# Excited-State Coupled Electronic-Structural Dynamics of Molecular Systems with DynEMol

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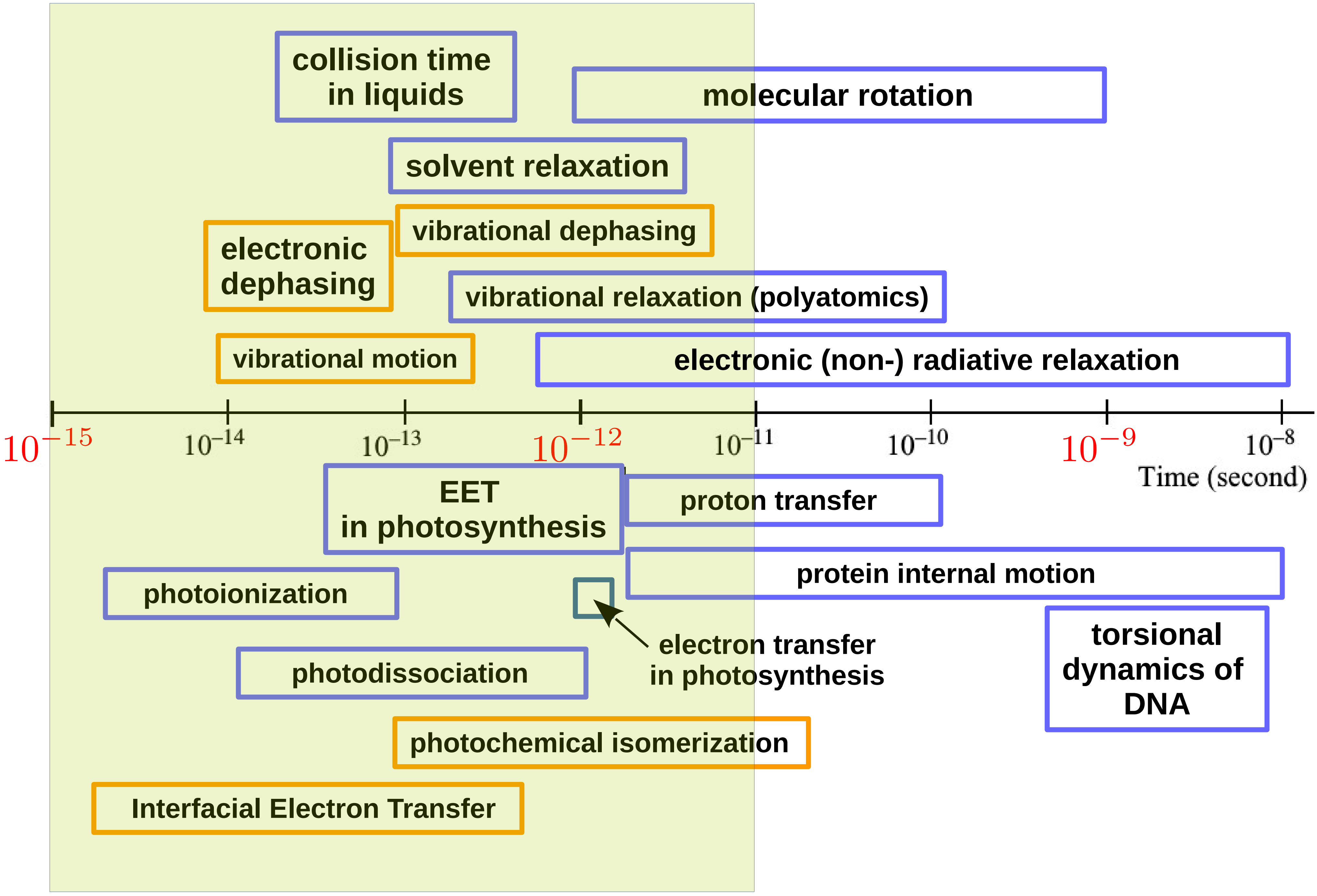


collision time in liquids

molecular rotation

solvent relaxation

vibrational dephasing

electronic dephasing

vibrational relaxation (polyatomics)

vibrational motion

electronic (non-) radiative relaxation

EET in photosynthesis

proton transfer

protein internal motion

photoionization

electron transfer in photosynthesis

torsional dynamics of DNA

photodissociation

photochemical isomerization

Interfacial Electron Transfer

Adapted from G.R. Fleming & P.G. Wolynes, Phys. Today (1990), vol. 43, p. 36

# DynEMol
# (Dynamics of Electrons in Molecules)

- *Motivation*
  - Self-Consistent Quantum-Classic Method for excited-state dynamics of Molecular and Extended Systems

