r};\mathbf{R})|H|\psi_j(\mathbf{r};\mathbf{R})\rangle \\ &= \boxed{\langle\psi_i(\mathbf{r};\mathbf{R})|T_N|\psi_j(\mathbf{r};\mathbf{R})\rangle} + V_i(\mathbf{R})\delta_{ij} \end{aligned}$$

coupled differential equations

$$\sum_j H_{ij}(\mathbf{R})\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

Born-Oppenheimer Approximation

elements of nuclear kinetic energy matrix

$$\begin{aligned}
\langle\psi_i|T_N|\psi_j\rangle &= \frac{-\hbar^2}{2M_k}\langle\psi_i|\nabla^2_{\mathbf{R}}|\psi_j\rangle \\
&= \frac{-\hbar^2}{2M_k}\left(\langle\psi_i|\nabla_{\mathbf{R}}\cdot\underline{\nabla_{\mathbf{R}}|\psi_j\rangle}\right) \\
&= \frac{-\hbar^2}{2M_k}\left(\underline{\langle\psi_i|\nabla_{\mathbf{R}}|\,\underline{[\nabla_{\mathbf{R}}\psi_j]\rangle}} + \underline{\langle\psi_i|\nabla_{\mathbf{R}}|\psi_j\rangle\underline{\nabla_{\mathbf{R}}}}\right) \\
&= \frac{-\hbar^2}{2M_k}\Big(\langle\psi_i|\,\underline{[\,\nabla^2_{\mathbf{R}}\psi_j]\rangle} + \langle\psi_i|\,\underline{[\nabla_{\mathbf{R}}\psi_j]\rangle\nabla_{\mathbf{R}}}+ \\
&\qquad \langle\psi_i|\,\underline{[\nabla_{\mathbf{R}}\psi_j]\rangle\nabla_{\mathbf{R}}} + \underline{\langle\psi_i|\psi_j\rangle\nabla^2_{\mathbf{R}}\Big)} \\
&= \frac{-\hbar^2}{2M_k}\left(\langle\psi_i|\,[\,\nabla^2_{\mathbf{R}}\psi_j]\rangle + 2\langle\psi_i|\,[\nabla_{\mathbf{R}}\psi_j]\rangle\nabla_{\mathbf{R}} + \langle\psi_i|\psi_j\rangle\nabla^2_{\mathbf{R}}\right) \\
&= \frac{-\hbar^2}{2M_k}\left(G_{ij} + 2\mathbf{F}\nabla_{\mathbf{R}}\right) + T_N \\
&= T_N\delta_{ij} - \Lambda_{ij}
\end{aligned}$$

Born-Oppenheimer Approximation

substitute and multiply from left by $\langle\psi_i|$ and integrate

$$\sum_j H_{ij}(\mathbf{R})\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

collect all couplings in special operator

$$H_{ij}(\mathbf{R}) = [T_N + V_i(\mathbf{R})]\,\delta_{ij} - \Lambda_{ij}$$

coupled equations

coupling between nuclear wavepackets on different electronic PES

coupling due to nuclear kinetic energy operator operating on electrons

kind of resonance with energy exchange

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

Born-Oppenheimer Approximation

coupled equations

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

non-adiabatic coupling operator matrix elements

$$\Lambda_{ij}(\mathbf{R}) = \sum_k \frac{\hbar^2}{\boxed{2M_k}}\left[2\mathbf{F}_{ij}^k(\mathbf{R})\nabla_{\mathbf{R}_k} + G_{ij}^k(\mathbf{R})\right]$$

with elements

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \langle\psi_i(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}_k}\psi_j(\mathbf{r};\mathbf{R})\rangle$$ non-adiabatic coupling vector

$$G_{ij}^k(\mathbf{R}) = \langle\psi_i(\mathbf{r};\mathbf{R})|\nabla^2_{\mathbf{R}_k}\psi_j(\mathbf{r};\mathbf{R})\rangle$$ scalar coupling

inversely proportional to nuclear mass!

small terms due to mass difference, but...

Born-Oppenheimer Approximation

non-adiabatic coupling vector

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} \psi_j(\mathbf{r};\mathbf{R}) \rangle$$

using the following relation

$$\nabla_{\mathbf{R}} H^e(\mathbf{r};\mathbf{R}) \psi_j(\mathbf{r};\mathbf{R}) = \nabla_{\mathbf{R}} V_j(\mathbf{R}) \psi_j(\mathbf{r};\mathbf{R})$$

and some lines of algebra to show that

Hellman-Feynmann term

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r};\mathbf{R}) \rangle}{V_j - V_i}$$

... coupling inversely proportional to energy gap!

Born-Oppenheimer Approximation

non-adiabatic coupling matrix element

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} \psi_j(\mathbf{r};\mathbf{R}) \rangle$$

no diagonal elements

$$\mathbf{F}_{ii}^{k}(\mathbf{R}) = 0$$

because

$$\begin{aligned} \nabla_{\mathbf{R}} \langle \psi_i | \psi_i \rangle &= 0 \\ \langle \nabla_{\mathbf{R}} \psi_i | \psi \rangle + \langle \psi_i | \nabla_{\mathbf{R}} \psi_i \rangle &= 0 \\ \langle \psi_i | \nabla_{\mathbf{R}} \psi \rangle + \mathrm{c.c} &= 0 \end{aligned}$$

Born-Oppenheimer Approximation

nuclear Schrödinger in Born representation

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

coupling between nuclear wavepackets on different PES

Born-Oppenheimer approximation: $\Lambda = \Lambda_{ii}$

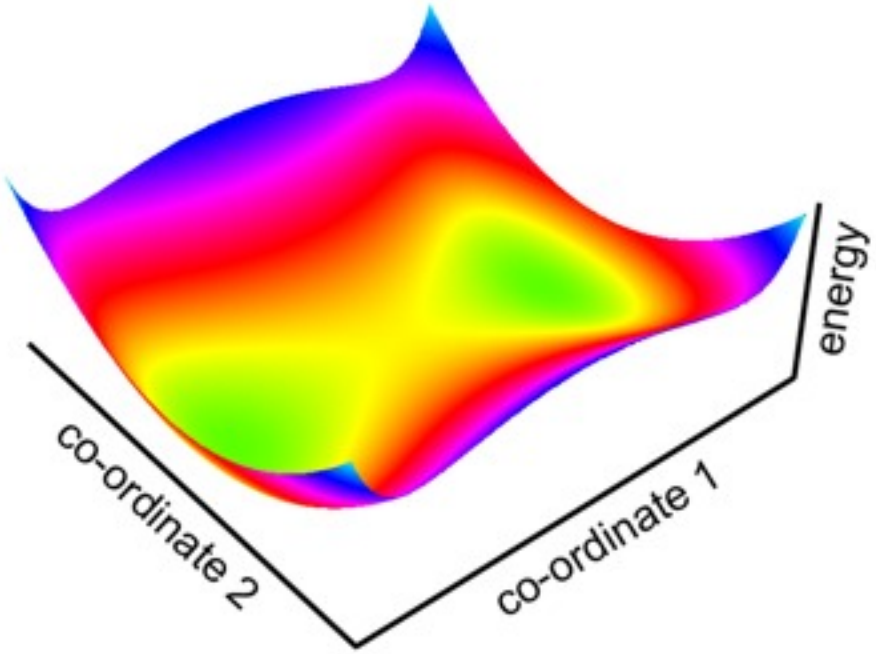
$$[T_N + V_i(\mathbf{R}) + \Lambda_{ii}]\,\chi_i(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

nuclear wavepackets restricted to single electronic PES

$$\Psi_i^{\mathrm{tot}}(\mathbf{R},\mathbf{r}) = \chi_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

adiabatic approximation: $\Lambda = 0$

$$[T_N + V_i(\mathbf{R})]\,\chi_i(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$



mostly used in quantum chemistry

Born-Oppenheimer Approximation

nuclear Schrödinger in Born representation

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_i(\mathbf{R})$$

using atomic units and scaled coordinates

$$T_N = -\frac{1}{M}\nabla^2_{\mathbf{R}}$$

$$\Lambda_{ij} = \frac{1}{2M}\left(2\mathbf{F}_{ij}\cdot\nabla_{\mathbf{R}} + G_{ij}\right))$$

$$\mathbf{F}_{ij} = \langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \qquad G_{ij} = \langle\psi_i|\nabla^2_{\mathbf{R}}\psi_j\rangle$$

Born-Oppenheimer Approximation

using atomic units and scaled coordinates

$$T_N = -\frac{1}{2M}\nabla_{\mathbf{R}}^2$$

$$\Lambda_{ij} = \frac{1}{2M}\left(2\mathbf{F}_{ij}\cdot\nabla_{\mathbf{R}} + G_{ij}\right)$$

$$\mathbf{F}_{ij} = \langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \qquad G_{ij} = \langle\psi_i|\nabla_{\mathbf{R}}^2\psi_j\rangle$$

using the relation

$$\mathbf{G} = \nabla_{\mathbf{R}}\cdot\mathbf{F} + \mathbf{F}\cdot\mathbf{F}$$

one arrives (after some frustration) at

$$\left[-\frac{1}{2M}\left(\nabla_{\mathbf{R}} + \mathbf{F}\right)^2 + \mathbf{V}\right]\chi = i\frac{\partial}{\partial t}\chi$$

Born-Oppenheimer Approximation

nuclear Schrödinger in vector notation

$$\left[\boxed{-\frac{1}{2M}\left(\nabla_{\mathbf{R}}+\mathbf{F}\right)^2}+\mathbf{V}\right]\chi = i\frac{\partial}{\partial t}\chi$$

dressed kinetic energy operator

$$\tilde{T}_N = -\frac{1}{2M}\left(\nabla_{\mathbf{R}}+\mathbf{F}\right)^2 \qquad \mathbf{F}_{ij} = \langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle$$

non local & non diagonal

couples nuclear dynamics on multiple electronic PES

induces radiationless transitions!

potential energy operator

local & diagonal

no coupling

Born-Oppenheimer Approximation

non-adiabatic coupling vector

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r};\mathbf{R}) \rangle}{V_j - V_i}$$

inversely proportional with gap!

break down of adiabatic approximation!

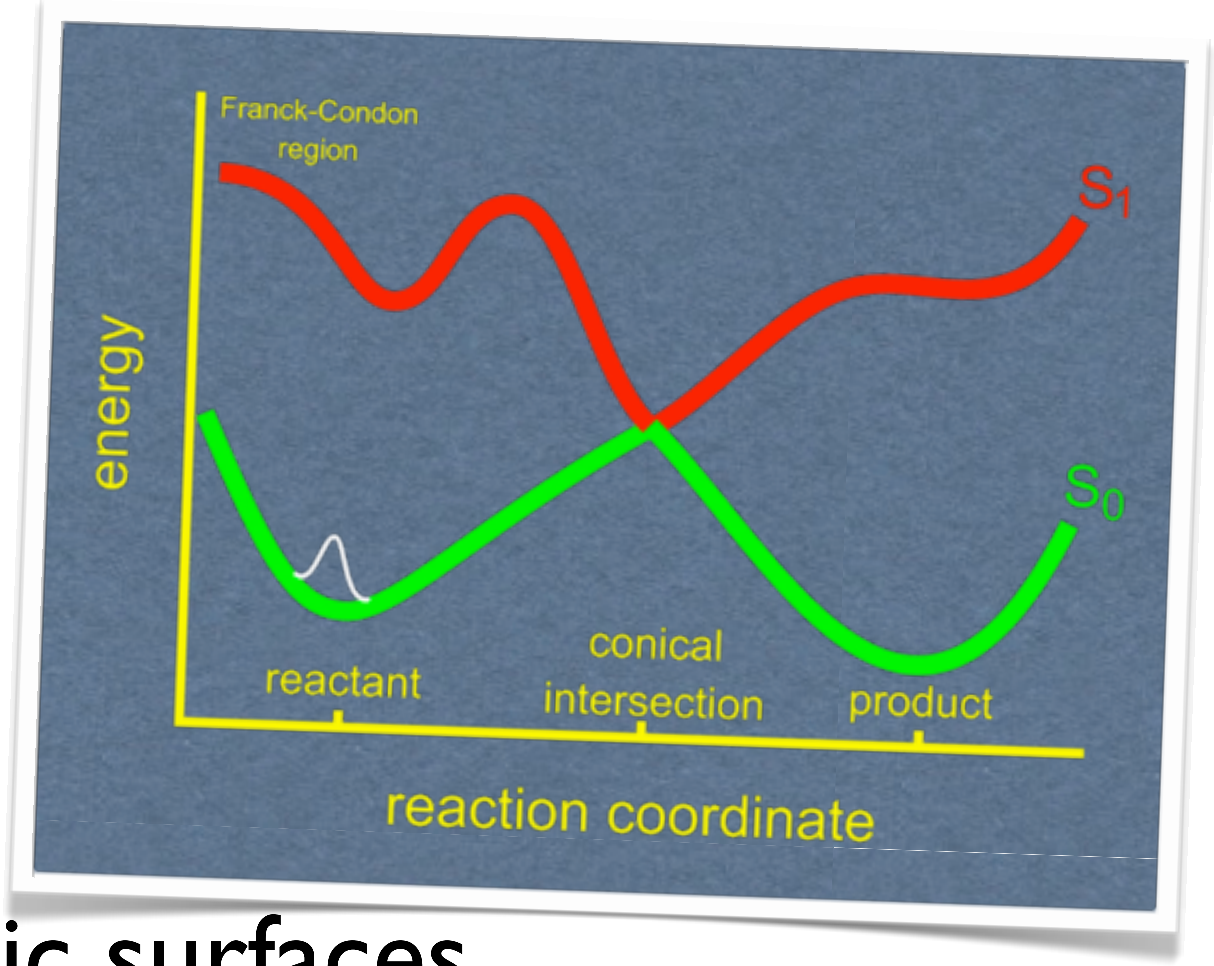
non-adiabatic dynamics

multiple surfaces

branching

interference/coherence

photochemistry



intersection between adiabatic surfaces

Born-Oppenheimer Approximation

adiabatic electronic basis

diagonal & local potential matrix

$$\langle \psi_i | H^e | \psi_j \rangle = \delta_{ij} V_j$$

non-diagonal & non-local nuclear kinetic energy matrix

$$\langle \psi_i | T_N | \psi_j \rangle = -\frac{1}{2M} \left(\nabla_{\mathbf{R}} + \boxed{\langle \psi_i | \nabla_{\mathbf{R}} | \psi_j \rangle} \right)^2$$

coupling in $\mathbf{F}$

diabatic representation

non-diagonal & local potential matrix

$$\langle \varphi_i | H^e | \varphi_j \rangle = W_{ij}$$

coupling in $\mathbf{W}$

diagonal nuclear kinetic energy matrix

$$\langle \varphi_i | T_N | \varphi_j \rangle = -\frac{\delta_{ij}}{2M} \nabla_{\mathbf{R}}^2$$

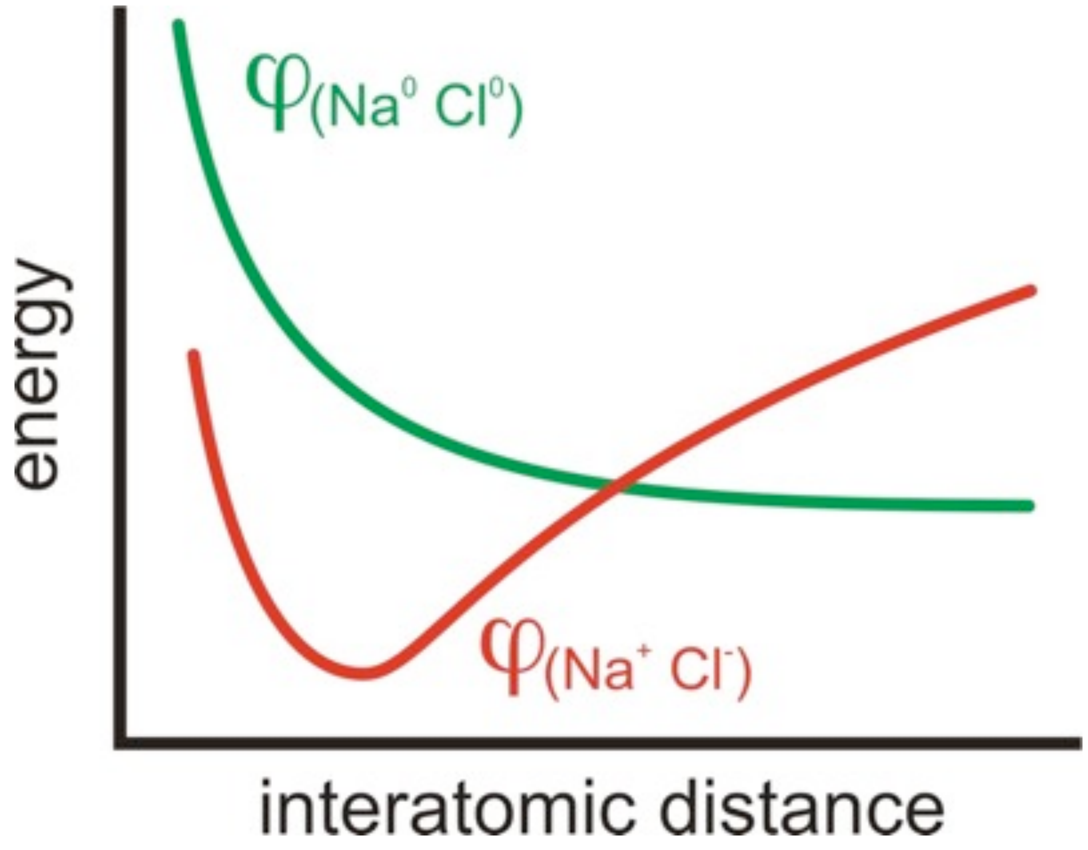
Born-Oppenheimer Approximation

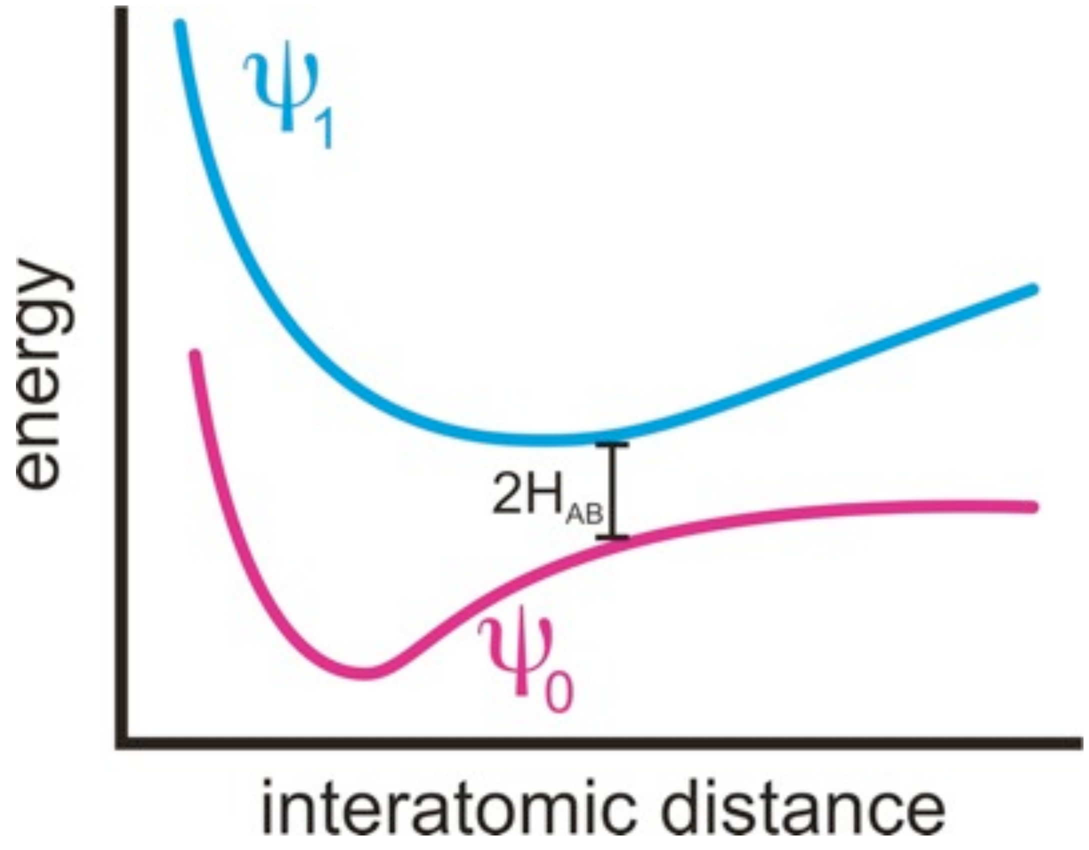
diabatic electronic basis

electronic character preserved

adiabatic electronic basis

electronic character mixed





Born-Oppenheimer Approximation

diabatic representation

non-diagonal & local potential matrix

$$\langle \varphi_i | H^e | \varphi_j \rangle = W_{ij}$$

diagonal nuclear kinetic energy matrix

$$\langle \varphi_i | T_N | \varphi_j \rangle = -\frac{\delta_{ij}}{2M} \nabla^2_{\mathbf{R}}$$

molecular Hamiltonian

$$H_{ij} = T_N \delta ij + W_{ij}$$

molecular Schrödinger equation

$$\sum_j H_{ij} \chi_j = T_N \chi_i + \sum_j W_{ij} \chi_j = i \frac{\partial}{\partial t} \chi_i$$

$$\mathbf{H} \boldsymbol{\chi} = \left[T_N \mathbf{I} + \mathbf{W}(\mathbf{R}) \right] \boldsymbol{\chi} = i \frac{\partial}{\partial t} \boldsymbol{\chi}$$

Born-Oppenheimer Approximation

construction of diabatic basis

unitary transformation for each nuclear configuration

$$\varphi_i(\mathbf{r};\mathbf{R}) = \sum_j \psi_j(\mathbf{r};\mathbf{R}) U_{ji}(\mathbf{R})$$

construction of diabatic Hamiltonian

potential matrix

$$\mathbf{W} = \mathbf{U}^T \mathbf{V} \mathbf{U}$$

kinetic energy (diagonal)

$$T_N \mathbf{I} = \mathbf{U^T} \mathbf{\tilde{T}_N} \mathbf{U}$$

Born-Oppenheimer Approximation

construction of diabatic basis

unitary transformation for each nuclear configuration

$$\varphi_i(\mathbf{r};\mathbf{R}) = \sum_j \psi_j(\mathbf{r};\mathbf{R}) U_{ji}(\mathbf{R})$$

construction of diabatic Hamiltonian

kinetic energy (diagonal)

$$T_N^d \mathbf{1} = \mathbf{U}^\dagger \tilde{\mathbf{T}}_N \mathbf{U}$$

dressed kinetic energy operator

$$\tilde{\mathbf{T}}_N = -\frac{1}{2M}\left(\nabla_{\mathbf{R}} + \mathbf{F}\right)^2 \qquad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

transformation should nullify non-adiabatic coupling

Born-Oppenheimer Approximation

construction of diabatic Hamiltonian

dressed kinetic energy operator

$$\tilde{\mathbf{T}}_N = -\frac{1}{2M}\left(\nabla_{\mathbf{R}} + \mathbf{F}\right)^2 \qquad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

transformation should nullify non-adiabatic coupling

$$\begin{aligned}
\langle \varphi_i | \nabla_{\mathbf{R}} \varphi_j \rangle &= \textstyle\sum_k \sum_l U_{ik}(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} U_{lj}(\mathbf{R}) \psi_l \rangle \\
&= \textstyle\sum_k \sum_l \left[U_{ik}(\mathbf{R} \langle \psi_k | \psi_l \rangle \nabla_{\mathbf{R}} U_{lj}(\mathbf{R}) + U_{ik}(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} | \psi_l \rangle U_{lj}(\mathbf{R}) \right] \\
&= \underline{\textstyle\sum_k U_{ik} \nabla_{\mathbf{R}} U_{kj}} + \underline{\textstyle\sum_k \sum_l U_{ik}(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} | \psi_l \rangle U_{lj}(\mathbf{R})}
\end{aligned}$$

find $\mathbf{U}$ such that

$$\underline{\mathbf{U}^{\mathbf{T}} \mathbf{F} \mathbf{U}} + \underline{\mathbf{U}^{\mathbf{T}} \nabla_{\mathbf{R}} \mathbf{U}} = \mathbf{0}$$

Born-Oppenheimer Approximation

- derivation
  - separation between fast and slow degrees of freedom
- nuclei move on single adiabatic PES
  - ignore non-adiabatic coupling
- breakdown
  - small energy gap between electronic PES
    - at intersections infinitenon-adiabatic coupling
  - nuclear displacement couple different adiabatic states
    - highly complicated nuclear wavefunction
- switch to diabatic basis
  - only electronic coupling
  - unitary transformation

Conical Intersection

- surface crossings
  - funnels for photochemical reactions
- conditions for crossing
  - adiabatic representation
    - two coordinates needed to locate intersection
    - two coordinates needed to lift degeneracy
- topology of intersection
  - double cone
  - $2N$-8 dimensional hyperline
- properties of intersection
  - Berry phase
    - singularity due to separation between electronic and nuclear motion
    - compensated by nuclear wavefunction (complicated!)

Conical Intersection

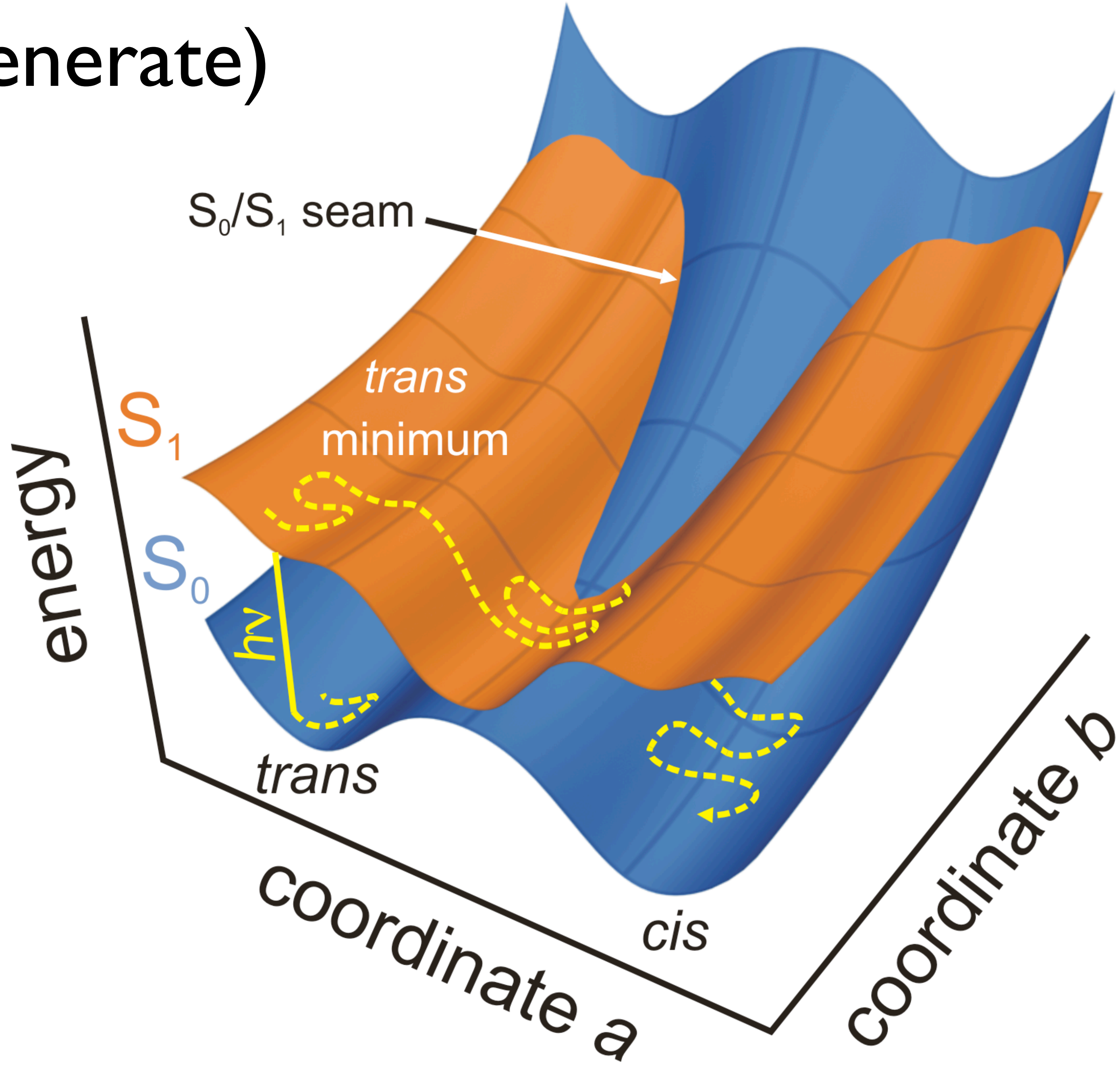
adiabatic surfaces

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

can cross (are degenerate)

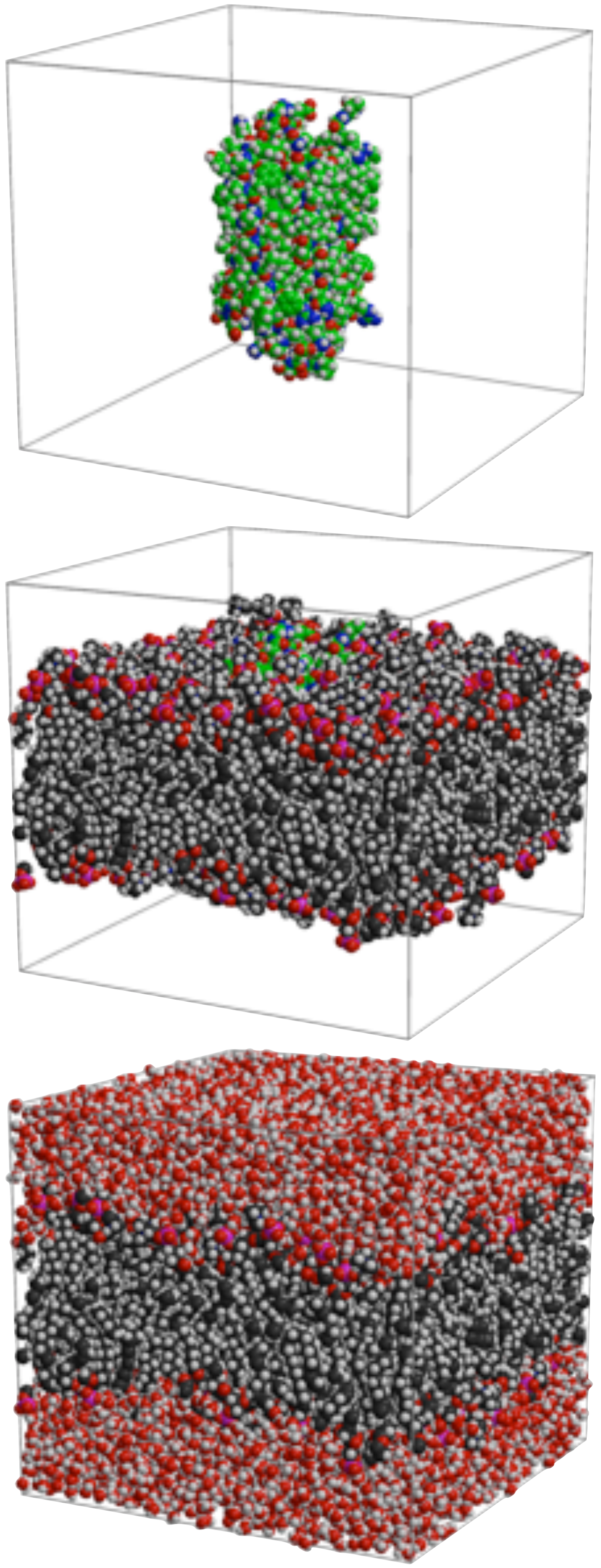
$$V_i(\mathbf{R}) = V_j(\mathbf{R})$$

radiationless decay



photoisomerization in bacteriorhodopsin

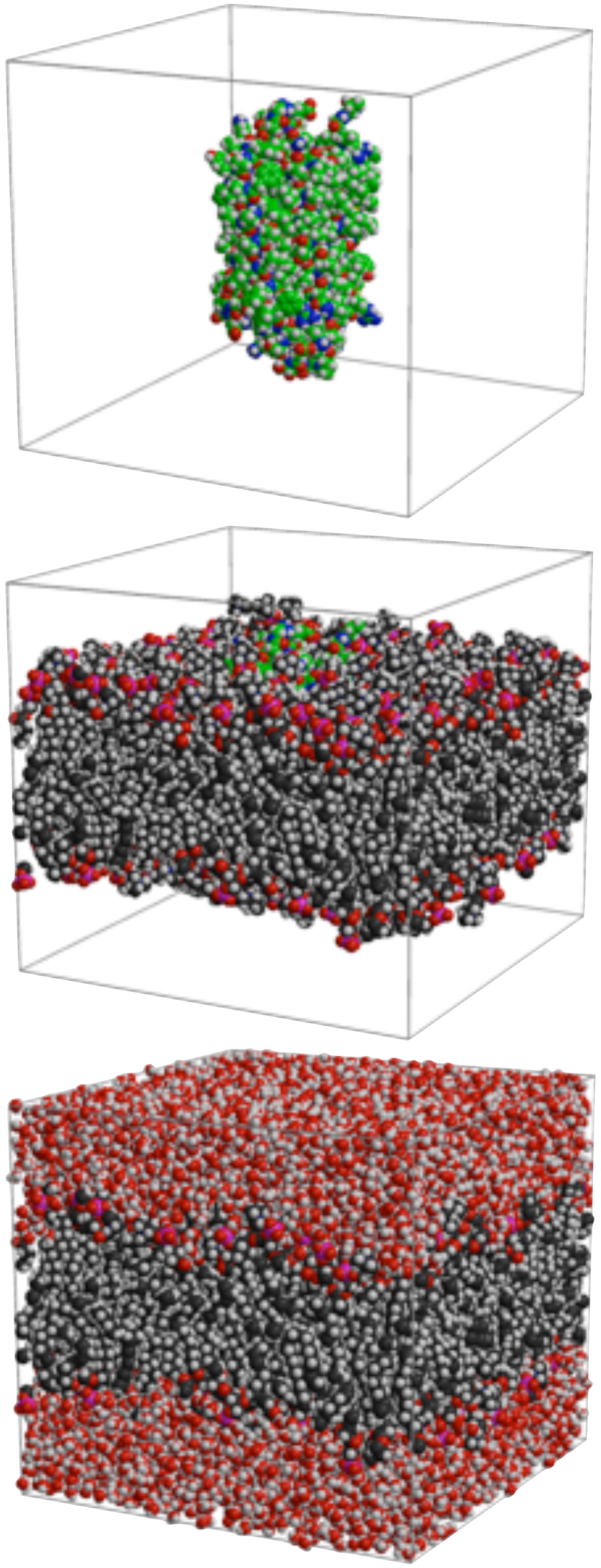
excited state decay via S_1/S_0 conical intersection

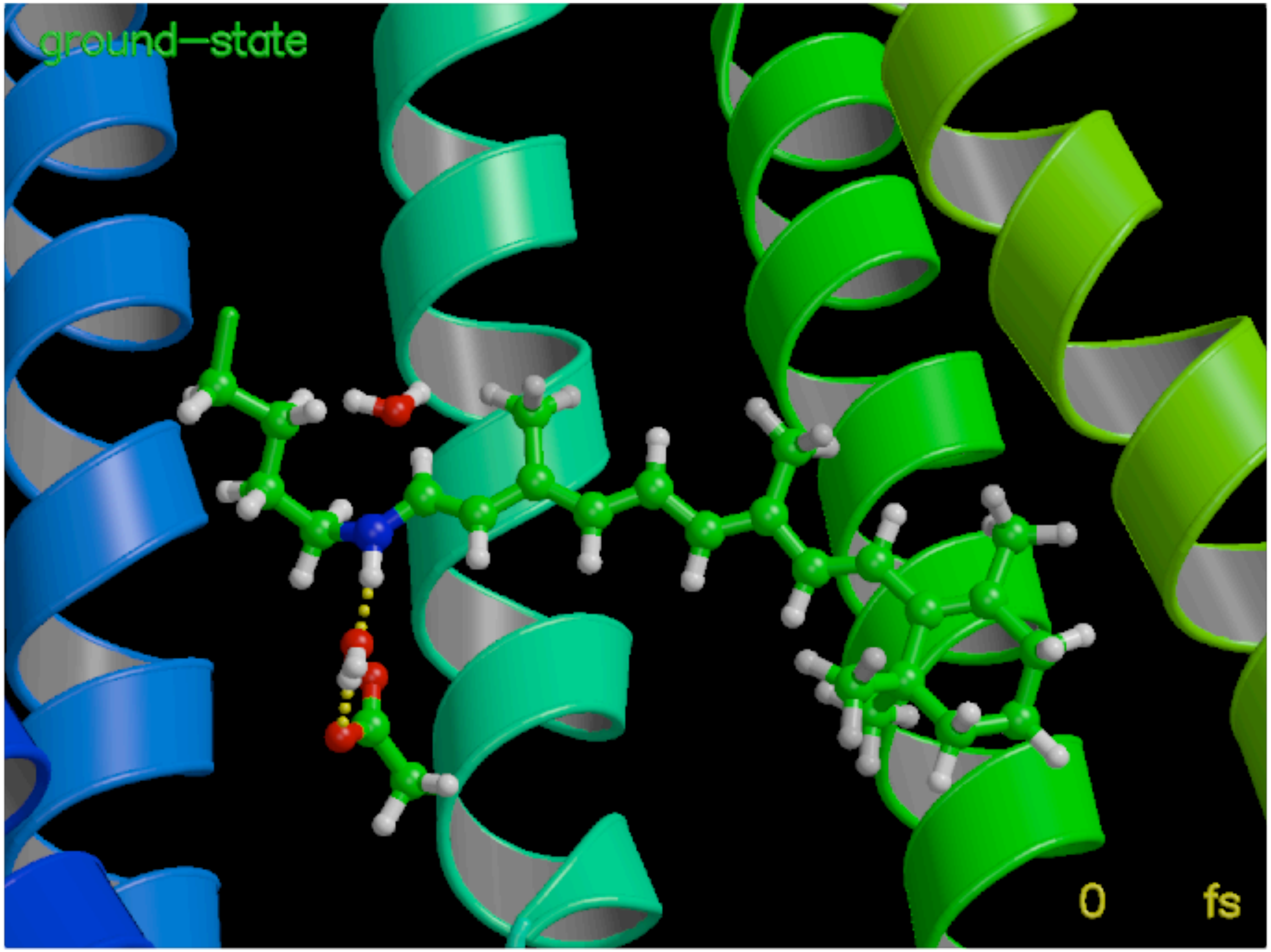


CASSCF/OPLS & diabatic hopping

photoisomerization in bacteriorhodopsin

excited state decay via S_1/S_0 conical intersection





CASSCF/OPLS & diabatic hopping

Conical Intersection

adiabatic surfaces

$$H^e\psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

can cross (are degenerate)

$$V_i(\mathbf{R}) = V_j(\mathbf{R})$$

break-down of Born-Oppenheimer

non-adiabatic coupling becomes infinite!

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \frac{\langle\psi_i(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}_k}H^e|\psi_j(\mathbf{r};\mathbf{R})\rangle}{V_j - V_i}$$

switch to diabatic basis

no non-adiabatic coupling

back to adiabatic basis by diagonalizing $\mathbf{W}$

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

$$V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

construct mixed diabatic/adiabatic basis at $\mathbf{R}_0$

via unitary transformation

$$\{\varphi_2, \varphi_1, \psi_3, ..., \psi_n\}$$

orthonormal

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} \quad \langle\varphi_I|\varphi_J\rangle = \delta_{IJ} \quad \langle\varphi_I|\psi_j\rangle = 0$$

diabatic and adiabatic energies for two lowest states

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_1(\mathbf{R}_0)$$

adiabatic wavefunctions

$$\psi_1 = c_{11}\varphi_1 + c_{12}\varphi_2 \qquad \psi_2 = c_{21}\varphi_1 + c_{22}\varphi_2$$

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

$$V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

transformation to mixed diabatic/adiabatic basis at $\mathbf{R}_0$

diabatic electronic energies

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_1(\mathbf{R}_0)$$

$$\mathbf{W}(\mathbf{R}_0) = \mathbf{V}(\mathbf{R_0})$$

$$W_{ij} = H_{ij} = \langle \varphi_i | H^e | \varphi_j \rangle$$

$$\mathbf{W}(\mathbf{R_0}) = \begin{pmatrix} H_{11}(\mathbf{R_0}) & H_{12}(\mathbf{R_0}) \\ H_{12}(\mathbf{R_0}) & H_{22}(\mathbf{R_0}) \end{pmatrix}$$

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

diabatic electronic energies

$$\mathbf{W}(\mathbf{R_0}) = \begin{pmatrix} H_{11}(\mathbf{R_0}) & H_{12}(\mathbf{R_0}) \\ H_{12}(\mathbf{R_0}) & H_{22}(\mathbf{R_0}) \end{pmatrix}$$

adiabatic electronic energies

diagonalize $\mathbf{W}$

$$V_1(\mathbf{R_0}) = \left(\frac{H_{11}+H_{22}}{2}\right) - \sqrt{\left(\frac{H_{11}-H_{22}}{2}\right)^2 + H_{12}^2}$$

$$V_2(\mathbf{R_0}) = \left(\frac{H_{11}+H_{22}}{2}\right) + \sqrt{\left(\frac{H_{11}-H_{22}}{2}\right)^2 + H_{12}^2}$$

degeneracy (crossing) if

$$H_{11} = H_{22} \wedge H_{12} = 0$$

independent: 2 coordinates required to locate degeneracy

degeneracy preserved in N-8 remaining internal coordinates

Conical Intersection

topology of intersection

expand $\mathbf{W}$ around $\mathbf{R}_0$

$$\mathbf{W}(\mathbf{R}-\mathbf{R}_0) = \mathbf{W}^{(0)} + \mathbf{W}^{(1)} + \mathbf{W}^{(2)} + \ldots$$

zeroth order term

$$\mathbf{W}^{(0)} = \frac{E_A + E_B}{2}\mathbf{1} + \begin{pmatrix} -\frac{E_B - E_A}{2} & 0 \\ 0 & \frac{E_B - E_A}{2} \end{pmatrix}$$

offset, set to zero for convenience

$$\mathbf{W}^{(0)} = \mathbf{0}$$

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}}\left(\frac{H_{11}+H_{22}}{2}\right)\cdot\Delta\mathbf{R} + \nabla_{\mathbf{R}}\left(\frac{H_{11}-H_{22}}{2}\right)\Delta\mathbf{R} & \nabla_{\mathbf{R}}H_{12}\cdot\Delta\mathbf{R} \\ \nabla_{\mathbf{R}}H_{12}\cdot\Delta\mathbf{R} & \nabla_{\mathbf{R}}\left(\frac{H_{11}+H_{22}}{2}\right)\cdot\Delta\mathbf{R} - \nabla_{\mathbf{R}}\left(\frac{H_{11}-H_{22}}{2}\right)\Delta\mathbf{R} \end{pmatrix}$$

$$\Delta\mathbf{R} = \mathbf{R}_0 - \mathbf{R}$$

Conical Intersection

topology of intersection

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}}\left(\frac{H_{11}+H_{22}}{2}\right)\cdot\Delta\mathbf{R} + \nabla_{\mathbf{R}}\left(\frac{H_{11}-H_{22}}{2}\right)\Delta\mathbf{R} & \nabla_{\mathbf{R}}H_{12}\cdot\Delta\mathbf{R} \\ \nabla_{\mathbf{R}}H_{12}\cdot\Delta\mathbf{R} & \nabla_{\mathbf{R}}\left(\frac{H_{11}+H_{22}}{2}\right)\cdot\Delta\mathbf{R} - \nabla_{\mathbf{R}}\left(\frac{H_{11}-H_{22}}{2}\right)\Delta\mathbf{R} \end{pmatrix}$$

$$\mathbf{W}^{(1)} = \begin{pmatrix} \mathbf{s}\cdot\Delta\mathbf{R} + \mathbf{g}\cdot\Delta\mathbf{R} & \mathbf{h}\cdot\Delta\mathbf{R} \\ \mathbf{h}\cdot\Delta\mathbf{R} & \mathbf{s}\cdot\boldsymbol{\Delta}\mathbf{R} - \mathbf{g}\cdot\boldsymbol{\Delta}\mathbf{R} \end{pmatrix}$$

average gradient vector

$$\mathbf{s} = \nabla_{\mathbf{R}}\frac{H_{11}+H_{22}}{2}|\mathbf{R}_0$$

gradient difference vector

$$\mathbf{g} = \nabla_{\mathbf{R}}\frac{H_{11}-H_{22}}{2}|\mathbf{R}_0$$

derivative coupling vector

$$\mathbf{h} = \nabla_{\mathbf{R}}H_{12}|\mathbf{R}_0$$

Conical Intersection

topology of intersection

keeping only terms to first order

$$\mathbf{W}(\Delta\mathbf{R}) \approx \mathbf{W}^{(0)} + \mathbf{W}^{(1)}$$

set zero$^{\text{th}}$ order term to zero (just an offset)

$$\mathbf{W}(\Delta\mathbf{R}) \approx \begin{pmatrix} \mathbf{s}\cdot\Delta\mathbf{R} + \mathbf{g}\cdot\Delta\mathbf{R} & \mathbf{h}\cdot\Delta\mathbf{R} \\ \mathbf{h}\cdot\Delta\mathbf{R} & \mathbf{s}\cdot\boldsymbol{\Delta}\mathbf{R} - \mathbf{g}\cdot\boldsymbol{\Delta}\mathbf{R} \end{pmatrix}$$

diagonalize to get adiabatic PES

$$V_1(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} - \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

$$V_2(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} + \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

Conical Intersection

topology of intersection

eigenvalues of $\mathbf{W}$

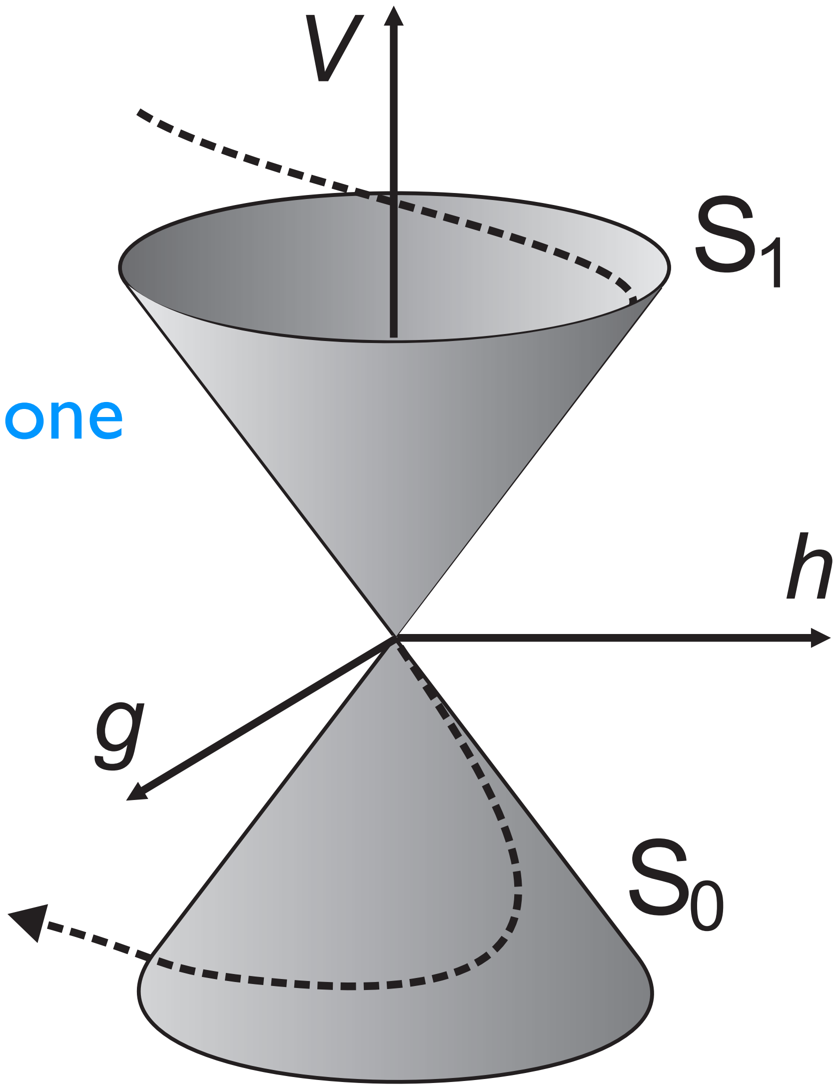
$$V_1(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} - \sqrt{(\boxed{\mathbf{g}\cdot}\Delta\mathbf{R})^2 + (\boxed{\mathbf{h}\cdot}\Delta\mathbf{R})^2}$$

$$V_2(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} + \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

double cone in branching space (g-h space)

adiabatic surfaces touch at tip

average gradient projected on g-h gives tilt of cone



Conical Intersection

back to adiabatic basis

degeneracy requires (to first order) that

$$\mathbf{g} \cdot \Delta\mathbf{R} = 0 \wedge \mathbf{h} \cdot \Delta\mathbf{R}$$

independent: accidental same-symmetry intersection

two coordinate need to change to locate intersection

single degree of freedom: non-crossing rule in diatomics

degeneracy lifted in branching space

degeneracy maintained in $3N$-8 remaining degree of freedom

Conical Intersection

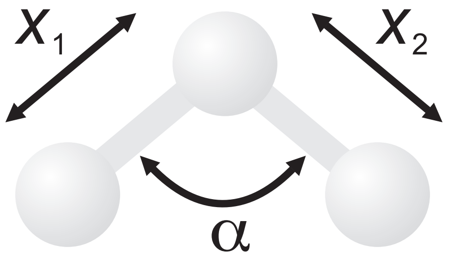
back to adiabatic basis

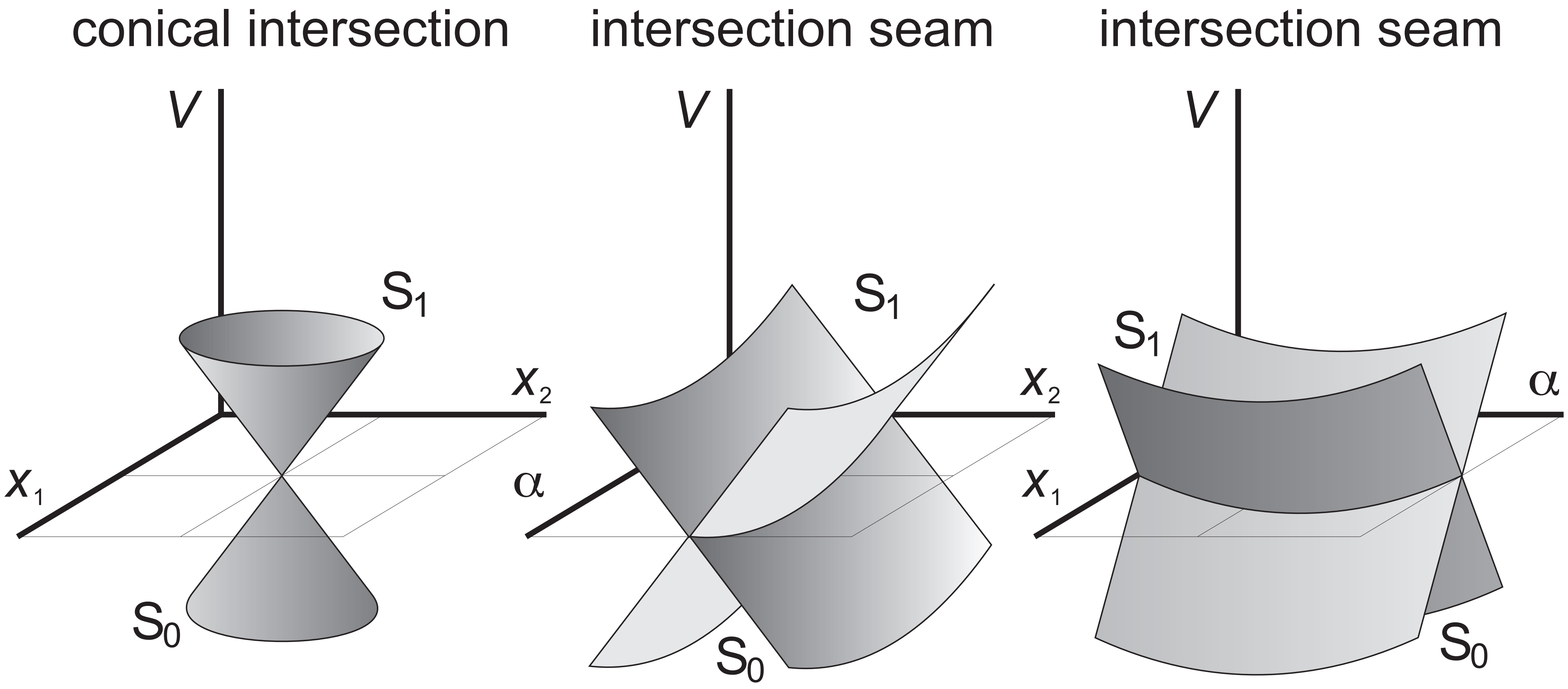
degeneracy lifted in branching space

$$\mathbf{x}_1 = \|\mathbf{g}\| \qquad \mathbf{x}_2 = \|\mathbf{h}\|$$

degeneracy maintained in $3N$-8 remaining degree of freedom

tri-atomics: hypothetical example




conical intersection

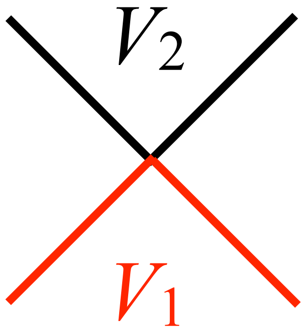
intersection seam

intersection seam

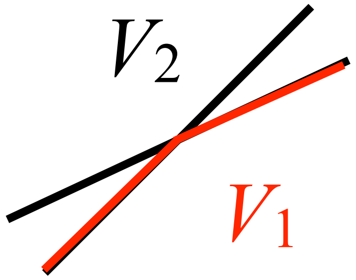
Conical Intersection

average gradient ($\mathbf{s}$)determines tilt of double cone

- peaked
  - photoreactivity
    $$\mathbf{s}\cdot\mathbf{g}\approx\mathbf{0}\quad\mathbf{s}\cdot\mathbf{h}\approx\mathbf{0}$$



- sloped
  - photostability
    $$\mathbf{s}\cdot\mathbf{g}>\mathbf{0}$$



all are $3N$-8 dimensional hyperlines

- impossible to hit
  - compare point in plane
- possible to get near
  - coupling strong enough for transition

Conical Intersection

they are everywhere!