- *Applications*
  - Intramolecular Vibration Relaxation (IVR)
  - Photoinduced Isomerization
  - Photoinduced Proton Transfer
  - Interfacial Electron Transfer
  - Spin Dynamics Effects

# Theoretical Method and Models

**Our goal:**

Modelling electron quantum dynamics in large molecular systems

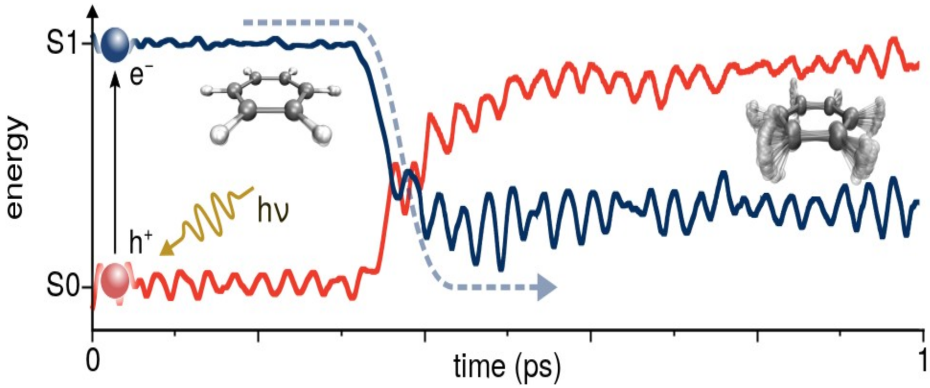
| | | |
|---|---|---|
| $< 10^2$ atoms | $10^2 - 10^4$ atoms | $\gg 10^4$ atoms |
| small to medium size | large size | Very large size |
| First principles<br>Quantum Mechanics<br>Molecular Dynamics | Quantum & Classical regimes | Classical Dynamics |
| $\tau \lesssim$ few picoseconds | $\tau < 10^2$ picoseconds | $\tau > 10^2$ picoseconds |

- Combines:

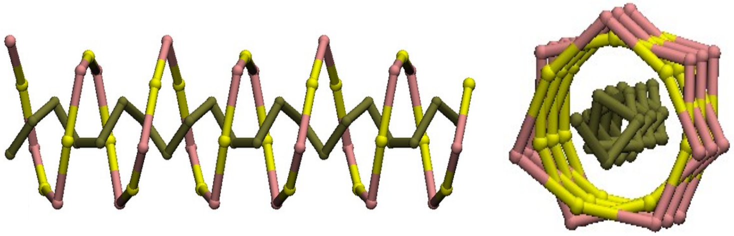
  Molecular Mechanics and tight-binding semi-empirical methods

- Wavepacket propagation of charge excitation

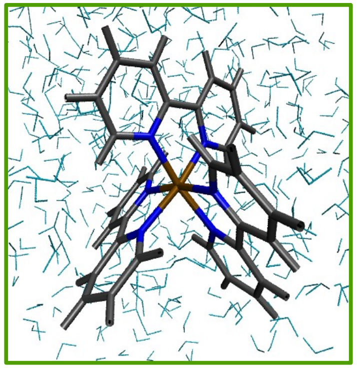
# Nonadiabatic Excited-State Dynamics with *Dynemol*



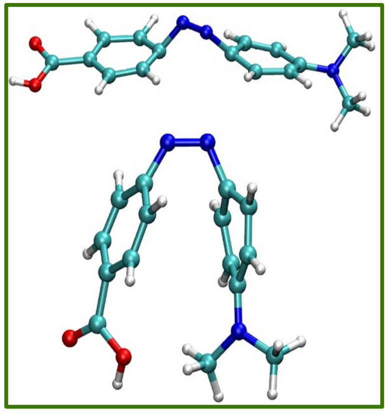
JPC-C 2016, **120**, 27688.