Conical Intersection

Berry phase

adiabatic wavefunctions

$$\psi_2 = c_{21}\varphi_1 + c_{22}\varphi_2 \qquad \psi_1 = c_{11}\varphi_1 + c_{12}\varphi_2$$

small displacement in 2D branching space (diabatic basis)

$$\mathbf{x}_1 = \|\mathbf{g}\| \qquad \mathbf{x}_2 = \|\mathbf{h}\|$$

polar coordinates

$$x_2 = R\sin\theta \quad x_1 = R\cos\theta \quad R = \sqrt{x_1^2 + x_2^2}$$

assume zero tilt angle

$$W \approx \begin{pmatrix} x_1 & x_2 \\ x_2 & -x_1 \end{pmatrix} = \begin{pmatrix} R\cos\theta & R\sin\theta \\ R\sin\theta & -R\cos\theta \end{pmatrix}$$

adiabatic energies

$$V_2 = R \qquad V_1 = -R$$

adiabatic eigenfunctions

$$\psi_1 = \sin\frac{\theta}{2}\varphi_1 - \cos\frac{\theta}{2}\varphi_2 \qquad \psi_2 = -\sin\frac{\theta}{2}\varphi_1 + \cos\frac{\theta}{2}\varphi_2$$

Conical Intersection

Berry phase

adiabatic wavefunctions

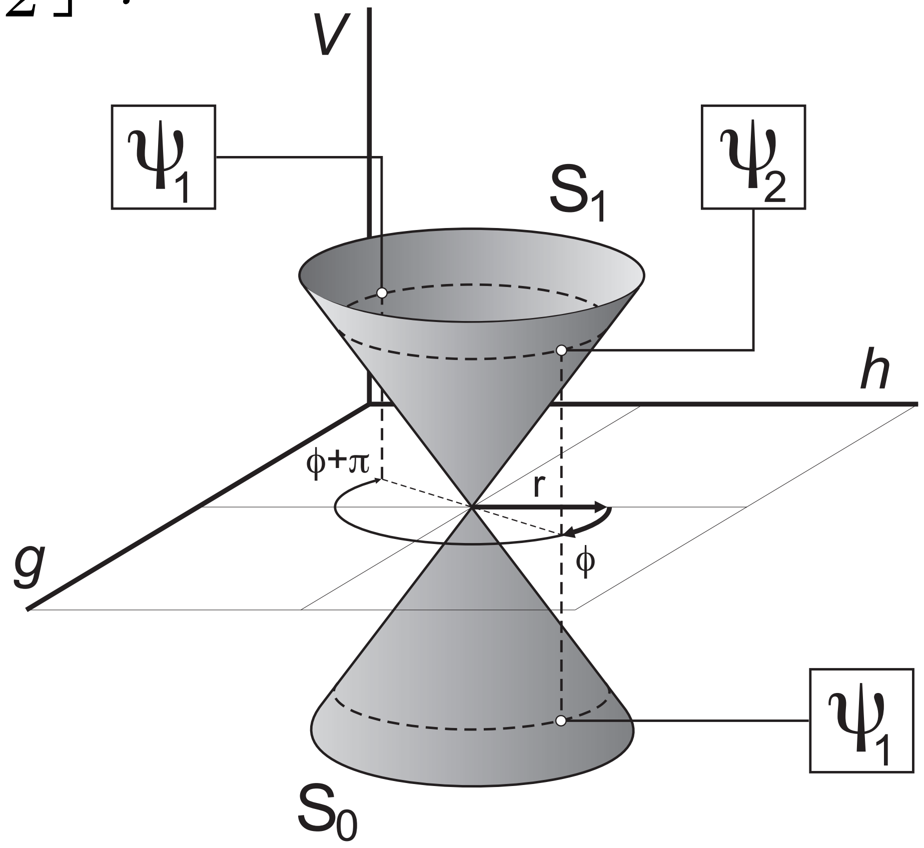
$$\psi_1 = \sin\frac{\theta}{2}\varphi_1 - \cos\frac{\theta}{2}\varphi_2 \qquad \psi_2 = -\sin\frac{\theta}{2}\varphi_1 + \cos\frac{\theta}{2}\varphi_2$$

rotate 360° around apex in branching space

$$\begin{aligned}\psi_1(\theta+2\pi) &= +\sin\left[\tfrac{\theta}{2}+\pi\right]\varphi_1 + \cos\left[\tfrac{\theta}{2}+\pi\right]\varphi_2 \\ &= -\sin\left[\tfrac{\theta}{2}\right]\varphi_1 + \cos\left[\tfrac{\theta}{2}\right]\varphi_2 \\ &= -\psi_1(\theta)\end{aligned}$$

singularity in electronic wavefunctions

separation of nuclear and electronic coordinate



Conical Intersection

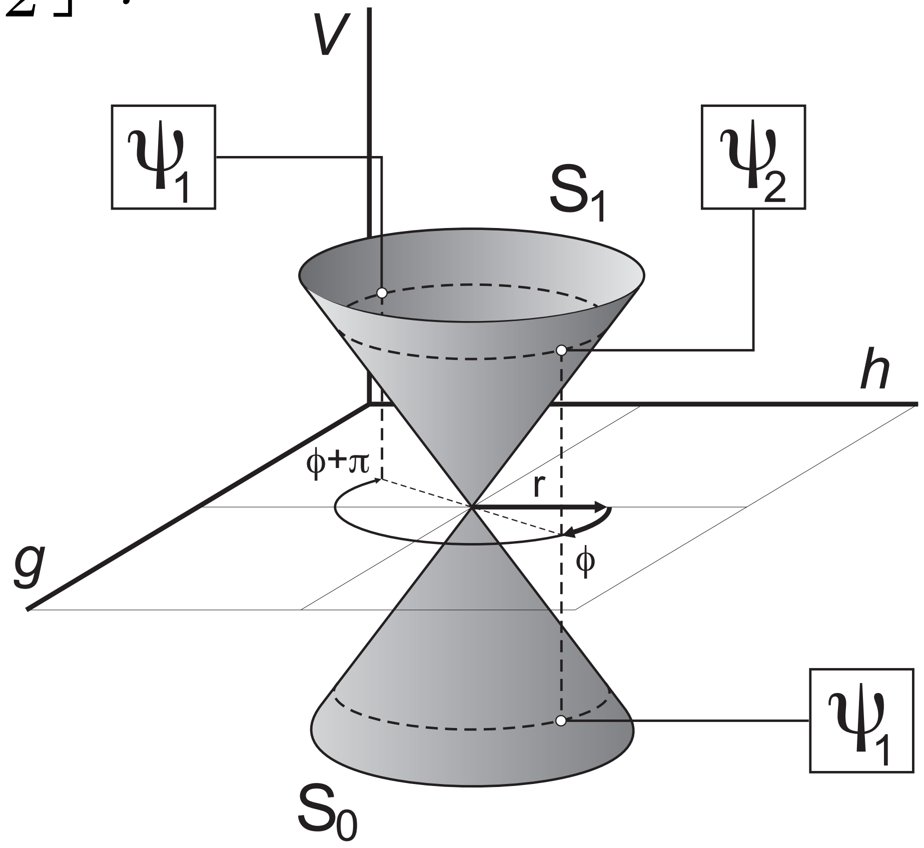
Berry phase

adiabatic wavefunctions

$$\psi_1 = \sin\frac{\theta}{2}\varphi_1 - \cos\frac{\theta}{2}\varphi_2 \qquad \psi_2 = -\sin\frac{\theta}{2}\varphi_1 + \cos\frac{\theta}{2}\varphi_2$$

rotate 360° around apex in branching space

$$\begin{aligned}\psi_2(\theta+2\pi) &= -\sin\left[\tfrac{\theta}{2}+\pi\right]\varphi_1 + \cos\left[\tfrac{\theta}{2}+\pi\right]\varphi_2\\ &= +\sin\left[\tfrac{\theta}{2}\right]\varphi_1 - \cos\left[\tfrac{\theta}{2}\right]\varphi_2\\ &= -\psi_2(\theta)\end{aligned}$$



singularity in electronic wavefunctions

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Conical Intersection

Berry phase

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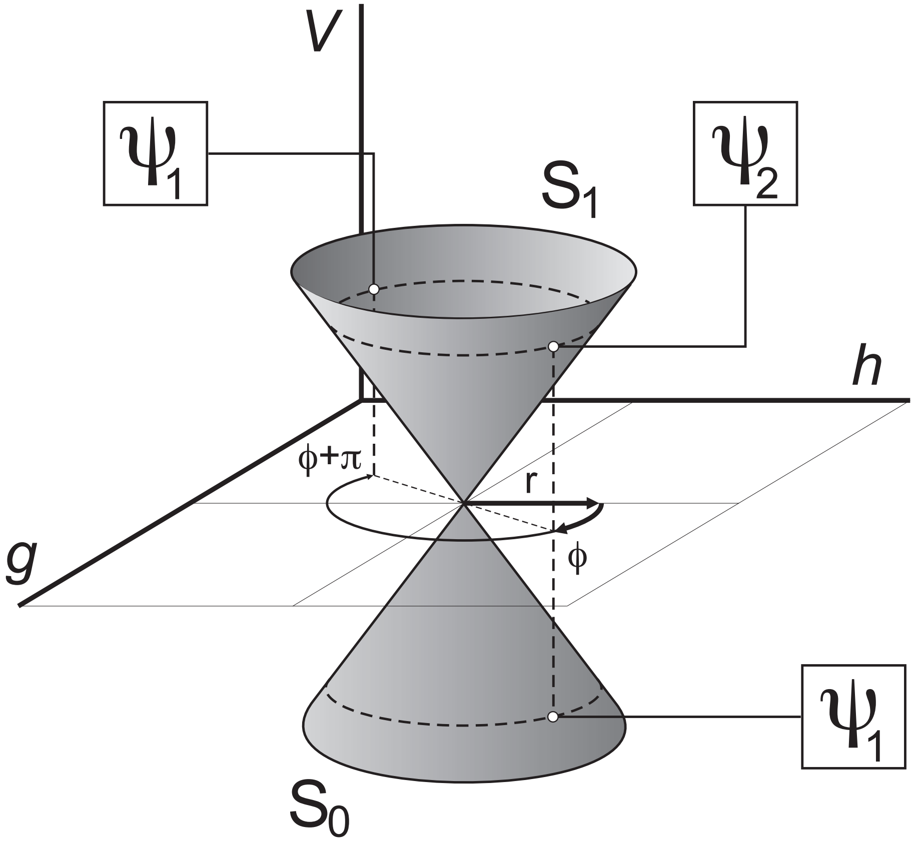
rotate 180° around apex in branching space

$$\begin{aligned}\psi_2(\theta+\pi) &= -\sin\left[\tfrac{\theta+\pi}{2}\right]\varphi_1 + \cos\left[\tfrac{\theta+\pi}{2}\right]\varphi_2 \\ &= \cos\left[\tfrac{\theta}{2}\right]\varphi_1 - \cos\left[\tfrac{\theta}{2}\right]\varphi_2 \\ &= -\psi_1(\theta)\end{aligned}$$

singularity in electronic wavefunctions

separation of nuclear and electronic coordinate



Conical Intersection

Berry phase

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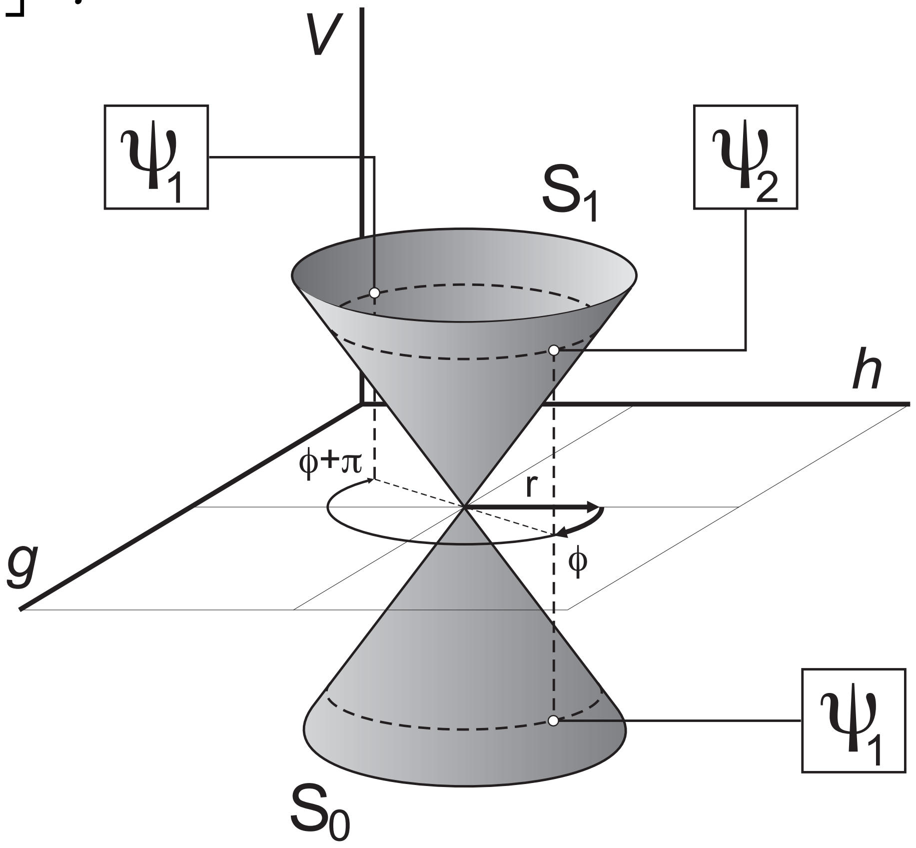

singularity in electronic wavefunctions

separation of nuclear and electronic coordinate

used for diabatic surface hopping

Conical Intersection

summary

- adiabatic states can become degenerate
  - two independent conditions
  - two coordinates to find/lift degeneracy: branching coordinates
  - degeneracy maintained in remaining degrees of freedom
- conical intersection
  - Berry phase
- modelling nuclear dynamics near conical intersection
  - non-adiabatic molecular dynamics

Non-adiabatic molecular dynamics

- incorporating electronic transitions
  - regions of non-adiabatic coupling
    - break down of Born-Oppenheimer approximation
    - conical intersections
- quantum dynamics
  - diabatic & adiabatic basis
- classical molecular dynamics with electronic transitions
  - only non-adiabatic quantum effects
    - no barrier tunneling
    - no zero-point energy

Non-adiabatic molecular dynamics

time-evolution of electrons and nuclei

Born Representation (no approximation)

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_j \chi_j(\mathbf{R})\psi_j(\mathbf{r};\mathbf{R}),$$

quantum mechanics for nuclear degrees of freedom

pre-computed potential energy surfaces

low dimensional systems: $N_{\mathrm{grid}}^{\mathrm{Dim}}$ computations

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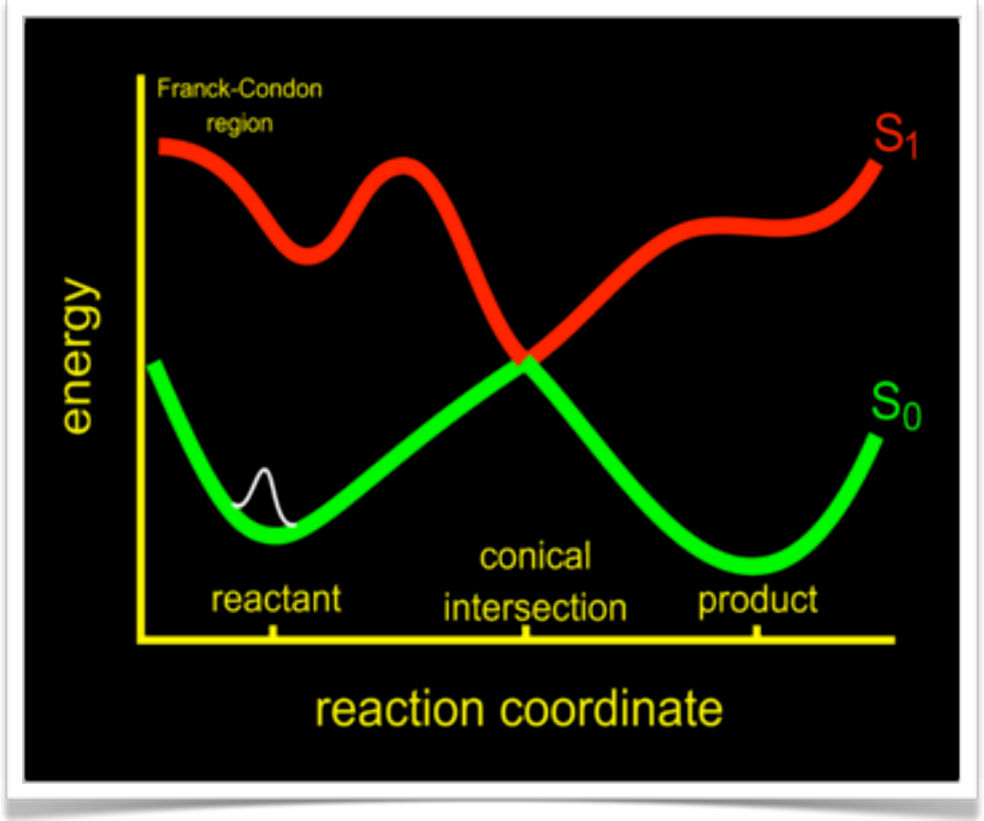


Non-adiabatic molecular dynamics

time-evolution of electrons and nuclei

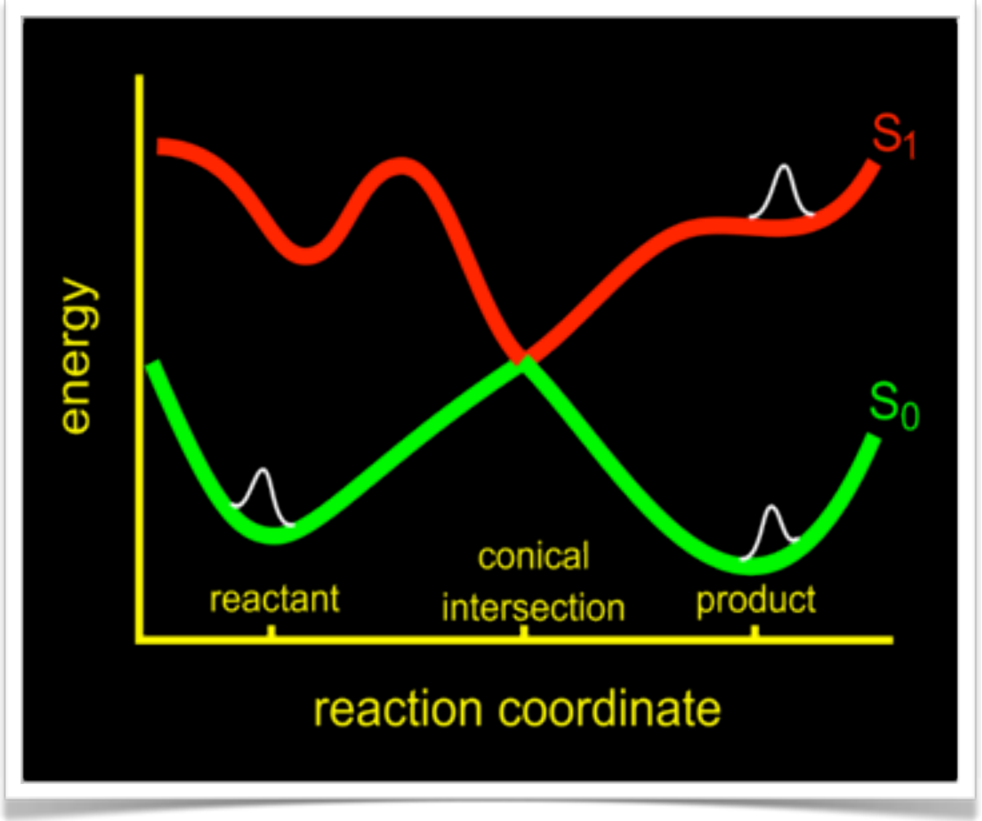
Born Representation (still correct)

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_j \chi_j(\mathbf{R})\psi_j(\mathbf{r};\mathbf{R}),$$

classical mechanics for nuclear degrees of freedom

on-the-fly: compute forces (and/or hessians) at each timestep

high dimensional systems: N_{steps}



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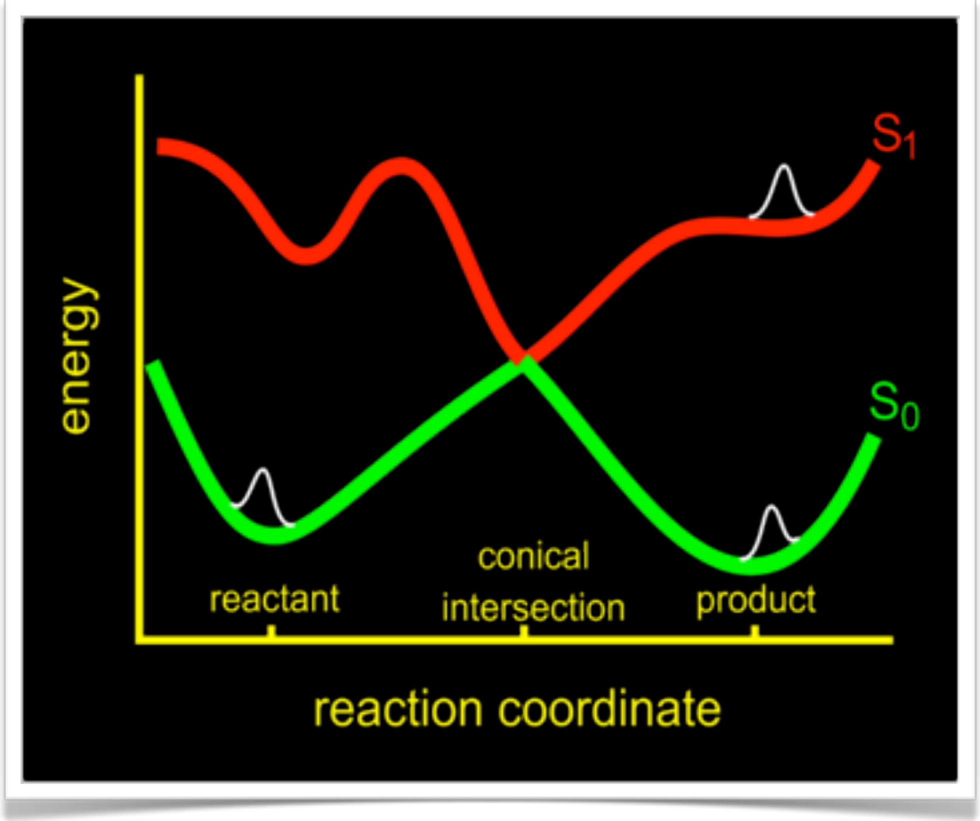
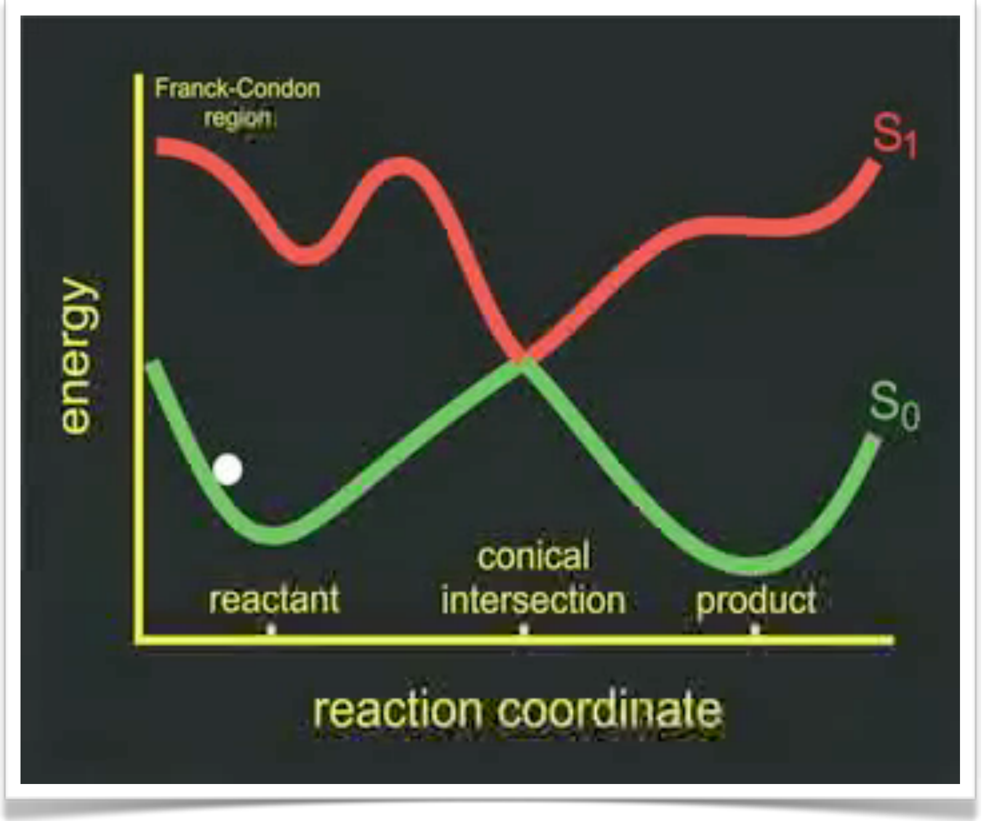




Non-adiabatic molecular dynamics

molecular dynamics with electronic transitions

- Ehrenfest dynamics
  - no detailed balance
  - incorrect asymptotic limit: mixed state
- fewest switches surface hopping (FSSH)
  - ensemble method
  - artificial coherence
  - *ad hoc* energy (& momentum) conservation
- full multiple spawning (FMS)
  - frozen gaussian wavepacket
  - centroid to evaluate forces and Hessian
  - multiple trajectories spawned
- diabatic hopping
  - approximate diabatic surfaces
  - energy & momentum conserved

Non-adiabatic molecular dynamics

Ehrenfest dynamics

time-dependent Schrödinger equation for electrons

expansion in adiabatic electronic basis

$$\phi(\mathbf{r},t;\mathbf{R}) = \sum_j c_j(t)\psi_j(\mathbf{r};\mathbf{R})$$

classical nuclei

$$\frac{\partial^2}{\partial t^2}\mathbf{R} = -\nabla_{\mathbf{R}} V^{tot}(\mathbf{R},t)$$

total energy expression

$$E = \underbrace{\langle\phi(\mathbf{r},t;\mathbf{R})|H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle}_{\text{electronic \& nuclear potential energy}} + \underbrace{\sum_i \frac{1}{2}M_i\left(\frac{\partial \mathbf{R}_i}{\partial t}\right)^2}_{\text{nuclear kinetic energy}}$$

conservation of energy

$$\frac{dE}{dt} = 0$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

conservation of energy

to derive equations of motion

$$\frac{d}{dt}\left[\langle\phi(\mathbf{r},t;\mathbf{R})|H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle+\sum_i\frac{1}{2}M_i\left(\frac{\partial\mathbf{R}_i}{\partial t}\right)^2\right]=0$$

using

$$\underline{\frac{d}{dt}=\frac{\partial}{\partial\mathbf{R}}\frac{\partial\mathbf{R}}{\partial t}}$$

to arrive at

$$\begin{aligned}\langle\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})|H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle+\langle\phi(\mathbf{r},t;\mathbf{R})|\underline{\nabla_{\mathbf{R}}H_e(\mathbf{R})}|\phi(\mathbf{r},t;\mathbf{R})\rangle\underline{\tfrac{\partial\mathbf{R}}{\partial t}}&\\ +\langle\phi(\mathbf{r},t;\mathbf{R})|H_e(\mathbf{R})|\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})\rangle+\textstyle\sum_i M_i\tfrac{\partial^2\mathbf{R}_i}{\partial t^2}\tfrac{\partial\mathbf{R}_i}{\partial t}&=0\end{aligned}$$

chain rule

Non-adiabatic molecular dynamics

Ehrenfest dynamics

conservation of energy

$$\begin{aligned}\langle \tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})|H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle + \langle \phi(\mathbf{r},t;\mathbf{R})|\nabla_{\mathbf{R}}H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle \tfrac{\partial \mathbf{R}}{\partial t} & \\ + \langle \phi(\mathbf{r},t;\mathbf{R})|H_e(\mathbf{R})|\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})\rangle + \textstyle\sum_i M_i \tfrac{\partial^2 \mathbf{R}_i}{\partial t^2}\tfrac{\partial \mathbf{R}_i}{\partial t} & = 0\end{aligned}$$

using time-dependent Schrödinger equation

$$\underline{H_e\phi = i\hbar\frac{\partial}{\partial t}\phi}$$

to arrive at

$$\begin{aligned}\underline{i\hbar}\langle \tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})|\underline{\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})\rangle} + \langle \phi(\mathbf{r},t;\mathbf{R})|\nabla_{\mathbf{R}}H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle \tfrac{\partial \mathbf{R}}{\partial t} & \\ \underbrace{-i\hbar\langle \tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})|\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})\rangle}_{\text{c.c.}} + \textstyle\sum_i M_i \tfrac{\partial^2 \mathbf{R}_i}{\partial t^2}\tfrac{\partial \mathbf{R}_i}{\partial t} & = 0\end{aligned}$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

conservation of energy

$$\begin{aligned}\cancel{i\hbar\langle \tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})|\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})\rangle} + \langle\phi(\mathbf{r},t;\mathbf{R})|\nabla_{\mathbf{R}}H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle\,\tfrac{\partial\mathbf{R}}{\partial t} & \\ \cancel{-i\hbar\langle \tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})|\tfrac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R})\rangle} + \textstyle\sum_i M_i\,\tfrac{\partial^2\mathbf{R}_i}{\partial t^2}\,\tfrac{\partial\mathbf{R}_i}{\partial t} &= 0\end{aligned}$$

$$\left[\langle\phi(\mathbf{r},t;\mathbf{R})|\nabla_{\mathbf{R}}H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle + \mathbf{M}\frac{\partial^2\mathbf{R}}{\partial t^2}\right]\frac{\partial\mathbf{R}}{\partial t} = 0$$

equations of motion

Newtonian dynamics with Hellmann-Feynman forces

$$\mathbf{M}\frac{\partial^2\mathbf{R}}{\partial t^2} = -\langle\phi(\mathbf{r},t;\mathbf{R})|\nabla_{\mathbf{R}}H_e(\mathbf{R})|\phi(\mathbf{r},t;\mathbf{R})\rangle$$

time-dependent Schrödinger equation along classical trajectory

$$i\hbar\frac{\partial}{\partial t}\phi(\mathbf{r},t;\mathbf{R}) = H^e(\mathbf{R})\phi(\mathbf{r},t;\mathbf{R})$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

equations of motion for electronic wavefunction

electronic wavefunction

$$\phi(\mathbf{r},t;\mathbf{R}) = \sum_j c_j(t)\psi_j(\mathbf{r};\mathbf{R})$$

time-dependent Schrödinger equation along classical trajectory $\mathbf{R}(t)$

$$i\hbar\frac{\partial}{\partial t}\phi(\mathbf{r},t,\mathbf{R}) = H^e(\mathbf{R})\phi(\mathbf{r},t,\mathbf{R})$$

time-dependence explicit in coefficients

$$i\hbar\frac{\partial}{\partial t}\sum_j c_j(t)\psi_j(\mathbf{r};\mathbf{R}) = H^e(\mathbf{R})\sum_j c_j(t)\psi_j(\mathbf{r};\mathbf{R})$$

multiply by adiabatic state i and integrate over electronic coordinates

$$i\hbar\sum_j \frac{\partial c_j}{\partial t}\langle\psi_i|\psi_j\rangle + i\hbar\sum_j c_j\langle\psi_i|\frac{\partial}{\partial t}\psi_j\rangle = \sum_j c_j\langle\psi_i|H^e|\psi_j\rangle$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

quantum dynamics for electrons

multiply by adiabatic state i and integrate

$$i\hbar \sum_j \frac{\partial c_j}{\partial t}\langle\psi_i|\psi_j\rangle + i\hbar \sum_j c_j \langle\psi_i|\frac{\partial}{\partial t}\psi_j\rangle = \sum_j c_j \langle\psi_i|H^e|\psi_j\rangle$$

again, use

$$\frac{d}{dt} = \frac{\partial}{\partial \mathbf{R}}\frac{\partial \mathbf{R}}{\partial t}$$

and orthogonality of adiabatic basis to arrive at

$$\frac{\partial c_i}{\partial t} = -\frac{i}{\hbar}V_i c_i(t) - \sum_j c_j(t)\langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \cdot \frac{\partial \mathbf{R}}{\partial t}$$

coupled first-order differential equations

Non-adiabatic molecular dynamics

Ehrenfest dynamics

mixed quantum/classical dynamics

time-dependent electronic wavefunction

$$\phi(\mathbf{r}, t; \mathbf{R}) = \sum_j c_j(t)\psi_j(\mathbf{r}; \mathbf{R})$$

classical nuclei

equations of motion

Newtonian dynamics with Hellmann-Feynman forces

$$\mathbf{M}\frac{\partial^2 \mathbf{R}}{\partial t^2} = -\langle \phi(\mathbf{r}, t; \mathbf{R})|\nabla_{\mathbf{R}} H_e(\mathbf{R})|\phi(\mathbf{r}, t; \mathbf{R})\rangle$$

coupled first-order differential equations

$$\frac{\partial c_i}{\partial t} = -\frac{i}{\hbar}V_i(\mathbf{R})c_i(t) - \sum_j c_j(t)\langle \psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \cdot \frac{\partial \mathbf{R}}{\partial t}$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

density matrix notation

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

populations of electronic states: diagonal

$$\rho_{kk}(t)$$

time evolution (Liouville-Von Neumann)

$$\begin{aligned}
\frac{\partial}{\partial t}\rho_{kl} &= c_l^* \frac{\partial}{\partial t} c_k + c_k \frac{\partial}{\partial t} c_l^* \\
&= -c_k c_l^* \frac{i}{\hbar} V_k - c_l^* \sum_j c_j \langle \psi_k | \nabla_{\mathbf{R}} \psi_j \rangle \cdot \frac{\partial \mathbf{R}}{\partial t} \\
&\quad + c_k c_l^* \frac{i}{\hbar} V_l - c_k \sum_j c_j^* \langle \psi_l | \nabla_{\mathbf{R}} \psi_j \rangle^* \cdot \frac{\partial \mathbf{R}}{\partial t}
\end{aligned}$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

density matrix notation

time-evolution

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{kl} &= -c_k c_l^* \frac{i}{\hbar} V_k - \sum_j c_j c_l^* \langle\psi_k|\nabla_{\mathbf{R}}\psi_j\rangle \cdot \frac{\partial \mathbf{R}}{\partial t} \\ &\quad + c_k c_l^* \frac{i}{\hbar} V_l - \sum_j c_k c_j^* \underline{\langle\psi_l|\nabla_{\mathbf{R}}\psi_j\rangle^*} \cdot \frac{\partial \mathbf{R}}{\partial t}\end{aligned}$$

adiabatic basis

$$\begin{aligned}\nabla_{\mathbf{R}}\langle\psi_l|\psi_j\rangle &= 0 \\ \langle\nabla_{\mathbf{R}}\psi_l|\psi_j\rangle + \langle\psi_l|\nabla_{\mathbf{R}}\psi_j\rangle &= 0 \\ \langle\nabla_{\mathbf{R}}\psi_l|\psi_j\rangle &= -\langle\psi_l|\nabla_{\mathbf{R}}\psi_j\rangle\end{aligned}$$

complex conjugate of non-adiabatic coupling vector

$$\begin{aligned}\underline{\langle\psi_l|\nabla_{\mathbf{R}}\psi_j\rangle}^* &= \langle\nabla_{\mathbf{R}}\psi_j|\psi_l\rangle \\ &= -\underline{\langle\psi_j|\nabla_{\mathbf{R}}\psi_l\rangle}\end{aligned}$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

density matrix notation

time-evolution

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{kl} &= -c_k c_l^* \frac{i}{\hbar} V_k - \sum_j c_j c_l^* \langle \psi_k | \nabla_{\mathbf{R}} \psi_j \rangle \cdot \frac{\partial \mathbf{R}}{\partial t} \\ &\quad + c_k c_l^* \frac{i}{\hbar} V_l \boxed{- \sum_j c_k c_j^* \underline{\langle \psi_l | \nabla_{\mathbf{R}} \psi_j \rangle}^*} \cdot \frac{\partial \mathbf{R}}{\partial t}\end{aligned}$$

using that in the adiabatic basis

$$\begin{aligned}\underline{\langle \psi_l | \nabla_{\mathbf{R}} \psi_j \rangle^*} &= \langle \nabla_{\mathbf{R}} \psi_j | \psi_l \rangle \\ &= \underline{-\langle \psi_j | \nabla_{\mathbf{R}} \psi_l \rangle}\end{aligned}$$

one arrives at

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{kl} &= -c_k c_l^* \frac{i}{\hbar} V_k - \sum_j c_j c_l^* \langle \psi_k | \nabla_{\mathbf{R}} \psi_j \rangle \cdot \frac{\partial \mathbf{R}}{\partial t} \\ &\quad + c_k c_l^* \frac{i}{\hbar} V_l \boxed{\underline{+} \sum_j c_k c_j^* \underline{\langle \psi_j | \nabla_{\mathbf{R}} \psi_l \rangle}} \cdot \frac{\partial \mathbf{R}}{\partial t}\end{aligned}$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

density matrix notation

time-evolution

$$\frac{\partial}{\partial t}\rho_{kl} \quad = \quad -c_k c_l^* \tfrac{i}{\hbar} V_k - \textstyle\sum_j c_j c_l^* \langle \psi_k | \nabla_{\mathbf{R}} \psi_j \rangle \cdot \frac{\partial \mathbf{R}}{\partial t}$$

$$+c_k c_l^* \tfrac{i}{\hbar} V_l + \textstyle\sum_j c_k c_j^* \langle \psi_j | \nabla_{\mathbf{R}} \psi_l \rangle \cdot \frac{\partial \mathbf{R}}{\partial t}$$

rearranging

$$\frac{\partial}{\partial t}\rho_{kl} = -\frac{i}{\hbar}\left[V_k - V_l\right]\rho_{kl} + \sum_j \left[\rho_{kj}\mathbf{F}_{jl} - \rho_{jl}\mathbf{F}_{kj}\right] \cdot \frac{\partial \mathbf{R}}{\partial t}$$

some more rearranging, and in different notation

$$i\hbar\dot{\rho}_{kl} = \sum_l \rho_{jl}\left\{\left[V_j\delta_{kj} - i\hbar\dot{\mathbf{R}} \cdot \mathbf{F}_{kj}\right] - \rho_{kj}\left[V_j\delta_{jl} - i\hbar\dot{\mathbf{R}} \cdot \mathbf{F}_{jl}\right]\right\}$$

where I used

$$\left[V_k - V_l\right]\rho_{kl} = \sum_j \left[\rho_{jl}V_j\delta_{kj} - \rho_{kj}V_j\delta_{jl}\right]$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

density matrix notation

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

populations of electronic states

$$\rho_{kk}(t)$$

Liouville-Von Neumann equation

$$i\hbar\dot{\rho}_{kl} = \sum_l \rho_{jl}\left\{\left[V_j\delta_{kj} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{F}_{kj}\right] - \rho_{kj}\left[V_j\delta_{jl} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{F}_{jl}\right]\right\}$$

Newton equation

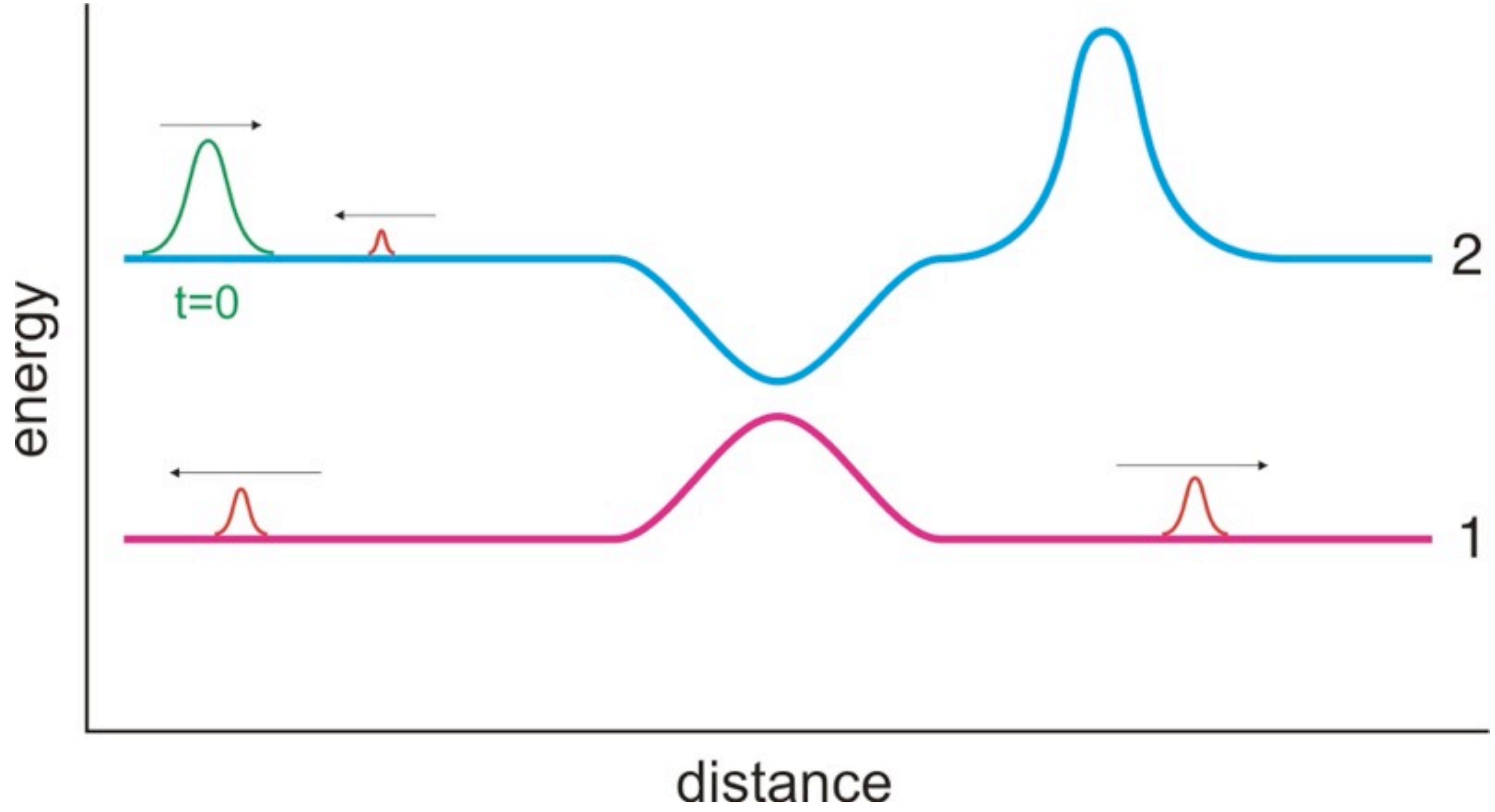
$$\begin{aligned}\mathbf{M}\ddot{\mathbf{R}} &= -\langle\phi|\nabla_{\mathbf{R}}H|\phi\rangle \\ &= -\sum_i\sum_j c_i^*(t)c_j(t)\langle\psi_i|\nabla_{\mathbf{R}}H|\psi_j\rangle \\ &= -\sum_i\sum_j \rho_{ji}(t)\langle\psi_i|\nabla_{\mathbf{R}}H|\psi_j\rangle = \sum_i \rho_{ii}\langle\psi_i|\nabla_{\mathbf{R}}H|\psi_i\rangle\end{aligned}$$

Non-adiabatic molecular dynamics

Ehrenfest dynamics

mixed electronic state

mixing due to non-adiabatic coupling



Non-adiabatic molecular dynamics

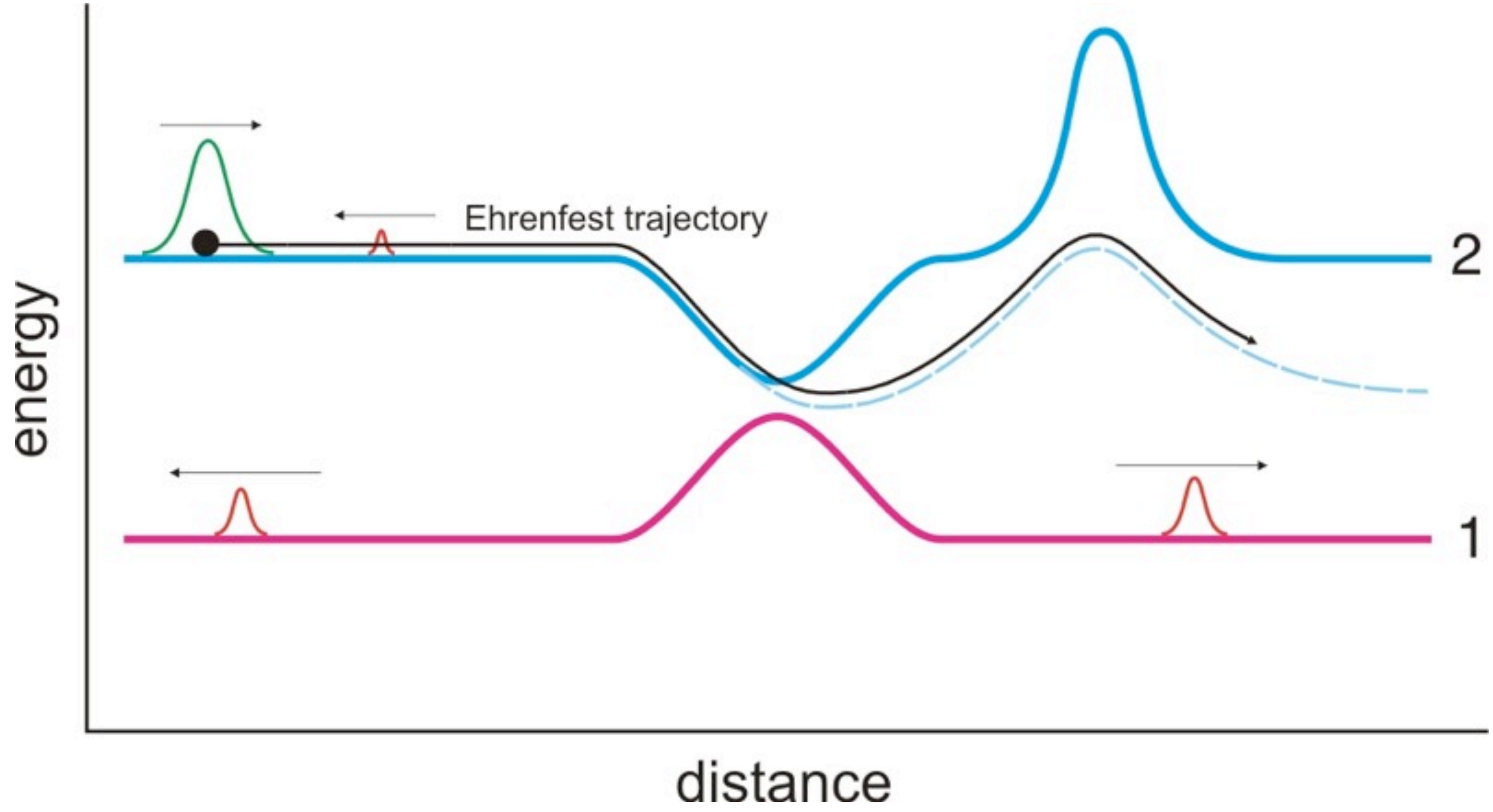
Ehrenfest dynamics

mixed electronic state

mixing due to non-adiabatic coupling

wrong asymptotic limit

no detailed balance: energy flows into electronic wavefunction



Non-adiabatic molecular dynamics

Ehrenfest dynamics

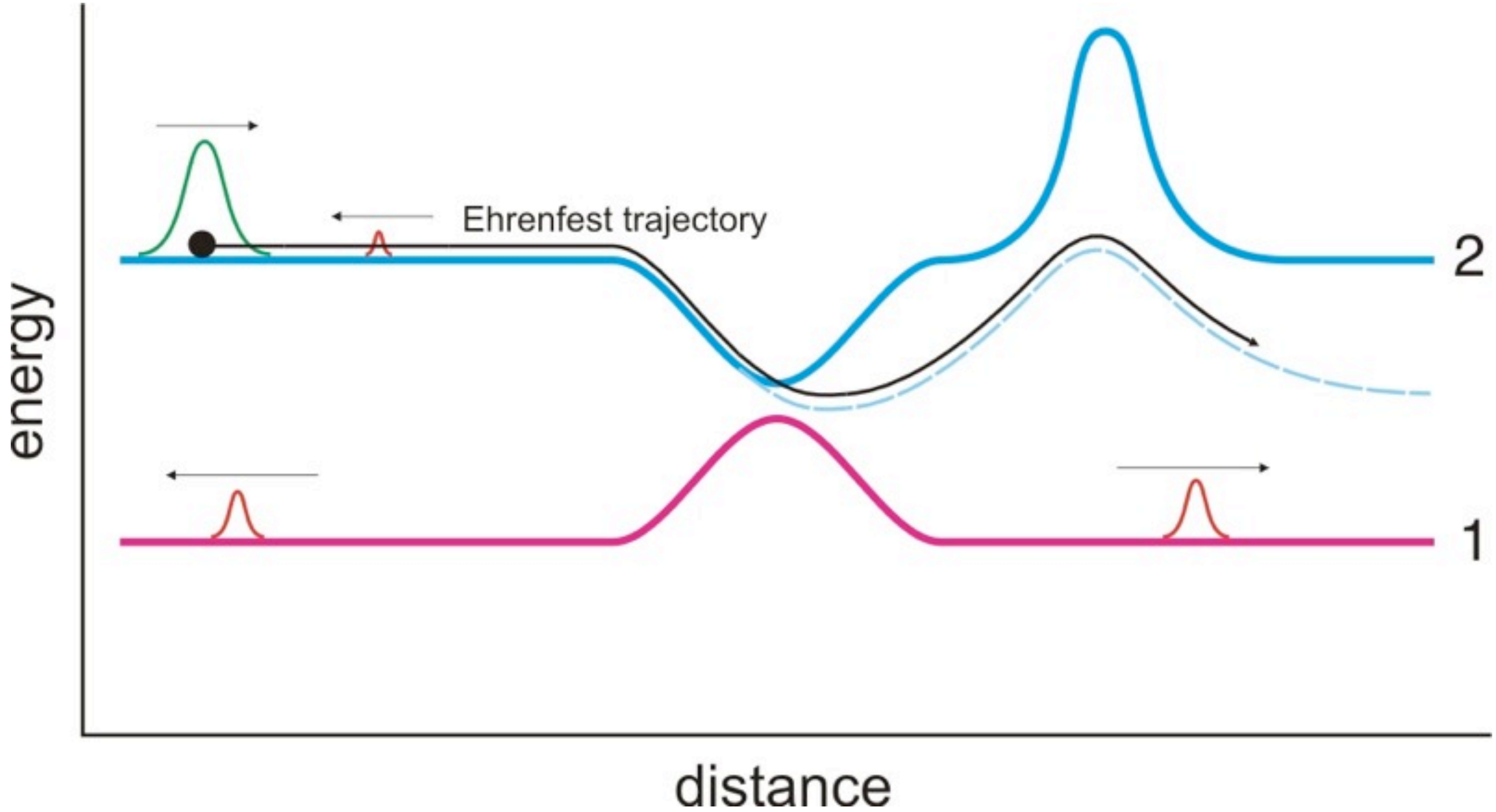
asymptotic limit

validity criteria (Prezhdo & Rossky)