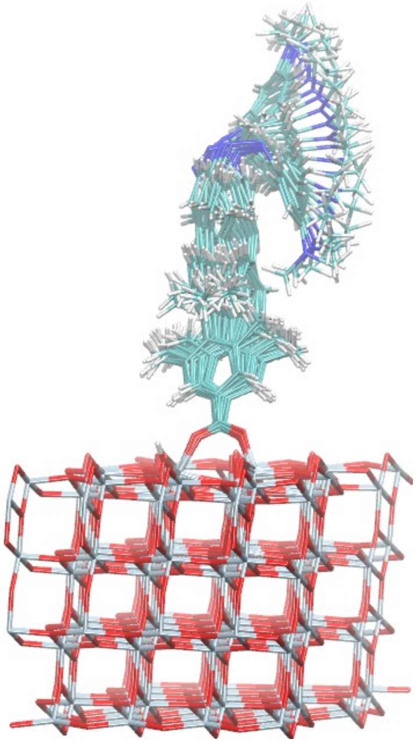
Nano Lett. 2021, 21, 8190.



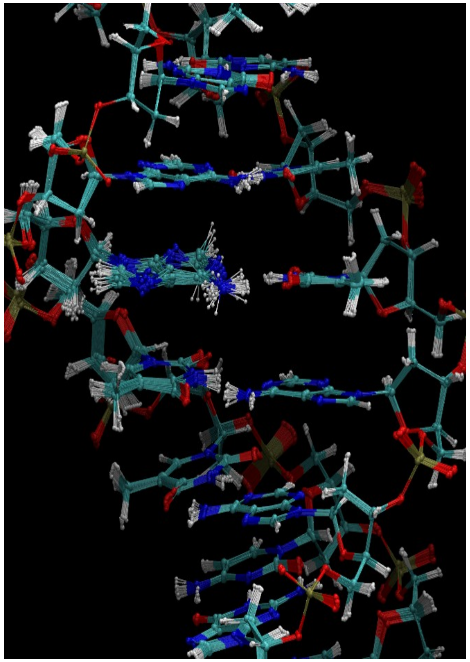
JPC-C 2011, **115**, 15617.



JPC-C, 2016, **120**, 27688.
JPC-L, 2018, **9**, 5926.



JPC-L, 2015, **6**, 4927.
JPC-C, 2019,**123**, 5692.



Effects of UV radiation
on DNA strands

# Quantum Dynamics of Electrons and Nuclei

Time-dependent *Schrödinger* equation (1926):

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(r,R,t)=\left[\frac{\hbar^2}{2m}\nabla_r^2+\frac{\hbar^2}{2M}\nabla_R^2+V(r,R)\right]\Psi(r,R,t)$$

*Paul Dirac* (1928):

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

# The electron-nucleus problem in molecular structures

Molecular Schrödinger Equation:

$$\hat{H}_{mol}(r,R)\Psi(r,R) = E\Psi(r,R)$$

$$\hat{H}_{mol}(r,R) = \hat{T}_e(r) + V_{eN}(r,R) + V_{ee}(r) + \hat{T}_N(R) + V_{NN}(R)$$

$$\hat{T}_N = \sum_{n}^{N_{nuc}} \frac{P_j^2}{2M_n} \qquad V_{NN} = \frac{1}{2}\sum_{n\neq m} \frac{Z_n Z_m e^2}{|\vec{R}_n - \vec{R}_m|} \qquad V_{eN} = -\sum_{j,n} \frac{Z_n e^2}{|\vec{r}_j - \vec{R}_n|}$$

$$\hat{T}_e = \sum_{j}^{N_e} \frac{p_j^2}{2m_e} \qquad V_{ee} = \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

The total Hamiltonian:

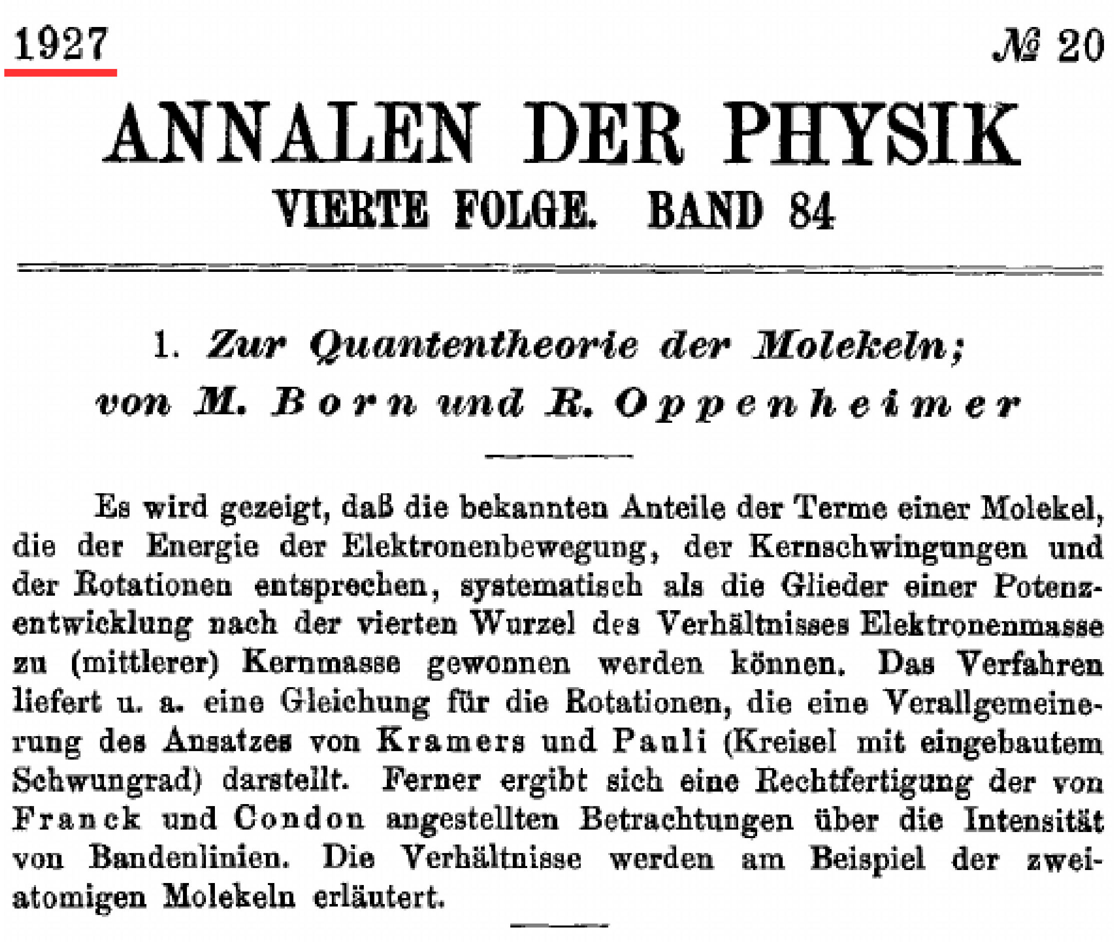
$$\hat{H} = \hat{H}_{el} + \hat{H}_{ph} + \hat{H}_{el-ph} = \sum_{\kappa} E_\kappa b_\kappa^\dagger b_\kappa + \sum_{\alpha}\left(\hat{n}_\alpha + \frac{1}{2}\right)\hbar\omega_\alpha + \hat{V}_{el-ph}$$

rigorous solution:

$$|\Psi\rangle = \sum_{\kappa,\mathbf{n}} C_{\kappa,\mathbf{n}} \left[ |\Phi_\kappa\rangle \prod_{\alpha=1}^{N} \frac{1}{\sqrt{n_\alpha !}} \left(a_\alpha^\dagger\right)^{n_\alpha} |0\rangle \right]$$

where $|\Phi_\kappa\rangle$ is a Slater determinant and $\mathbf{n} \equiv (n_1, n_2, \cdots, n_N)$