$$\frac{|\mathbf{P}_j - \mathbf{P}_i|}{|\mathbf{P}_j + \mathbf{P}_i|} \ll 1 \qquad \frac{|\mathbf{R}_j - \mathbf{R}_i|}{a_0} \ll 1$$

reset populations when criteria are violated

Bohr radius



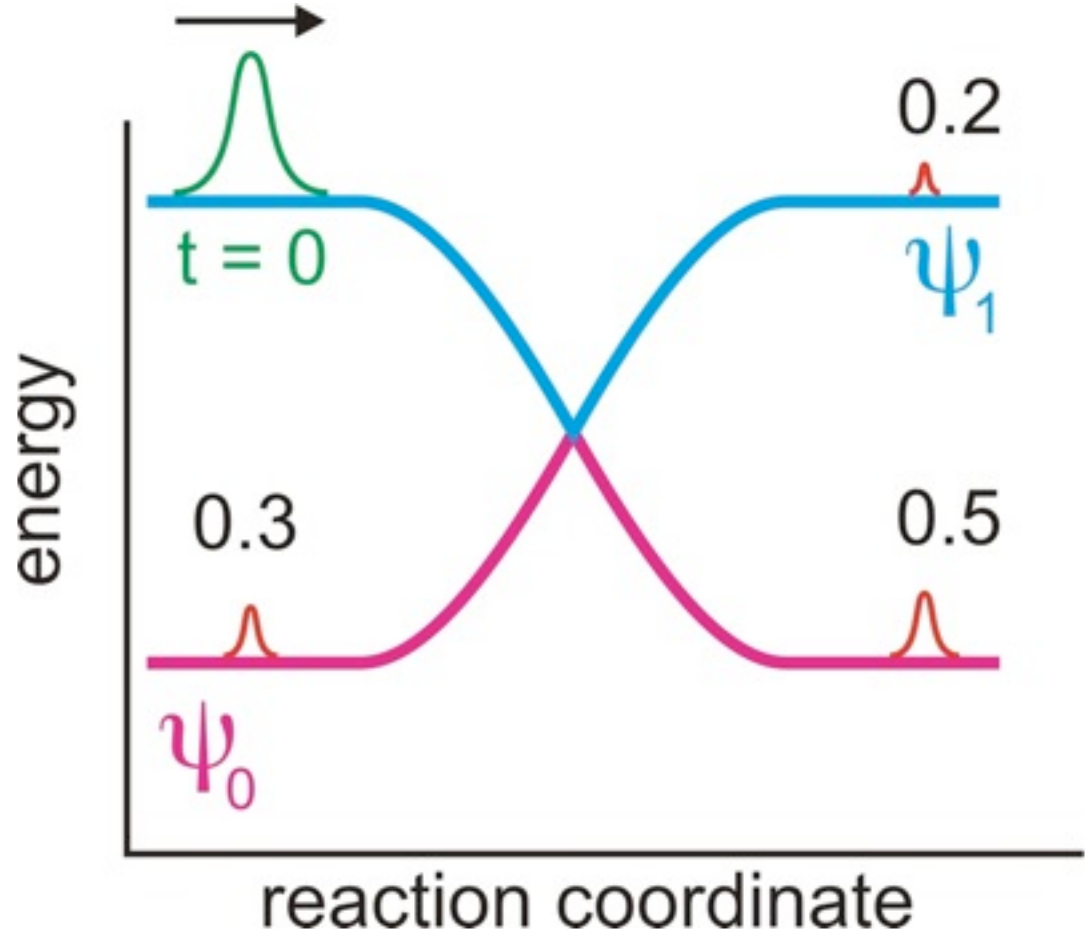
Non-adiabatic molecular dynamics

surface hopping

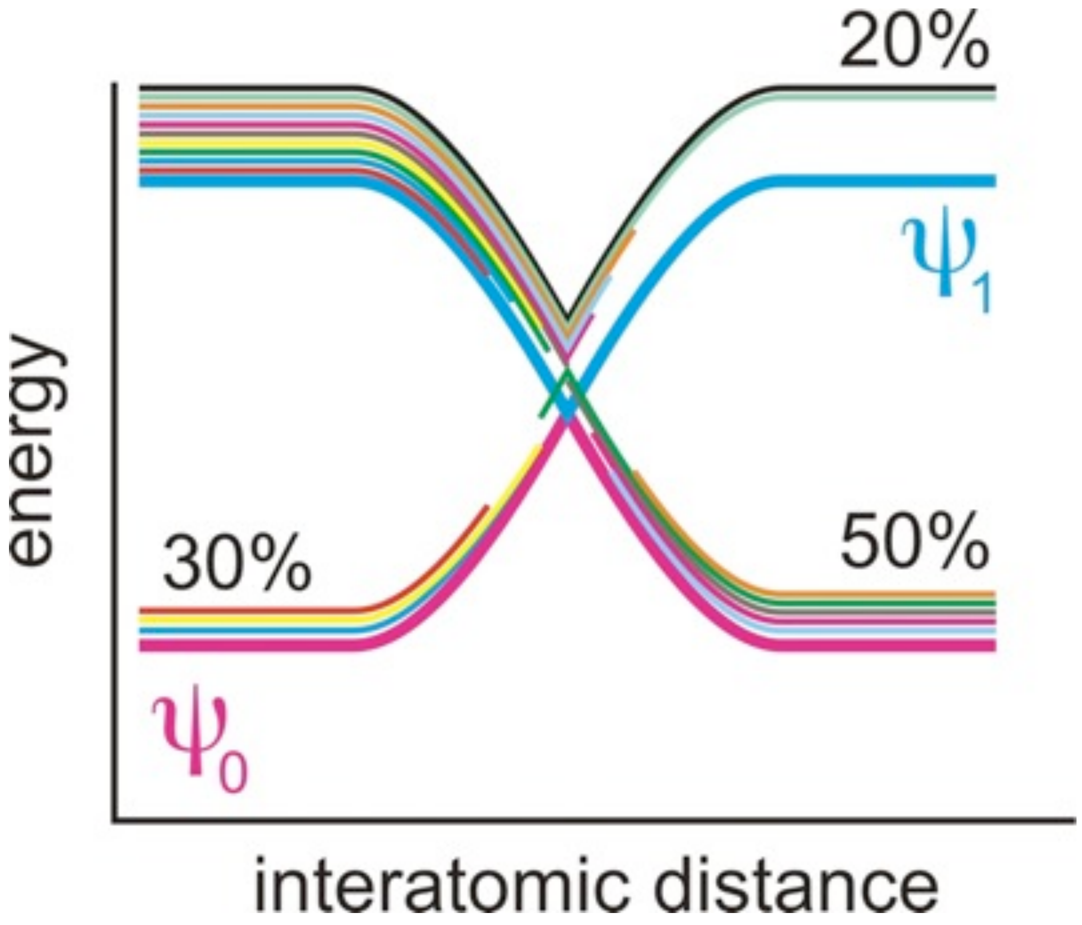
classical propagation of nuclei on single adiabatic PES

stochastic hops between electronic state

classical ensemble (‘swarm’) reproduce quantum populations



quantum dynamics



surface hopping trajectories

Non-adiabatic molecular dynamics

surface hopping

electronic dynamics

primary wavefunction in adiabatic basis

$$\phi(\mathbf{r}, t; \mathbf{R}) = \sum_j c_j(t)\psi_j(\mathbf{r}; \mathbf{R})$$

time-evolution

$$\frac{\partial c_i}{\partial t} = -\frac{i}{\hbar} V_i c_i(t) - \sum_j c_j(t)\langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \cdot \frac{\partial \mathbf{R}}{\partial t}$$

nuclear dynamics

classical dynamics on single adiabatic potential energy surface

$$\mathbf{M}\frac{\partial^2}{\partial t^2}\mathbf{R} = -\langle\psi_i|\nabla_{\mathbf{R}}|\psi_i\rangle$$

make random hops between adiabatic surfaces according to

$$p_i(t) = |c_i(t)|^2$$

average ensemble of trajectories to get quantum probabilities

Non-adiabatic molecular dynamics

surface hopping

electronic dynamics

primary wavefunction in adiabatic basis

$$\phi(\mathbf{r},t;\mathbf{R}) = \sum_j c_j(t)\psi_j(\mathbf{r};\mathbf{R})$$

density matrix evolution

$$i\hbar\dot{\rho}_{kl} = \sum_l \rho_{jl}\left\{\left[V_j\delta_{kj} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{F}_{kj}\right] - \rho_{kj}\left[V_j\delta_{jl} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{F}_{jl}\right]\right\}$$

nuclear dynamics

classical dynamics on single adiabatic potential energy surface

$$\mathbf{M}\frac{\partial^2}{\partial t^2}\mathbf{R} = -\langle\psi_i|\nabla_{\mathbf{R}}|\psi_i\rangle$$

make random hops between adiabatic surfaces according to

$$p_i(t) = \rho_{ii}(t)$$

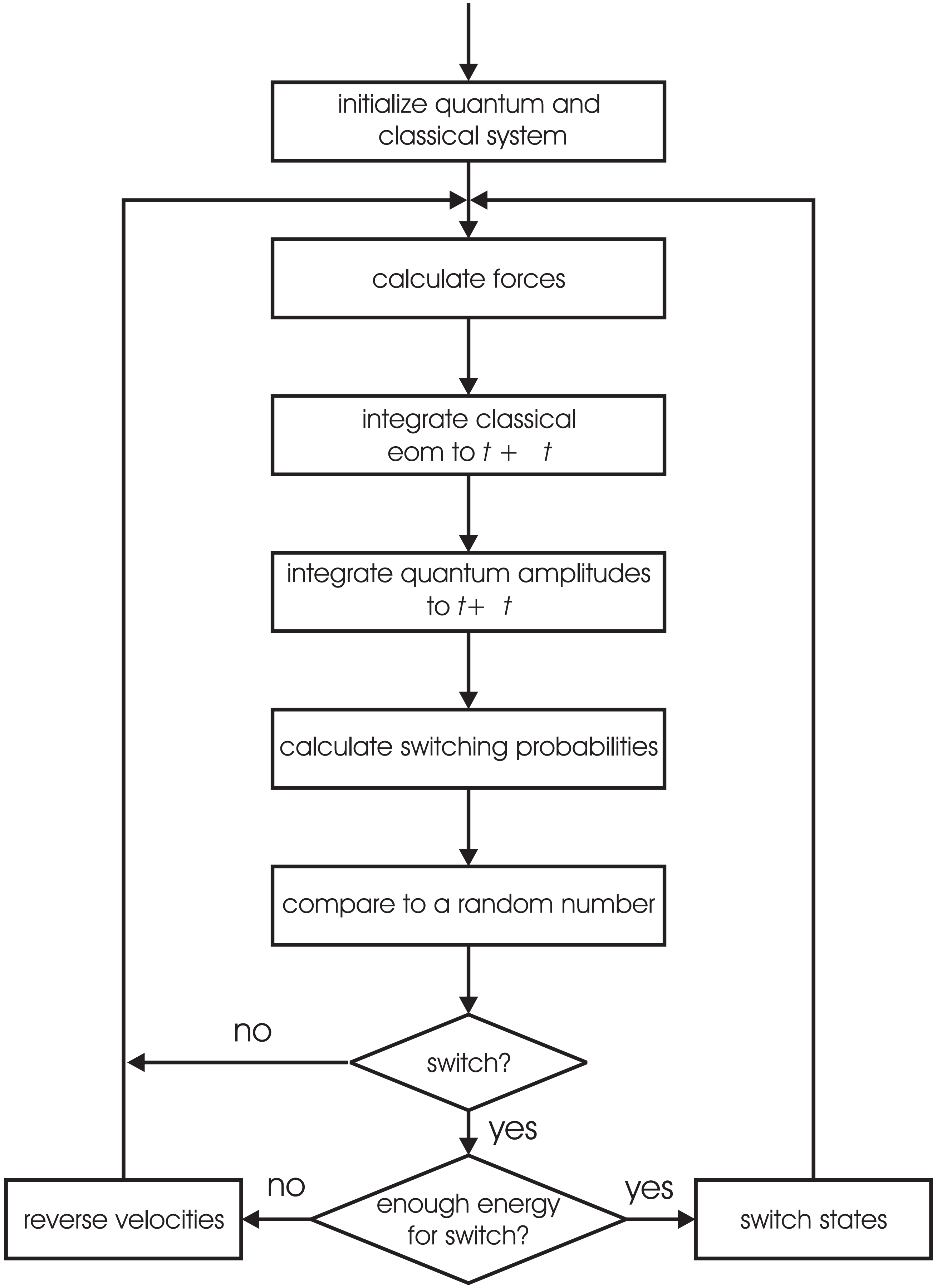
average ensemble of trajectories to get quantum probabilities

Non-adiabatic molecular dynamics

surface hopping

basic algorithm

hopping probabilities?



initialize quantum and classical system

calculate forces

integrate classical eom to *t* +   *t*

integrate quantum amplitudes to *t*+   *t*

calculate switching probabilities

compare to a random number

switch?

no

yes

enough energy for switch?

no

yes

reverse velocities

switch states

Non-adiabatic molecular dynamics

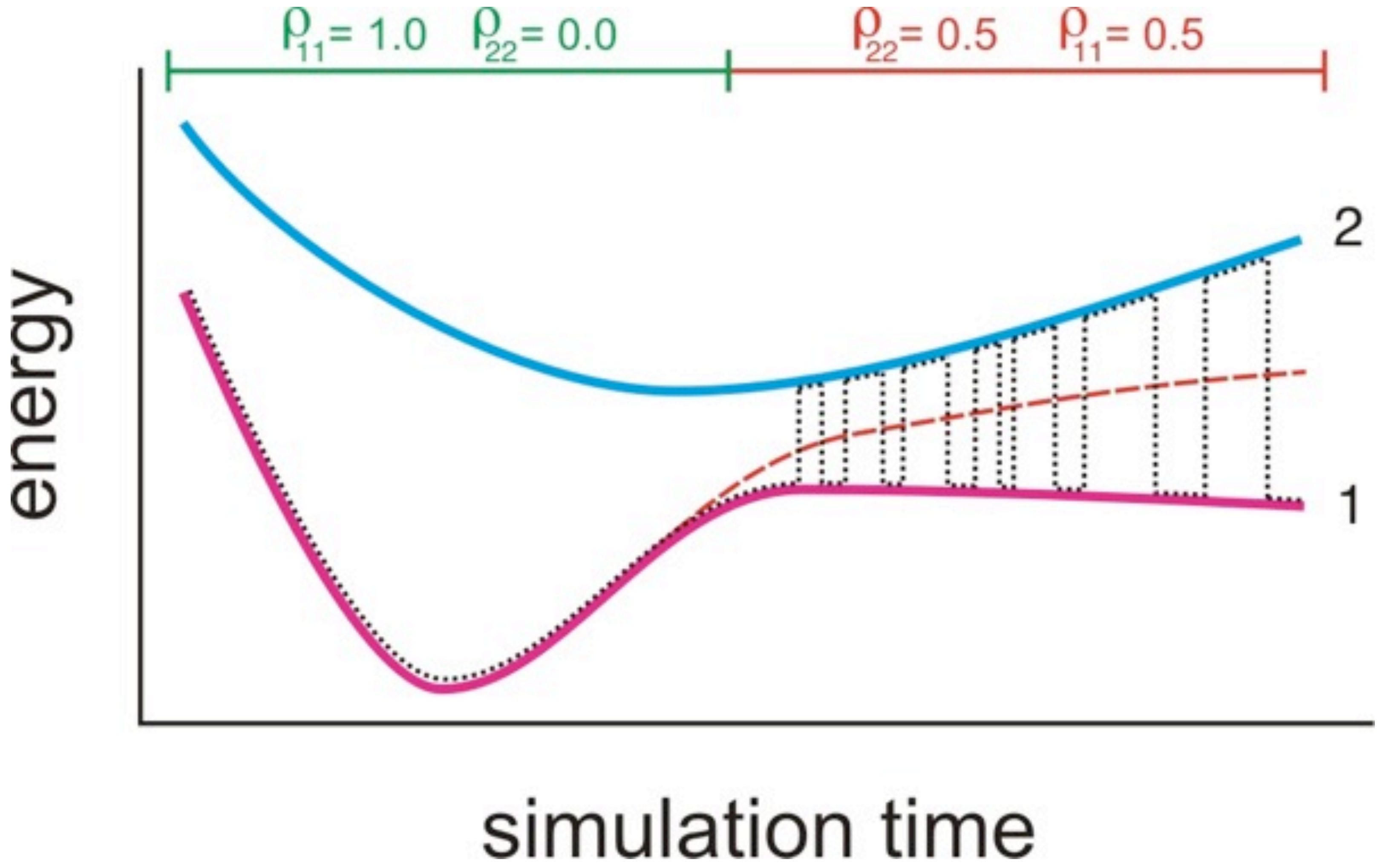
population-based surface hopping

naive algorithm

stochastic hop with probabilities

$$p_{i\to j}(t) \propto \rho_{jj}(t)$$

coherent propagation electronic wavefunction: keep hopping



Non-adiabatic molecular dynamics

fewest switches surface hopping (Tully)

minimize the number of switches from state l to k

during small time interval

$$\delta\rho_{kk} \approx \dot{\rho}_{kk}\delta t$$

$$\delta\rho_{ll} \approx -\delta\rho_{kk}\delta t$$

time-derivative of density matrix

$$\frac{\partial}{\partial t}\rho_{kl} = -\frac{i}{\hbar}\left[V_k - V_l\right]\rho_{kl} + \sum_j \left[\rho_{kj}\mathbf{F}_{jl} - \rho_{jl}\mathbf{F}_{kj}\right]\cdot\frac{\partial\mathbf{R}}{\partial t}$$

Non-adiabatic molecular dynamics

fewest switches surface hopping (Tully)

minimize the number of switches from state *l* to *k*

time-derivative of density matrix

$$\frac{\partial}{\partial t}\rho_{kl} = -\frac{i}{\hbar}\left[V_k - V_l\right]\rho_{kl} + \sum_j \left[\rho_{kj}\mathbf{F}_{jl} - \rho_{jl}\mathbf{F}_{kj}\right] \cdot \frac{\partial \mathbf{R}}{\partial t}$$

diagonal elements (populations)

$$\frac{\partial}{\partial t}\rho_{kk} = \sum_j \left[\rho_{kj}\mathbf{F}_{jk} - \rho_{jk}\mathbf{F}_{kj}\right] \cdot \frac{\partial \mathbf{R}}{\partial t}$$

using again that in adiabatic basis

$$\mathbf{F}^*_{kj} = -\mathbf{F}_{jk}$$

we arrive at

$$\frac{\partial}{\partial t}\rho_{kk} = -\sum_j 2\Re\left\{\rho_{jk}\mathbf{F}_{kj}\right\} \cdot \frac{\partial \mathbf{R}}{\partial t} = \sum_j b_{kj}$$

Non-adiabatic molecular dynamics

fewest switches surface hopping (Tully)

minimize the number of switches from state l to k

during small time interval (trajectory is on l)

$$\delta\rho_{kk} \approx \dot{\rho}_{kk}\delta t = b_{kl}\delta t \qquad b_{kl} = -2\Re\left\{\rho_{lk}\mathbf{F}_{kl}\right\}\cdot\dot{\mathbf{R}}$$

$$\delta\rho_{ll} \approx -\delta\rho_{kk} = -b_{kl}\delta t$$

number of hops from l to k must exceed number hops from k to l

$$N^{\text{hops}}_{l\to k} - N^{\text{hops}}_{k\to l} = N_{\text{ens}}b_{kl}\delta t$$

minimal number of hops if

$$N^{\text{hops}}_{k\to l} = 0$$

then

$$p_{l\to k} = \frac{N_{\text{ens}}b_{kl}}{N_{\text{ens}}\rho_{ll}}\delta t = \frac{b_{kl}}{\rho_{ll}}\delta t \qquad p_{l\to k} = \max\left[0, \frac{b_{kl}}{\rho_{ll}}\Delta t\right]$$

MD timestep

Non-adiabatic molecular dynamics

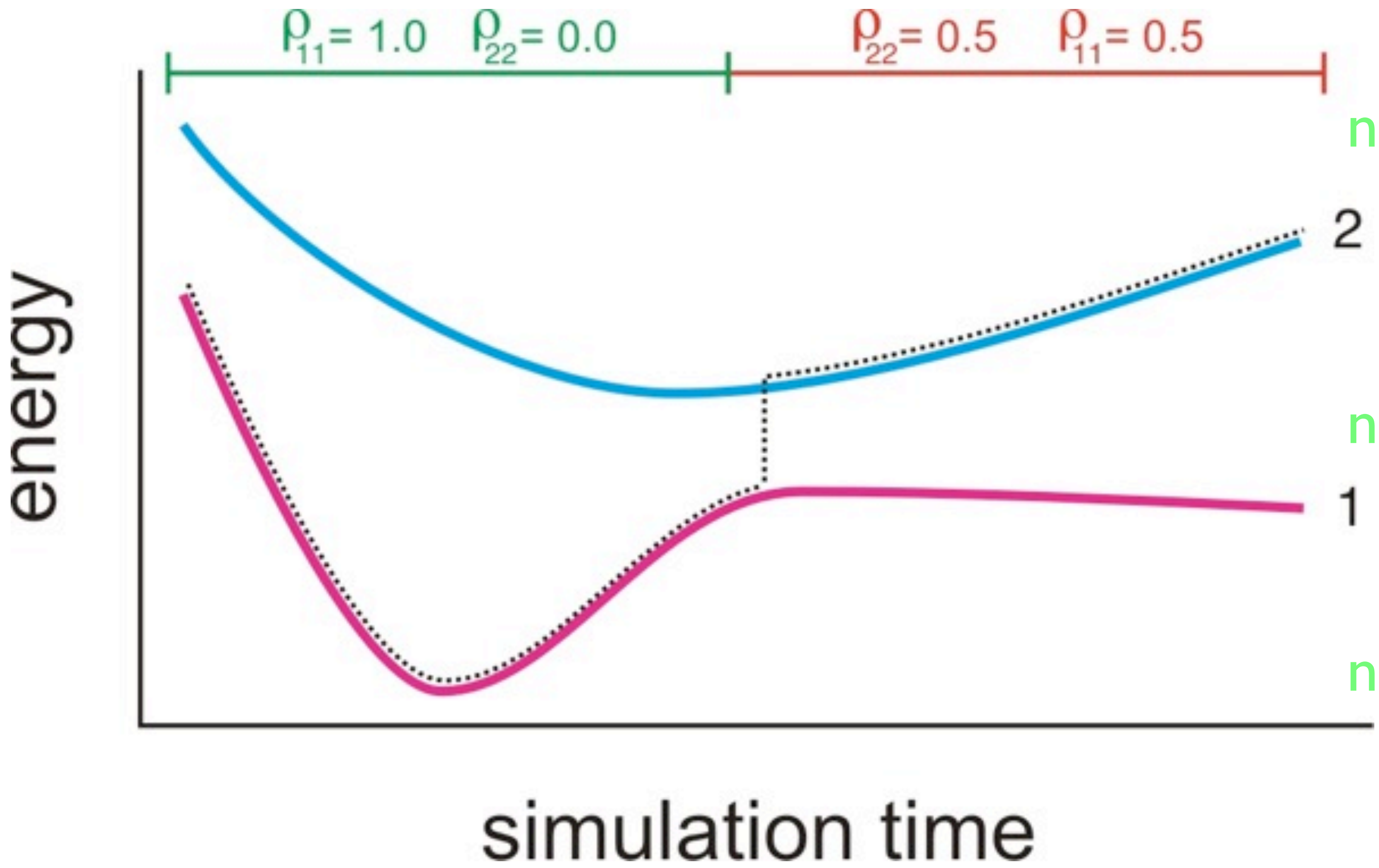
fewest switches surface hopping

basic algorithm

stochastic hop with probabilities

$$p_{l\to k} = \max\left[0, \frac{b_{kl}}{\rho_{ll}}\Delta t\right] \qquad b_{kl} = -2\Re\left\{\rho_{lk}\mathbf{F}_{kl}\right\}\cdot\dot{\mathbf{R}}$$

coherent propagation of electronic wavefunction



no coupling:

$$\langle\psi_2|\nabla_{\mathbf{R}}\psi_1\rangle = 0$$

no derivative:

$$\dot{\rho}_{11} = 0$$

no hopping

Non-adiabatic molecular dynamics

fewest switches surface hopping

conservation of energy after hopping

adjust velocity parallel to non-adiabatic coupling vector

non-adiabatic force does (pos/neg) work to bring about transition

non-adiabatic force should change in momentum of nuclei

$$\dot{\mathbf{R}}_i^{\mathrm{new}} = \dot{\mathbf{R}}_i - \gamma_{kj}\frac{\mathbf{F}_{kj}^i}{M_i}$$

kinetic energy after hopping

$$\sum_i \frac{1}{2}M_i(\dot{\mathbf{R}}_i^{\mathrm{new}})^2 = \sum_i \frac{1}{2}M_i\dot{\mathbf{R}}_i^2 + (V_k - V_j)$$

$$\sum_i \frac{1}{2}M_i\left(\dot{\mathbf{R}}_i - \gamma_{kj}\frac{\mathbf{F}_{kj}^i}{M_i}\right)^2 = \sum_i \frac{1}{2}M_i\dot{\mathbf{R}}_i^2 + (V_k - V_j)$$

Non-adiabatic molecular dynamics

fewest switches surface hopping

conservation of energy after hopping

adjust velocity parallel to non-adiabatic coupling vector

$$\sum_i \frac{1}{2} M_i \left(\dot{\mathbf{R}}_i - \gamma_{kj} \frac{\mathbf{F}^i_{kj}}{M_i} \right)^2 = \sum_i \frac{1}{2} M_i \dot{\mathbf{R}}_i^2 + (V_k - V_j)$$

$$\sum_i \frac{1}{2} M_i \left(\dot{\mathbf{R}}_i^2 - 2\gamma_{kj} \frac{\mathbf{F}_{kj} \cdot \dot{\mathbf{R}}_i}{M_i} + \gamma_{kj}^2 \frac{|\mathbf{F}^i_{kj}|^2}{M_i^2} \right) = \sum_i \frac{1}{2} M_i \dot{\mathbf{R}}_i^2 + (V_k - V_j)$$

Non-adiabatic molecular dynamics

fewest switches surface hopping

conservation of energy after hopping

adjust velocity parallel to non-adiabatic coupling vector

$$\sum_i \frac{1}{2} M_i \left(\cancel{\dot{\mathbf{R}}_i^2} - 2\gamma_{kj} \frac{\mathbf{F}_{kj} \cdot \dot{\mathbf{R}}_i}{M_i} + \gamma_{kj}^2 \frac{|\mathbf{F}^i_{kj}|^2}{M_i} \right) = \cancel{\sum_i \frac{1}{2} M_i \dot{\mathbf{R}}_i^2} + (V_k - V_j)$$

$$\underline{\sum_i \frac{1}{2}} \gamma_{kj}^2 \underline{\frac{|\mathbf{F}^i_{kj}|^2}{M_i}} - \underline{\sum_i} \gamma_{kj} \underline{\mathbf{F}^i_{kj} \cdot \dot{\mathbf{R}}_i} - (V_k - V_j) = 0$$

introducing some definitions to make the thing readable

$$\underline{a_{kj}} \gamma_{kj}^2 - \underline{b_{kj}} \gamma_{kj} - (V_k - V_j) = 0$$

Non-adiabatic molecular dynamics

fewest switches surface hopping

conservation of energy after hopping

adjust velocity parallel to non-adiabatic coupling vector

$$a_{kj}\gamma_{kj}^2 - b_{kj}\gamma_{kj} - (V_k - V_j) = 0$$

solution

$$\gamma_{kj} = \begin{cases} \frac{b_{kj}+\sqrt{b_{kj}^2+4a_{kj}[V_k(\mathbf{R})-V_j(\mathbf{R})]}}{2a_{kj}} & , \quad b_{kj} < 0 \\ \frac{b_{kj}-\sqrt{b_{kj}^2+4a_{kj}[V_k(\mathbf{R})-V_j(\mathbf{R})]}}{2a_{kj}} & , \quad b_{kj} \geq 0 \end{cases}$$

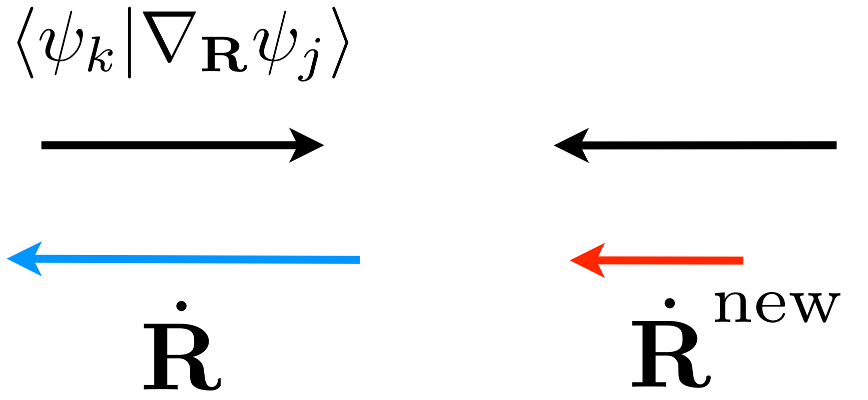
Non-adiabatic molecular dynamics

fewest switches surface hopping

non-adiabatic coupling acts as a force

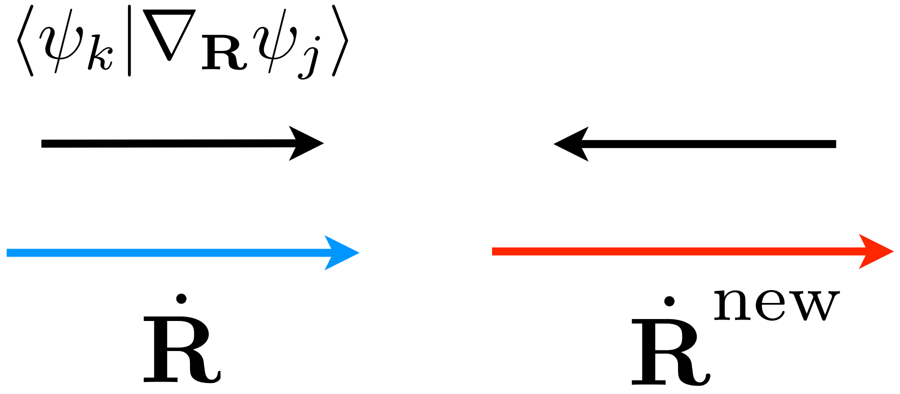
situation A

$$\Delta V_{kj} > 0$$



situation B

$$\Delta V_{kj} < 0$$



not sufficient kinetic energy

reject hop

keep velocities

reverse velocities

inconsistencies with quantum mechanics

Non-adiabatic molecular dynamics

fewest switches surface hopping

- coherent propagation
  - artificial coherence far from non-adiabatic region
  - problematic for new encounters
- washing out coherence
  - (i) reset density matrix after hop

$$\rho_{kk} = 1 \wedge \rho_{ij} = 0$$

Non-adiabatic molecular dynamics

fewest switches surface hopping

coherent propagation

artificial coherence far from non-adiabatic region

problematic for new encounters

washing out coherence

(i) reset density matrix after hop

(ii) damp off-diagonal elements of density matrix (Tully)

$$i\hbar\dot{\rho}_{kl} = \textstyle\sum_l \rho_{jl}\left\{\left[V_j\delta_{kj} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{F}_{kj}\right] - \rho_{kj}\left[V_j\delta_{jl} - i\hbar\dot{\mathbf{R}}\cdot\mathbf{F}_{jl}\right]\right\}$$

$$-i\hbar\zeta(1-\delta_{kl})\rho_{kl}$$

“friction”

Non-adiabatic molecular dynamics

fewest switches surface hopping

coherent propagation

artificial coherence far from non-adiabatic region

problematic for new encounters

washing out coherence

(i) reset density matrix after hop

(ii) damp off-diagonal elements of density matrix (Tully)

(iii) damp coefficients (Truhlar, Granucci/Persico)

$$c'_k = c_k \exp[-\frac{\Delta t}{\tau_{km}}]$$

$$c'_m = c_m \sqrt{\left[\frac{1 - \sum_{k\neq m} |c'_k|^2}{|c_m|^2}\right]}$$

$$\tau_{km} = \frac{\hbar}{|V_k - V_m|}\left(1 + \frac{C}{E_{\text{kin}}}\right)$$

Non-adiabatic molecular dynamics

diabatic hopping

Landau-Zener model

one dimensional surface crossing: staying on diabatic surface

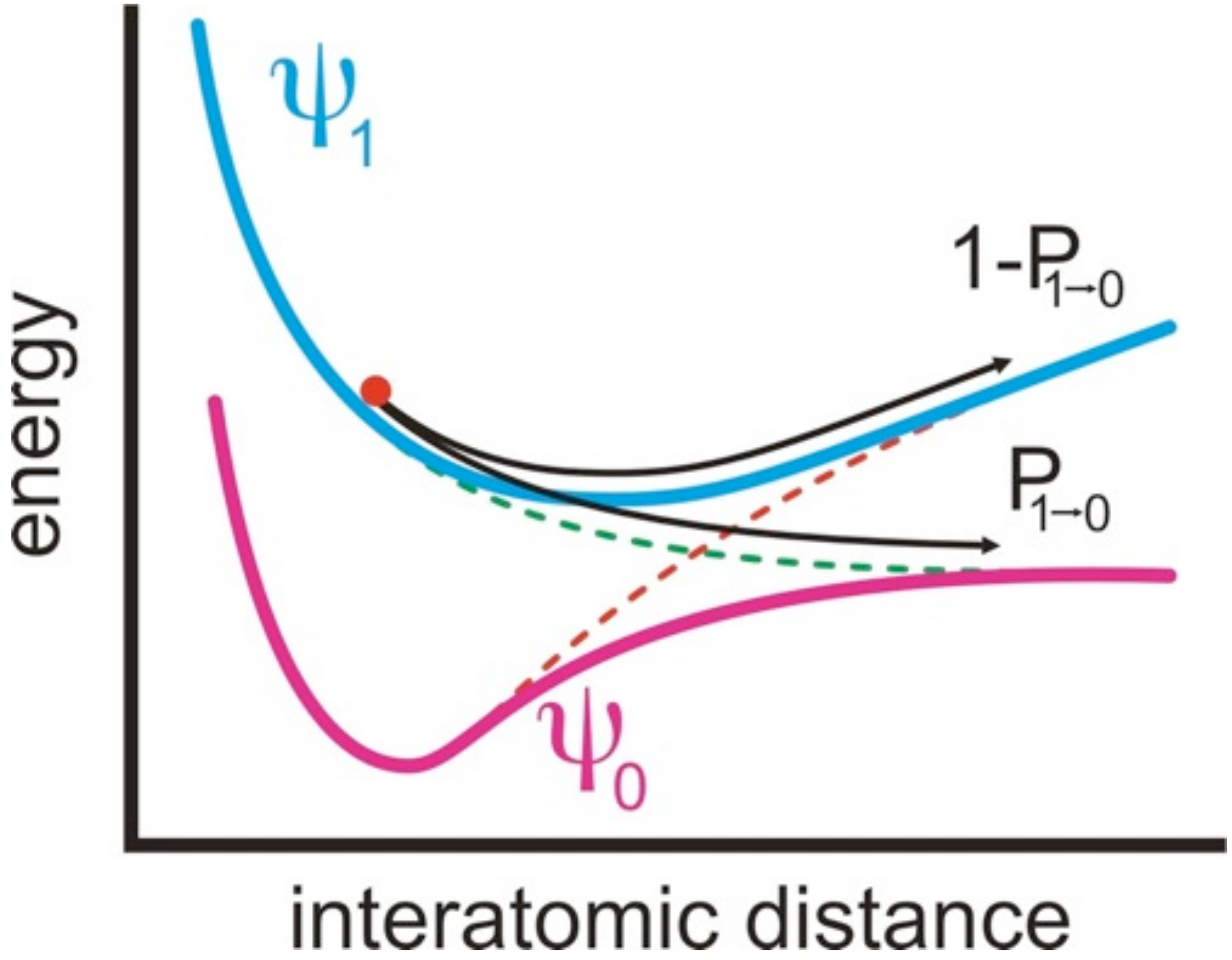
$$P_{1\to 0} = \exp\left[-\frac{1}{4}\pi\xi\right]$$

Massey parameter

$$\xi = \frac{\Delta E}{\hbar \mathbf{F}_{01} \partial Q/\partial t}$$

$$\mathbf{F}_{01} = \langle \psi_0 | \nabla_Q \psi_1 \rangle$$

probability of diabatic hop



Non-adiabatic molecular dynamics

diabatic hopping

Landau-Zener model

one dimensional surface crossing

$$P_{1\to 0} = \exp\left[-\frac{1}{4}\pi\xi\right]$$

Massey parameter

$$\xi = \frac{\Delta E}{\hbar \mathbf{F}_{01} \partial Q/\partial t} \qquad \mathbf{F}_{01} = \langle \psi_0 | \nabla_Q \psi_1 \rangle$$

using

$$\langle \psi_0 | \frac{\partial}{\partial t} \psi_1 \rangle = \langle \psi_0 | \nabla_Q \psi_1 \rangle \frac{\partial}{\partial t} Q$$

to rewrite Massey parameter

$$\xi = \frac{\Delta E}{\hbar \langle \psi_0 | \partial/\partial t \psi_1 \rangle}$$

Non-adiabatic molecular dynamics

diabatic hopping

Landau-Zener model

one dimensional surface crossing

$$P_{1\to 0} = \exp\left[-\frac{1}{4}\pi\xi\right]$$

Massey parameter

$$\xi = \frac{\Delta E}{\hbar\langle\psi_0|\partial/\partial t\psi_1\rangle}$$

surface hopping algorithm

compute probability at every step to decide on hopping

how to compute the denominator?

$$\langle\psi_0|\partial/\partial t\psi_1\rangle$$

Non-adiabatic molecular dynamics

diabatic hopping

computing denominator $\langle\psi_0|\partial/\partial t\psi_1\rangle$

at any time we have

$\psi_1(t)$ and $\psi_0(t)$

during integration step these states mix due to non-adiabatic coupling

$$\psi_0(t+\Delta t) = \psi_0(t) + \beta\psi_1(t)$$
$$\psi_1(t+\Delta t) = \psi_1(t) - \beta\psi_0(t)$$

numerical differentiation (finite differencing)

$$\frac{\partial}{\partial t}\psi_1(t) \approx \frac{\psi_1(t+\Delta t) - \psi_1(t)}{\Delta t} = -\frac{\beta\psi_0}{\Delta t}$$
$$\langle\psi_0|\frac{\partial}{\partial t}\psi_1\rangle \approx -\frac{\beta}{\Delta t}$$

we also have that

$$\langle\psi_0(t)|\psi_1(t+\Delta t)\rangle = -\beta$$

Non-adiabatic molecular dynamics

diabatic hopping

computing denominator $\langle\psi_0|\partial/\partial t\psi_1\rangle$

numerical differentiation (finite differencing)

$$\langle\psi_0|\frac{\partial}{\partial t}\psi_1\rangle \approx -\frac{\beta}{\Delta t}$$

since

$$\langle\psi_0(t)|\psi_1(t+\Delta t)\rangle = -\beta$$

we can use the following approximation

$$\langle\psi_0|\frac{\partial}{\partial t}\psi_1\rangle \approx \psi_0(t)|\psi_1(t+\Delta t)\rangle/\Delta t$$

in principle hopping everywhere

in practice hopping restricted at intersection seam

Non-adiabatic molecular dynamics

diabatic hopping

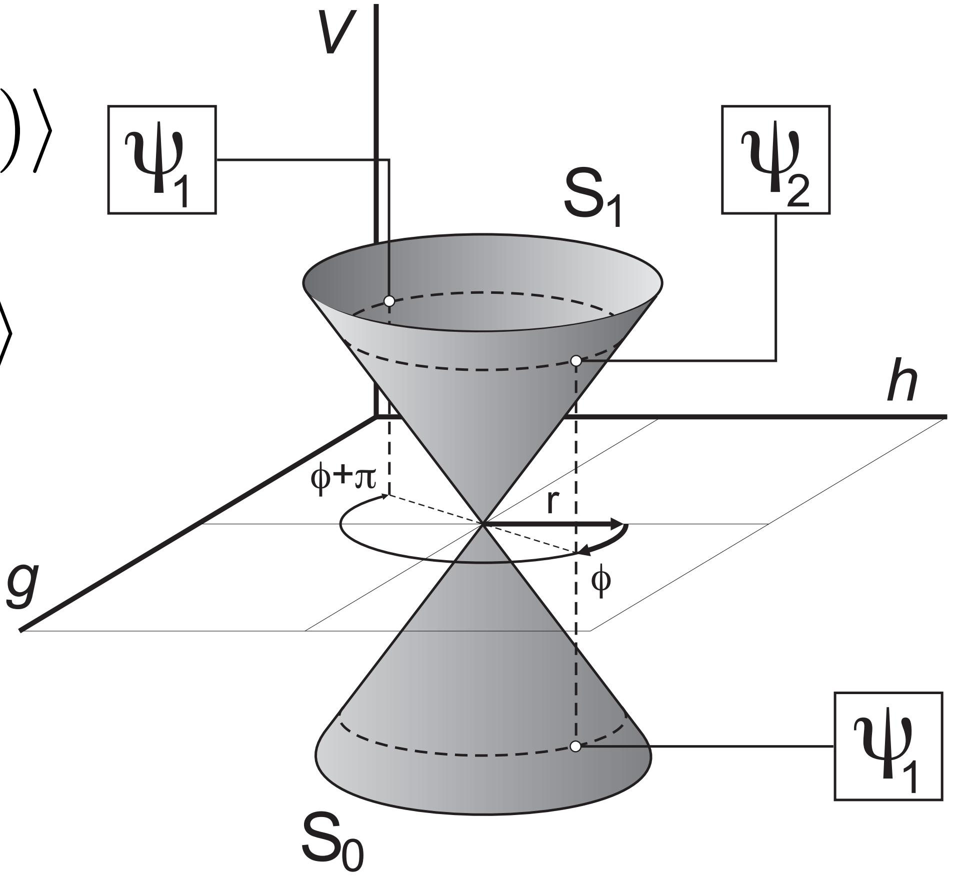
practical algorithm

restrict hopping to the seam: stay on ‘diabatic’ surface

monitor energy gap

upon passing seam in simulation we have from the Berry phase

$$\begin{aligned}\langle\psi_0(t)|\psi_1(t+\Delta t)\rangle &= \langle\psi_0(\phi)|\psi_1(\phi+\pi)\rangle\\ &= -\langle\psi_0(\phi)|\psi_0(\phi)\rangle\\ &= -\langle\psi_0(t)|\psi_0(t)\rangle\\ &= -1\end{aligned}$$



conservation of momentum and energy

no quantum coherence

Non-adiabatic molecular dynamics

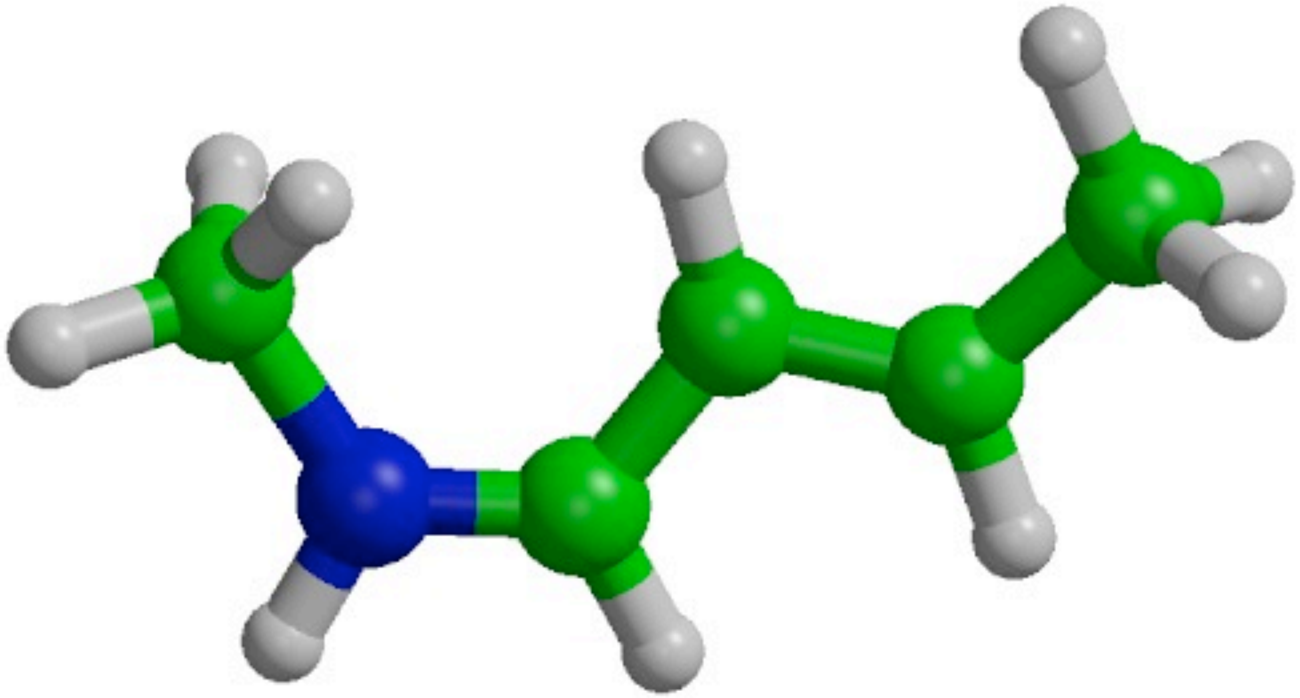
comparing diabatic hopping with fewest switches

photoisomerization of protonated Schiff base

aim a: find out if initial conditions determine outcome

aim b: control outcome

aim c: compare hopping algorithms



simulations

CASSCF(4,4)/6-31G*, diabatic & fewest switches surface hopping

QY: 44.6%/42.4%

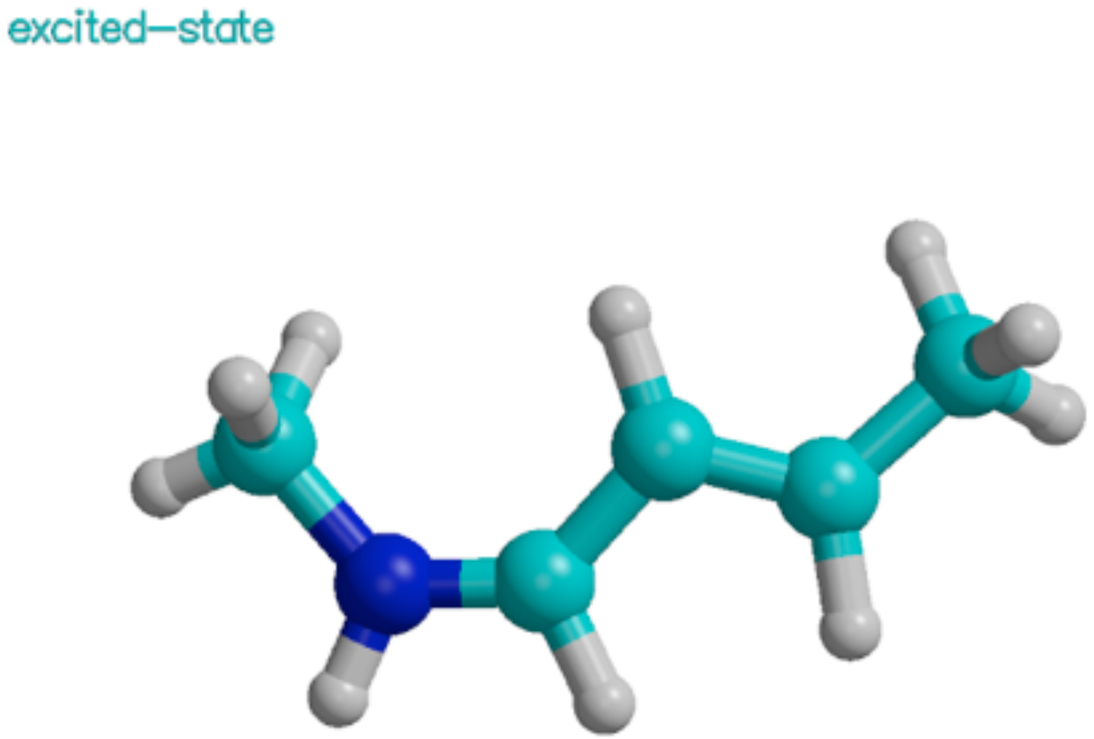
average lifetime: 115.8 fs/75.2 fs

QY: 35.5%/34.8%

average lifetime: 139.5 fs/83.7 fs

QY (both): 19.9 %/22.8%

average lifetime: 60.2 fs/54.6 fs



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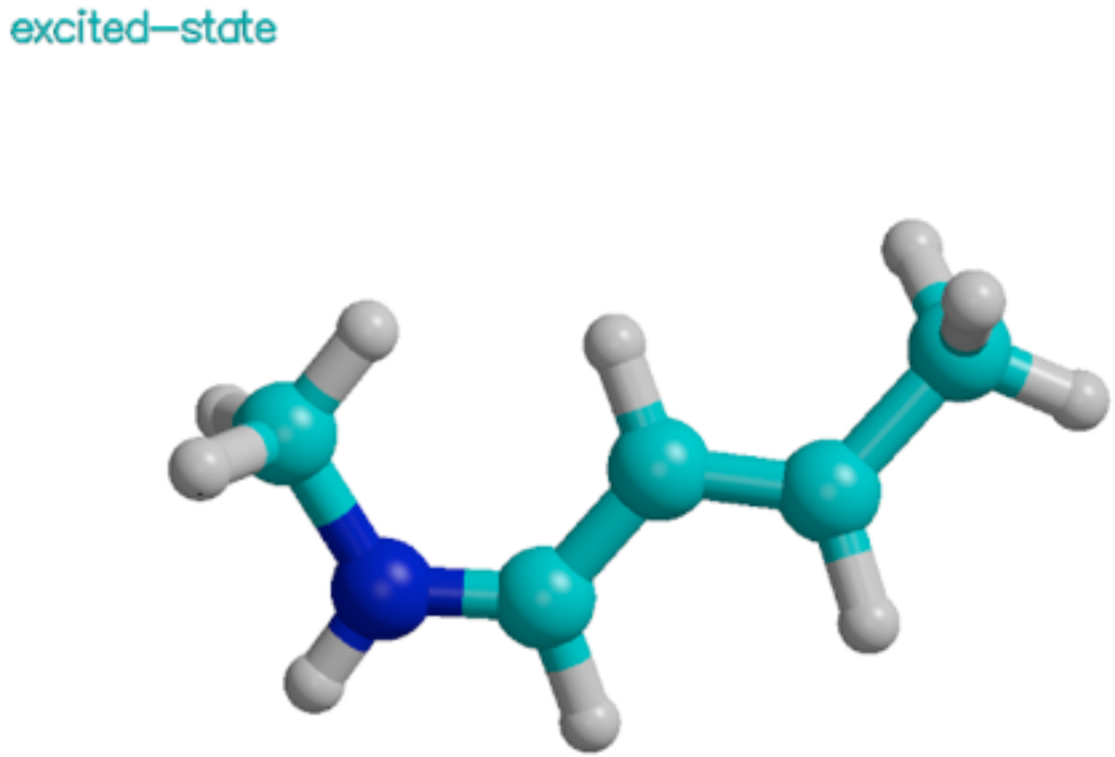

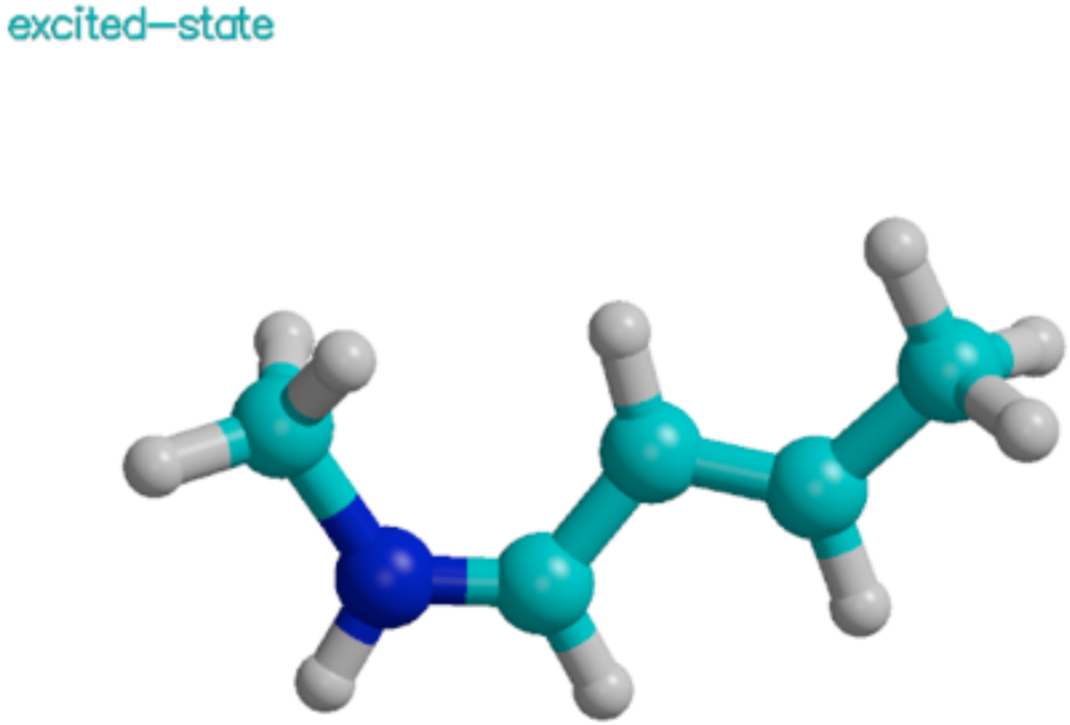

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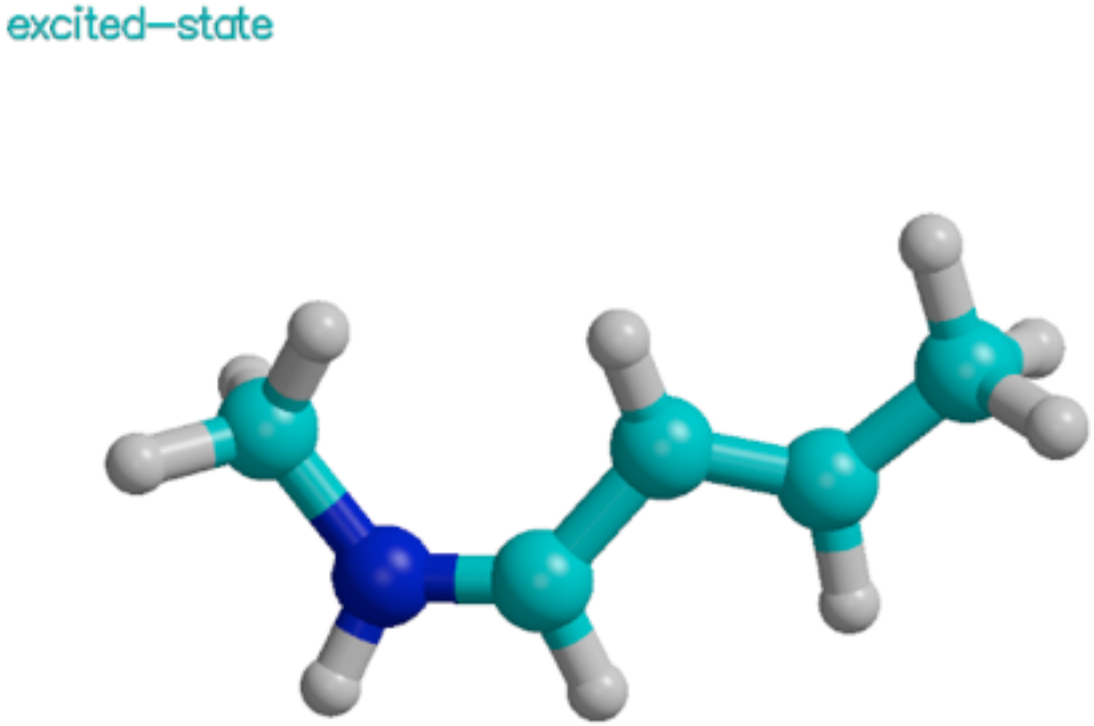

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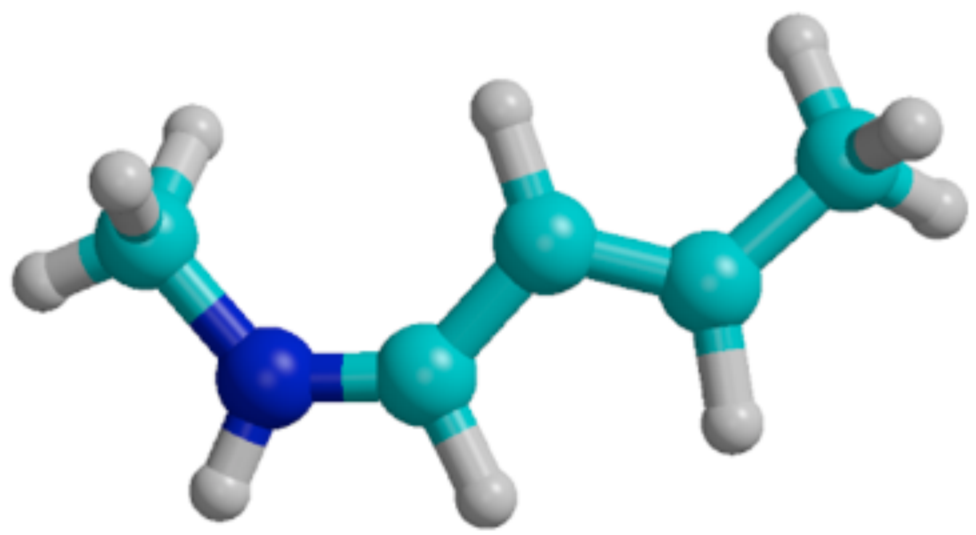

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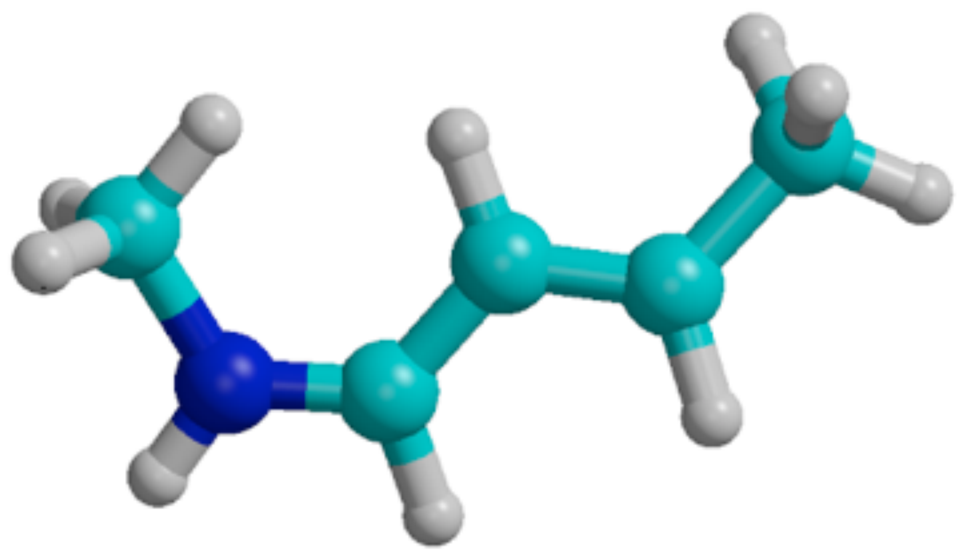

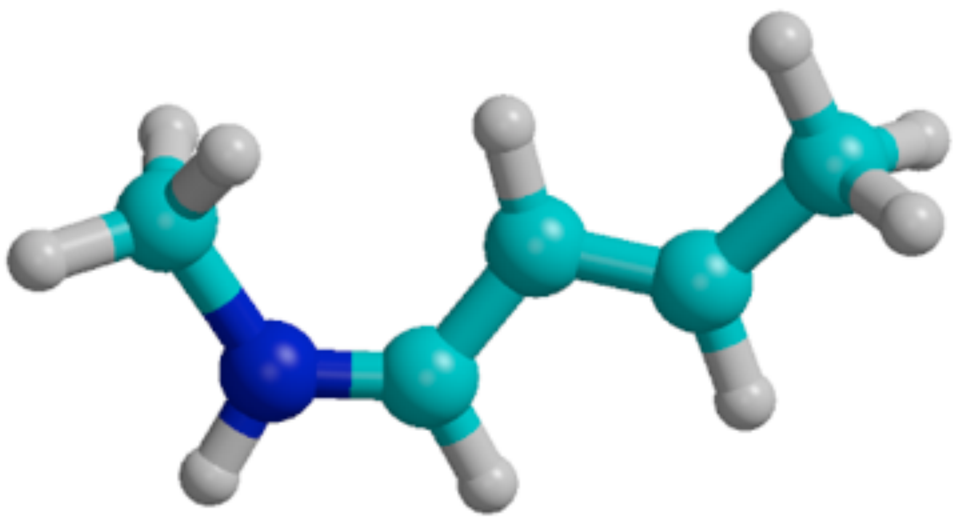

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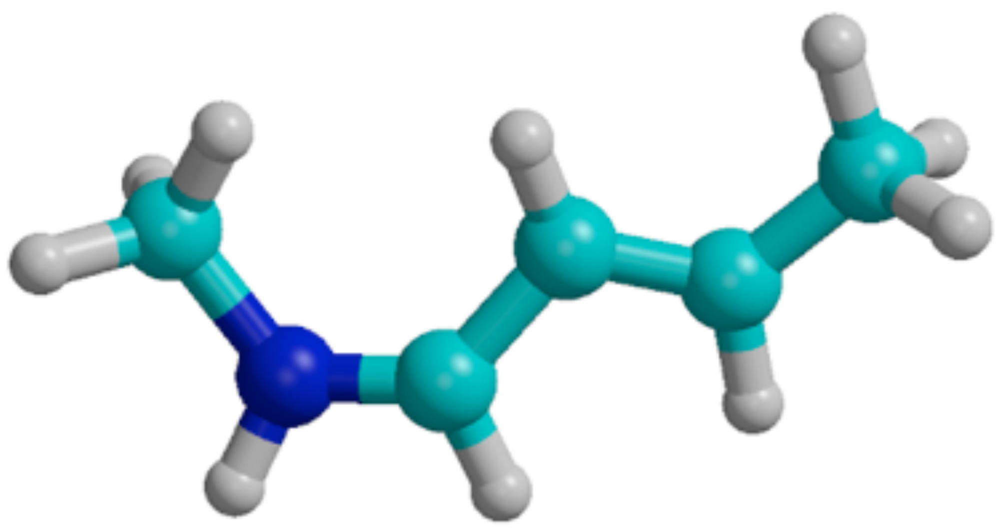

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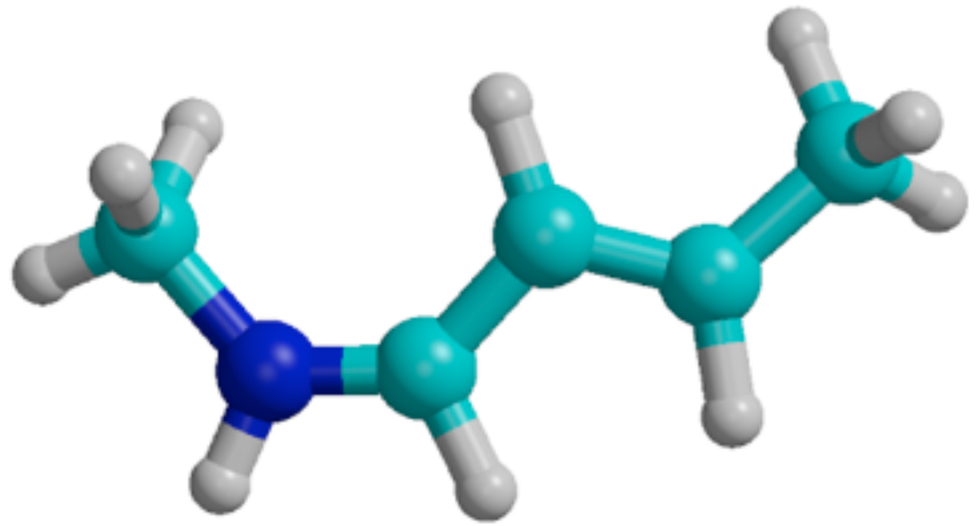

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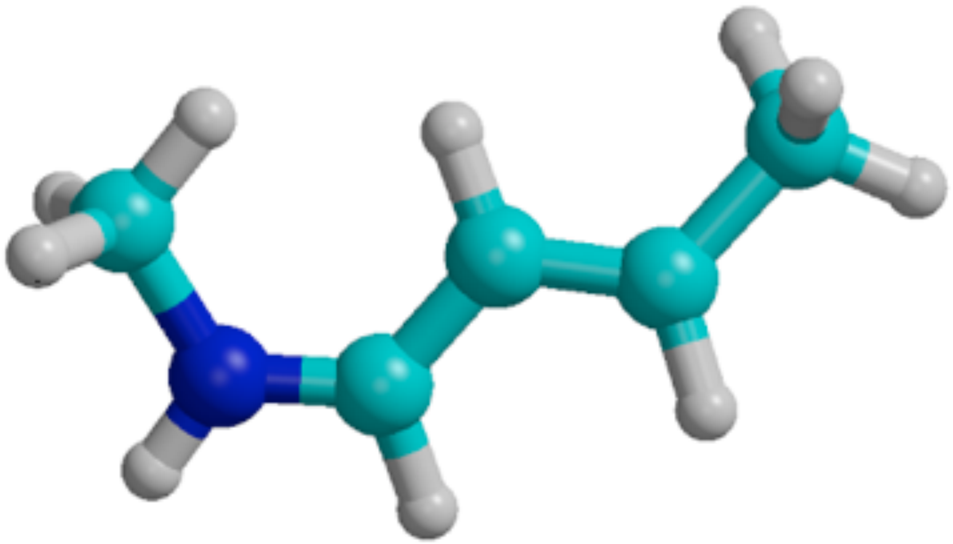

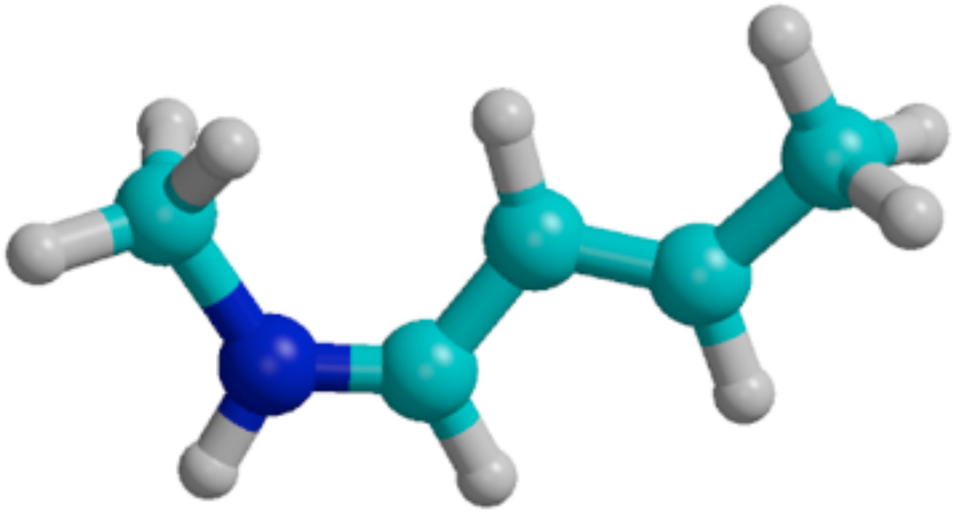

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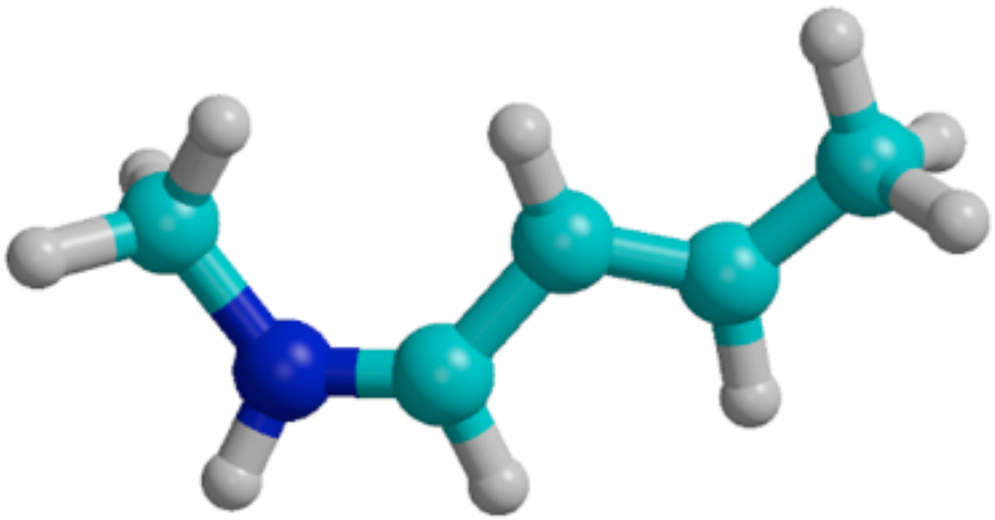

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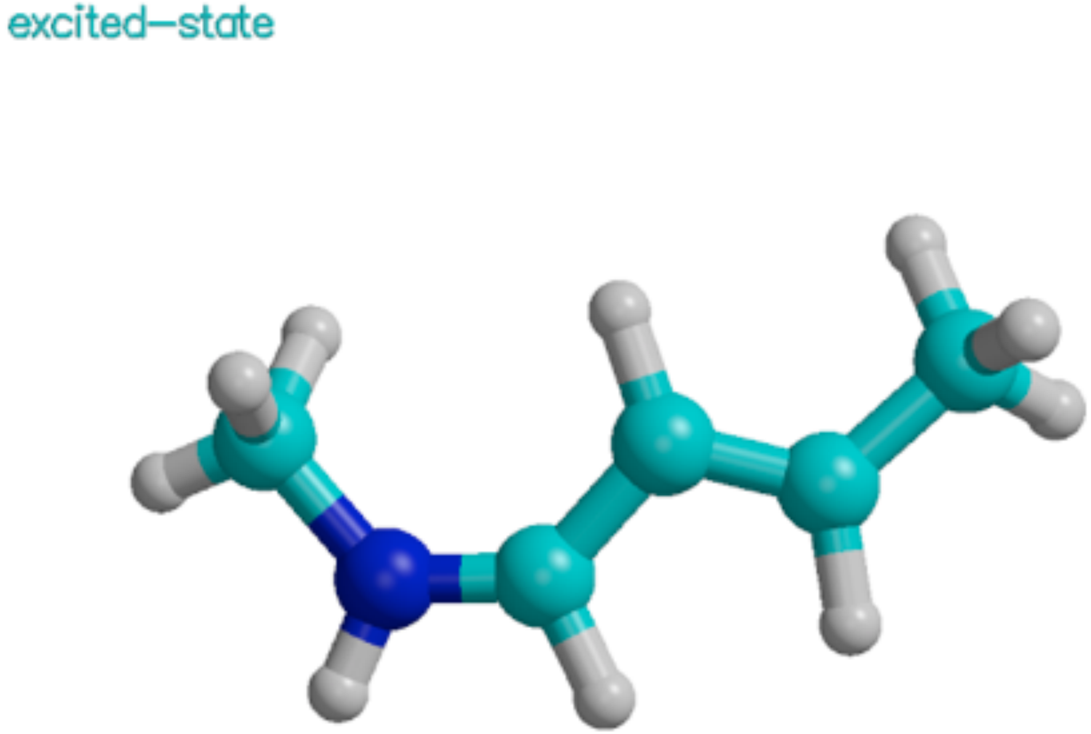

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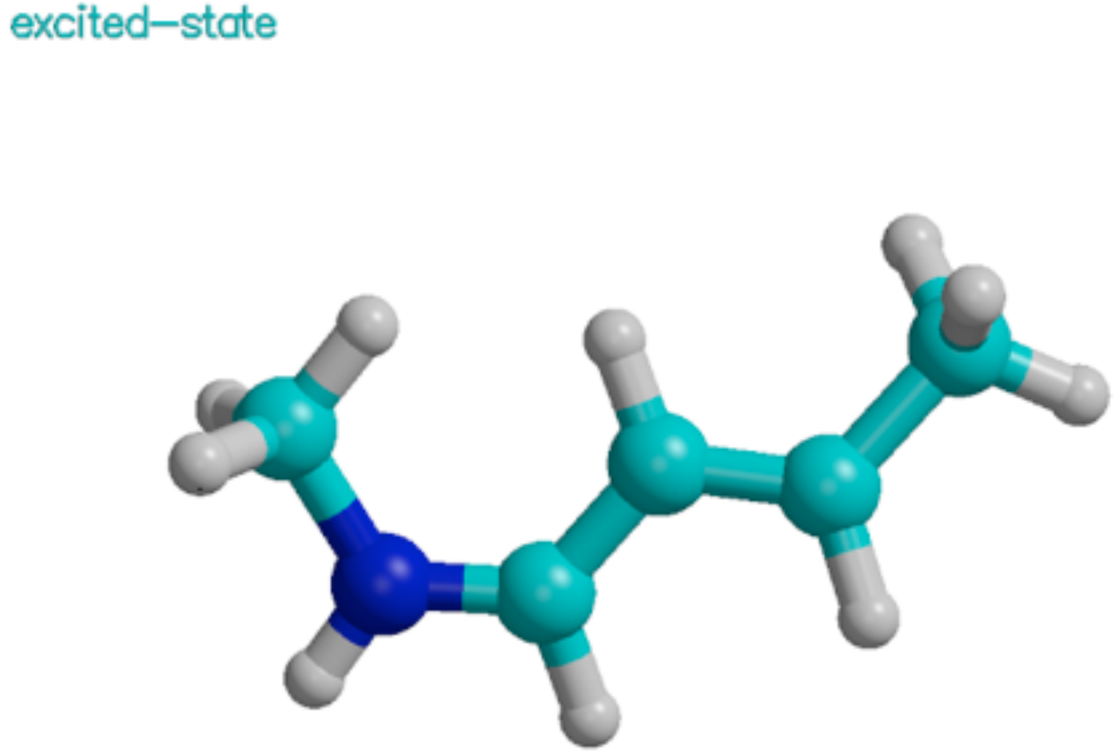

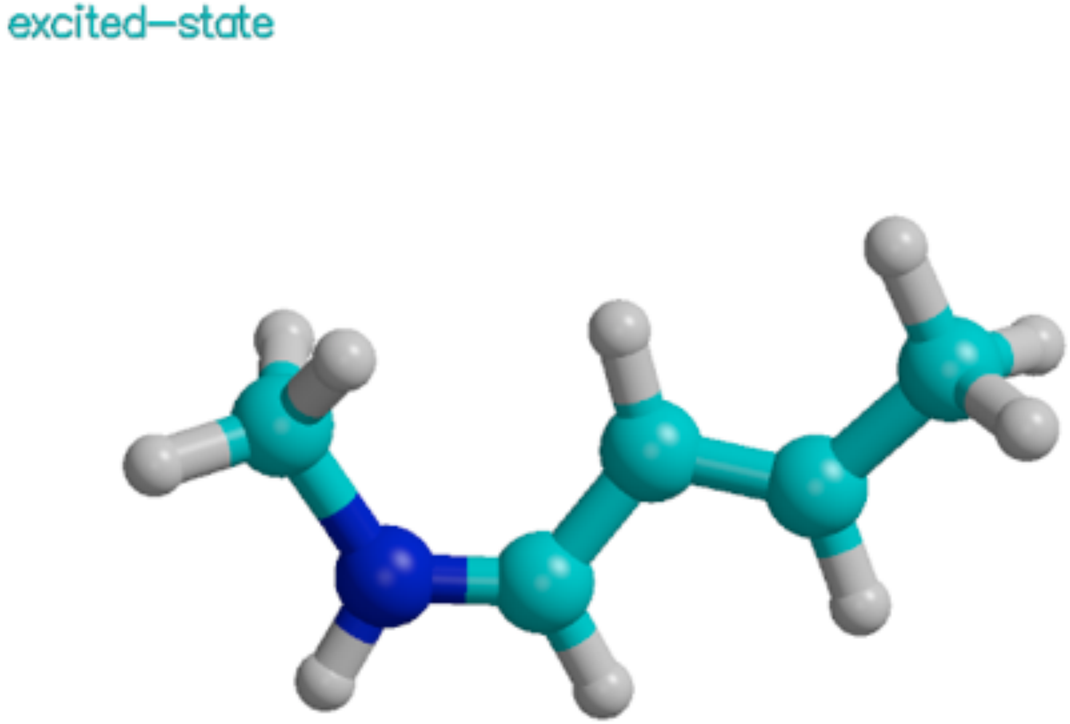

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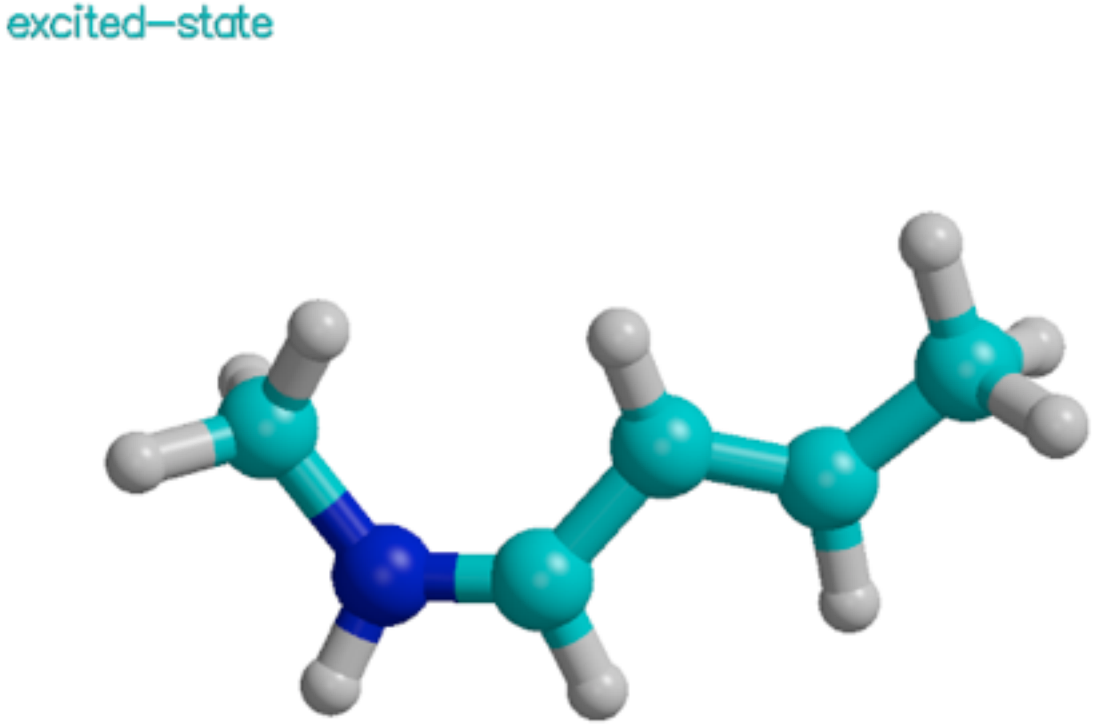


QY (both): 19.9 %/22.8%

average lifetime: 60.2 fs/54.6 fs

Non-adiabatic molecular dynamics

- classical/quantum dynamics
  - electrons: time-dependent Schrödinger equation
  - nuclei: Newton equation
- Ehrenfest dynamics
  - mean field: state-averaged adiabatic surface
- surface hopping
  - diabatic hopping
  - Tully's fewest switches surface hopping
- main problem: accuracy of PES
  - excited state electronic structure

excited state electronic structure

- response based single reference methods
  - time-dependent HF
  - time-dependent DFT
    - Runge-Gross theorem
  - eom-coupled cluster
- multi-configuration methods
  - full and truncated CI
  - MCSCF
    - CASSCF, RASSCF
- multi-reference approaches
  - MRCI(SD)
  - CASPT2
- quantum Monte Carlo

excited state electronic structure

response based single reference methods

time-dependent HF

time-dependent DFT

Runge-Gross theorem

eom-coupled cluster

gradients

non-adiabatic coupling

multi-configuration methods

full and truncated CI

MCSCF

CASSCF, RASSCF

gradients

non-adiabatic coupling

S_1/S_0 degeneracy

multi-reference approaches

MRCI(SD)

CASPT2

gradients

non-adiabatic coupling

S_1/S_0 degeneracy

quantum Monte Carlo

S_1/S_0 degeneracy

excited state electronic structure

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Fock operator

$$f_{ij} = \langle\phi_i(\mathbf{r}_1)|h(\mathbf{r}_1)|\phi_j(\mathbf{r}_1)\rangle + \sum_k \left\langle \phi_i(\mathbf{r}_1)\phi_k(\mathbf{r}_2) \left| \frac{2-\hat{p}_{12}}{|\mathbf{r}_1-\mathbf{r}_2|} \right| \phi_k(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \right\rangle$$

basisset

$$\phi_i(\mathbf{r}_1) = \sum_\alpha c_{i\alpha}\chi_\alpha(\mathbf{r}_1)$$

$$\hat{f} = h + \frac{1}{2}\sum_\lambda\sum_\sigma P_{\lambda\sigma}\left\langle \chi_\sigma \left| \frac{2-\hat{p}_{12}}{|\mathbf{r}_1-\mathbf{r}_2|} \right| \chi_\lambda \right\rangle$$

density matrix

$$P_{\mu\nu} = 2\sum_a^{\frac{1}{2}n_e} c_{\mu a}c^*_{\nu a}$$

iterative self-consistent solution procedure

excited state electronic structure

- restricted Hartree Fock in nutshell
  - one particle, mean field theory
    - Slater determinant

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

- electron-electron correlation
  - static correlation
    - large separation of electrons in pair
    - near degeneracies: different spatial wavefunctions
    - multi-configuration SCF
  - dynamic correlation
    - short distance: cusp
    - not so dependent on orbitals/density
    - perturbation theory
  - simple distinction not always possible

excited state electronic structure

configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

expansion of coefficients in one-electron functions

$$a(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

so that

$$\phi(x_1, x_2) = \sum_i \sum_j b_{ij} \chi_i(x_1) \chi_j(x_2)$$

excited state electronic structure

configuration interaction

functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} \left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]$$

in determinants

$$\phi(x_1, x_2) = \sum_i \sum_j \frac{1}{\sqrt{2}} b_{ij} \det\left[\chi_i(x_1)\chi_j(x_2)\right]$$

in general

n-electron wavefunction

$$\Psi_i = \sum_j C_{ij}\psi_j = C_{i0}\psi_0 + \sum_{ra} C_{ia}^{r}\psi_a^r + \sum_{\substack{a\,<\,b\\ r\,<\,s}} C_{iab}^{rs}\psi_{ab}^{rs} + \ldots$$

excited state electronic structure

- full configuration interaction
  - exact solution (within finite basisset)

$$\Psi_i = \sum_j C_{ij}\psi_j = C_{i0}\psi_0 + \sum_{ra} C_{ia}^{r}\psi_a^{r} + \sum_{\substack{a<b\\ r<s}} C_{iab}^{rs}\psi_{ab}^{rs} + \ldots$$

- truncated configuration interaction
  - CISingles
    - excited states (higher roots)
    - no correlation in ground state
  - CISinglesDoubles
    - stronger correlation in ground state
  - CISinglesDoublesTriples
    - stronger correlation in excited states than in ground state
  - ...
    - too expensive: number of configurations blows up

excited state electronic structure

- truncated configuration interaction
  - CISingles, Double, Triples ...
    - systematic
    - number of configurations blows up
- multi-configuration SCF
  - multiple configurations
    - free to choose, not black box!
    - optimize both CI and MO coefficients
  - basis for higher level methods
    - MultiReferenceCI

$$\Psi_i = \sum_{j}^{M} C_{ij}\psi_j .$$

Slater

single excitations

double excitations

$$\Phi = \sum_I (K_I\Psi_I + \sum_{i,a} K_{Iia}\Psi_{Iia} + \sum_{i,a,j,b} K_{Iiajb}\Psi_{Iiajb} + \dots)$$

a root in MCSCF

of Slaters in each configuration in root

excited state electronic structure

- truncated configuration interaction
  - CISingles, Double, Triples ...
    - systematic
    - number of configurations blows up
- multi-configuration SCF
  - multiple configurations
    - free to choose, not black box!
    - optimize both CI and MO coefficients
  - basis for higher level methods
    - MultiReferenceCI
    - perturbation theory: CASPT2

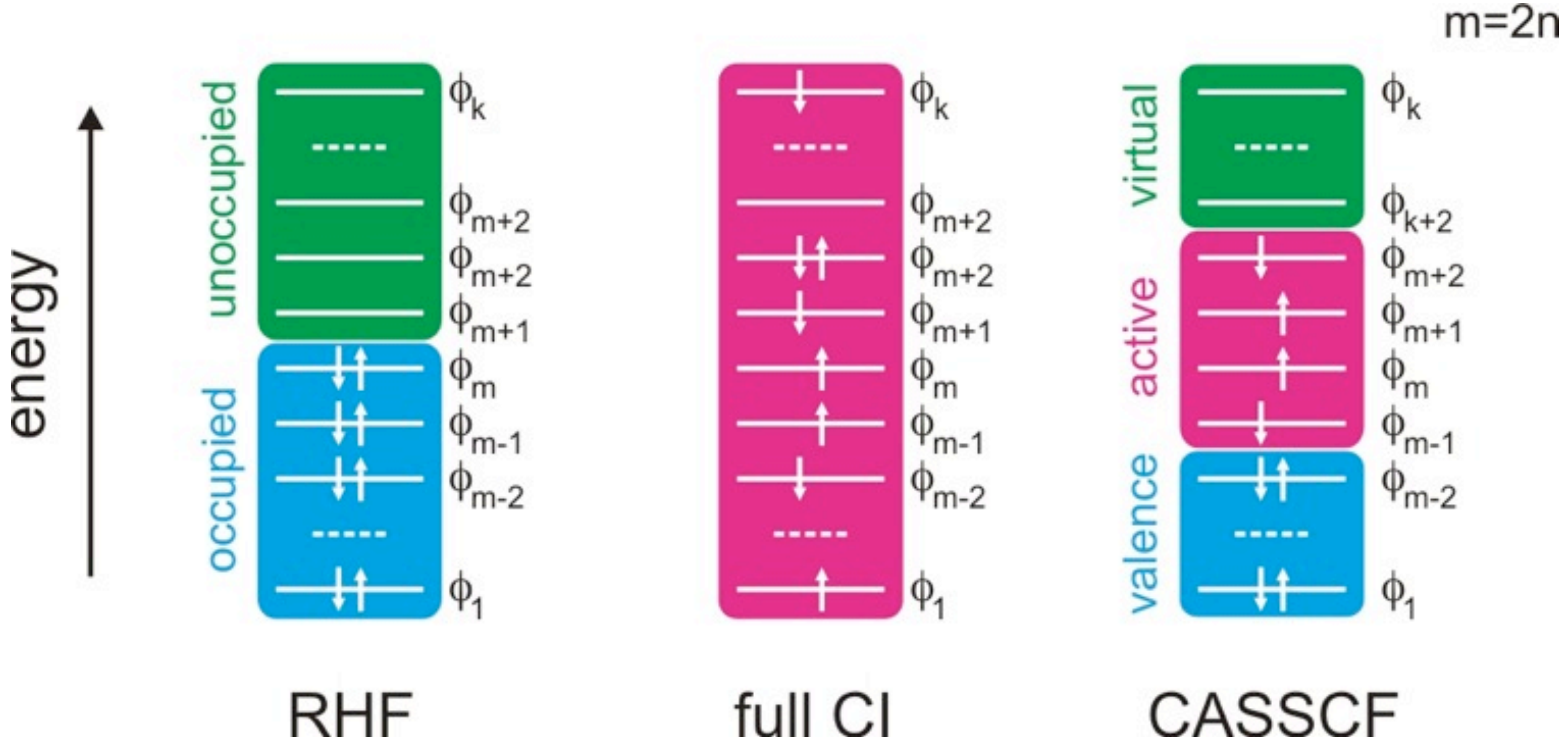
$$\Psi_i = \sum_j^M C_{ij}\psi_j.$$

$$\Phi = \sum_I (K_I \Psi_I + \sum_{i,a} K_{Iia}\Psi_{Iia} + \sum_{i,a,j,b} K_{Iiajb}\Psi_{Iiajb} + \dots)$$

excited state electronic structure

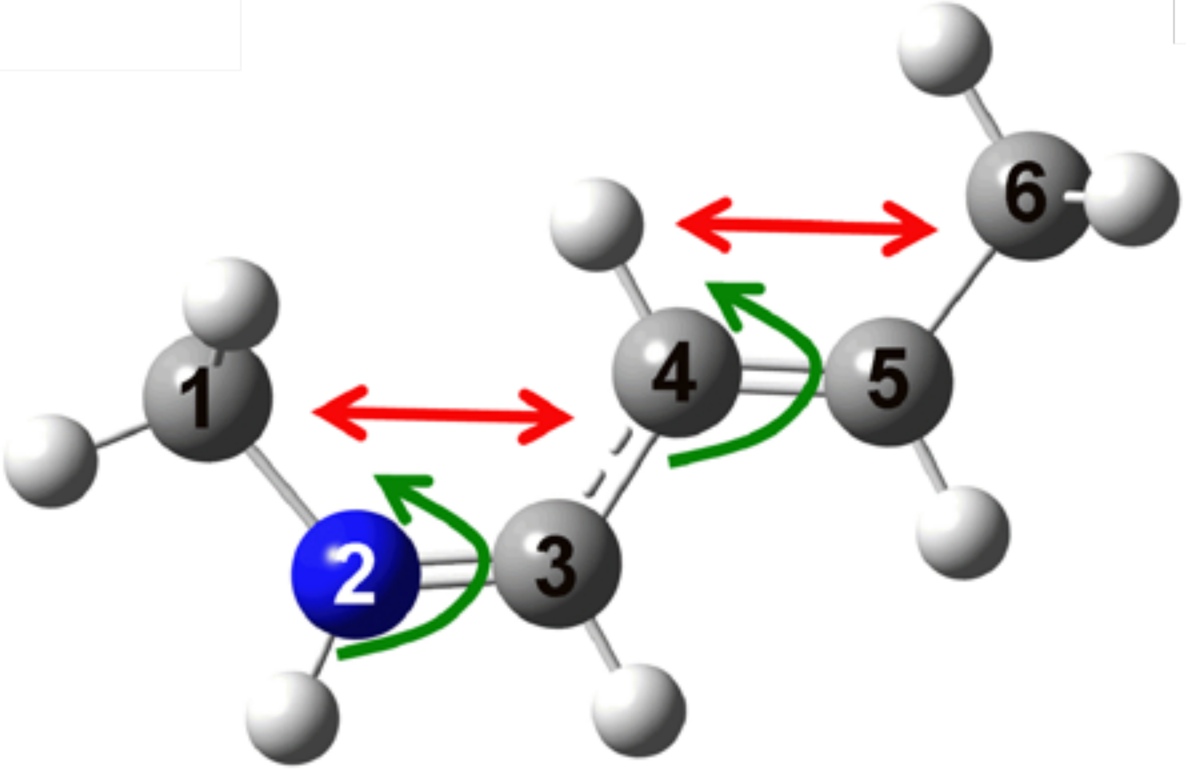
multi-configuration SCF

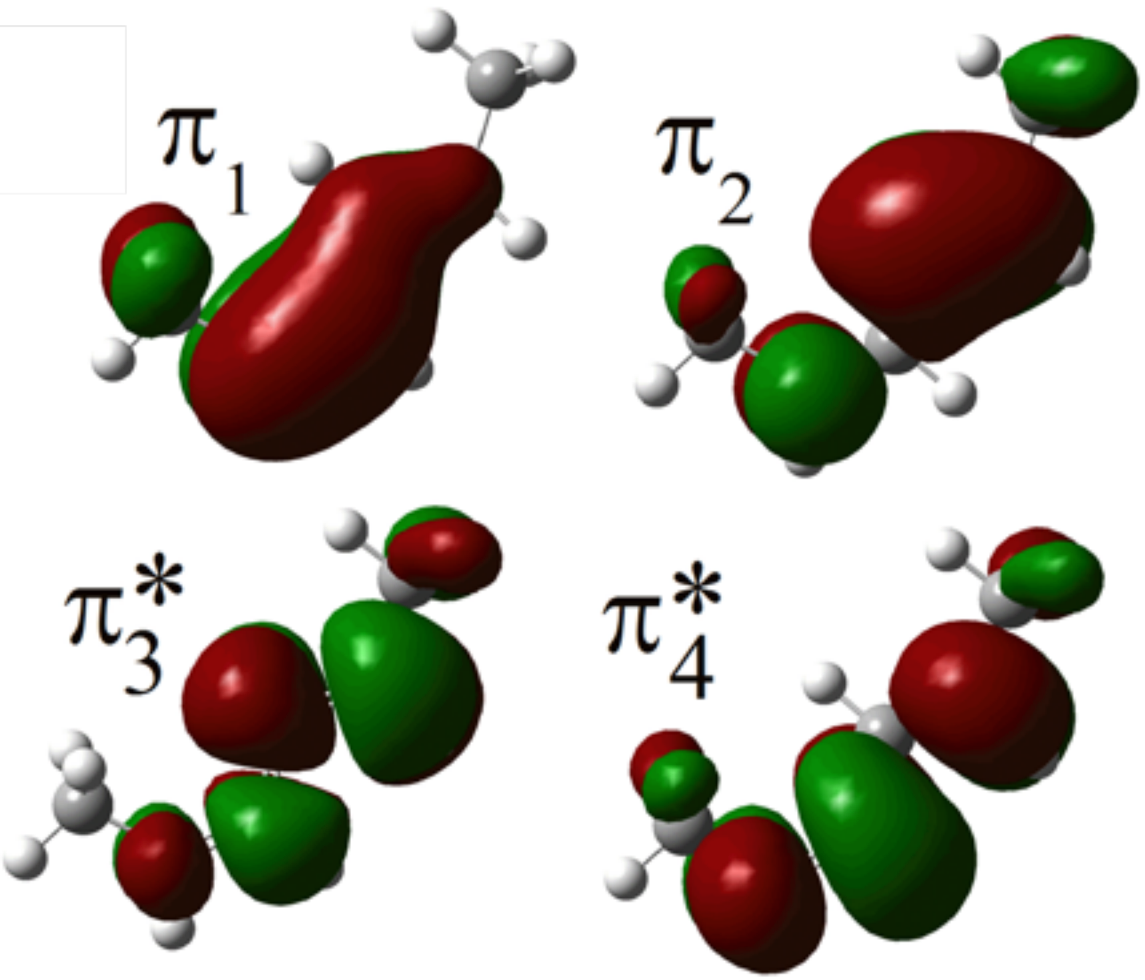
- multiple configurations
  - free to choose
  - not black box
- Complete Active Space SCF
  - select orbitals for full CI



excited state electronic structure

- multi-configuration SCF
  - Complete Active Space SCF
    - select electrons and orbitals for full CI (HF, NBO)
    - knowledge/intuition/luck/good co-workers
  - example
    - protonated schiff base
    - CAS(4,4) with all π orbitals





excited state electronic structure

CASSCF

- recovers static correlation
  - near degeneracy
- excited states
  - optimize second root in CI
  - problem: need expectation values involving both states

$$\langle \psi_{S_0} | \nabla_{\mathbf{R}} H | \psi_{S_1} \rangle$$

  - problem: root flipping
- state average CASSCF
  - same molecular orbitals for all states
  - optimize the weighted average energy

$$E^{\mathrm{SA}} = \sum_i \omega_i E_i$$

  - average density matrix

excited state electronic structure

SA-CASSCF

same molecular orbitals for all states

sometimes orbitals change drastically upon excitation

wavefunction is not variational minimum

$$\begin{aligned}\nabla_{\mathbf{R}}E &= \nabla_{\mathbf{R}}\langle\psi|H|\psi\rangle \\ &= \langle\nabla_{\mathbf{R}}\psi|H|\psi\rangle + \langle\psi|\nabla_{\mathbf{R}}H|\psi\rangle + \langle\psi|H|\nabla_{\mathbf{R}}\psi\rangle\end{aligned}$$

$$\begin{aligned}\langle\nabla_{\mathbf{R}}\psi|H|\psi\rangle = & \langle\nabla_{\mathbf{c}_{\mathrm{MO}}}\psi|H|\psi\rangle\nabla_{\mathbf{R}}\mathbf{c}_{\mathrm{MO}} + \\ & \langle\nabla_{\mathbf{c}_{\mathrm{CI}}}\psi|H|\psi\rangle\nabla_{\mathbf{R}}\mathbf{c}_{\mathrm{CI}} +\end{aligned}$$

excited state electronic structure

SA-CASSCF

quantities for surface hopping

expression for non-adiabatic coupling

$$\mathbf{F}_{ij}(\mathbf{R}) = \frac{\mathbf{h}_{ij}(\mathbf{R})}{V_i - V_j} + \sum_{a,b} c^*_{ia}(\mathbf{R}) c_{jb}(\mathbf{R}) \langle \psi_a | \nabla_{\mathbf{R}} \psi_b \rangle$$

$$\mathbf{h}_{ij}(\mathbf{R}) = \mathbf{C}_i^\dagger(\mathbf{R}) \nabla_{\mathbf{R}} \mathbf{H}^{\mathrm{cf}} \mathbf{C}_j(\mathbf{R})$$

$$\nabla_{\mathbf{R}} H^{\mathrm{cf}}_{ab}(\mathbf{R}) = \nabla_{\mathbf{R}} \langle \psi_a | H^e(\mathbf{r}, \mathbf{R} | \psi_b \rangle$$

expression for diabatic hop

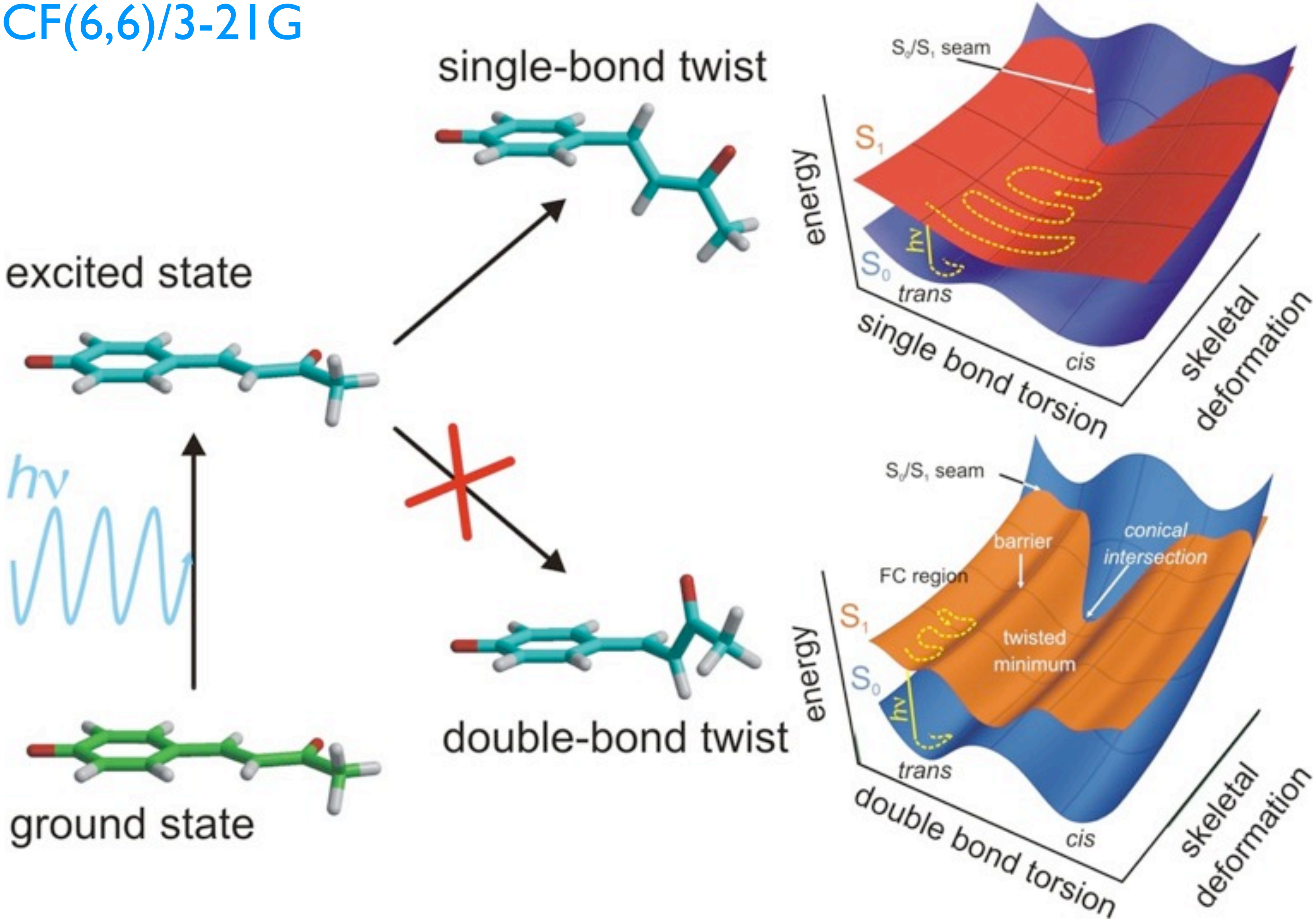
$$\langle \psi_1(t) | \psi_2(t + \Delta t) \rangle = \mathbf{C}_1^t \cdot \mathbf{C}_2^{t+\Delta t}$$

Validation of quantum chemistry method

effect of level of theory on S_1 surface

isolated pCK$^-$ chromophore

SA-CASSCF(6,6)/3-21G



Validation of quantum chemistry method

effect of level of theory on S_1 surface

isolated pCK$^-$ chromophore

	level of theory	SB barrier (kJ/mol)	DB barrier(kJ/mol)
	CASSCF(6,6)/3-21G	0.0	3.810
	CASSCF(12,11)/6-31G(d)	0.007	9.442
	CASSCF(12,11)/aug-cc-pVDZ	2.175	5.665
!	CASPT2/aug-cc-pVDZ	0.778	28.592
!	EOM-CCSD/aug-cc-pVDZ	3.859	14.698

consistent: PES seem qualitative correct

competing processes: barrier heights critical for branching!

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