# The electron-nucleus problem in molecular structures:
# Born-Oppenheimer (Adiabatic) Approximation



1927 № 20

ANNALEN DER PHYSIK

VIERTE FOLGE. BAND 84

1. *Zur Quantentheorie der Molekeln;*

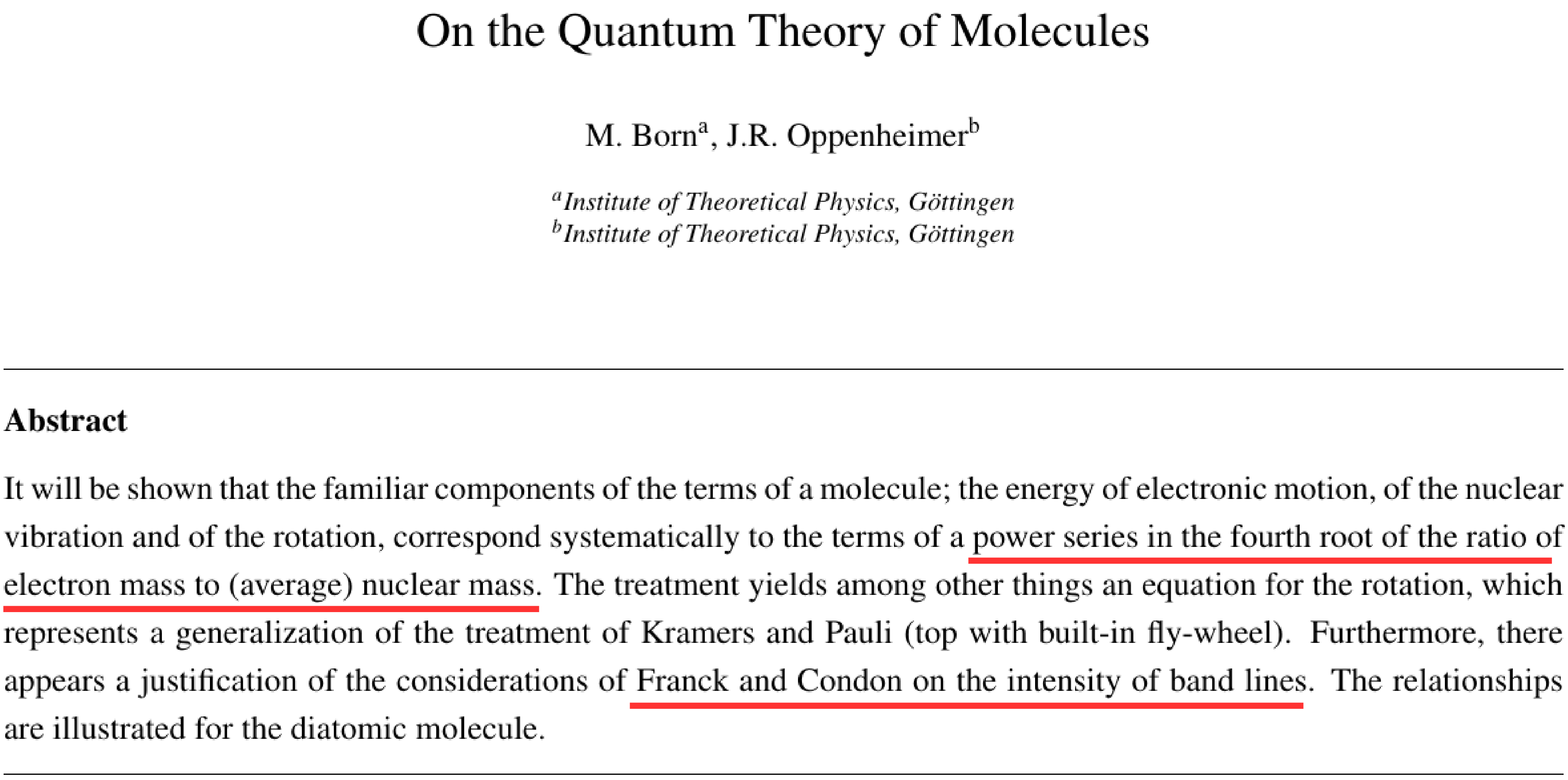
*von M. Born und R. Oppenheimer*

Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel, die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von Kramers und Pauli (Kreisel mit eingebautem Schwungrad) darstellt. Ferner ergibt sich eine Rechtfertigung der von Franck und Condon angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Molekeln erläutert.

Historical note, the band theory of crystals appeared in 1928:

“On the quantum mechanics of electrons in crystal lattices”, Felix Bloch (1928)

# The electron-nucleus problem in molecular structures: Born-Oppenheimer (Adiabatic) Approximation



## On the Quantum Theory of Molecules

M. Born[a], J.R. Oppenheimer[b]

[a] *Institute of Theoretical Physics, Göttingen*
[b] *Institute of Theoretical Physics, Göttingen*

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**Abstract**

It will be shown that the familiar components of the terms of a molecule; the energy of electronic motion, of the nuclear vibration and of the rotation, correspond systematically to the terms of a power series in the fourth root of the ratio of electron mass to (average) nuclear mass. The treatment yields among other things an equation for the rotation, which represents a generalization of the treatment of Kramers and Pauli (top with built-in fly-wheel). Furthermore, there appears a justification of the considerations of Franck and Condon on the intensity of band lines. The relationships are illustrated for the diatomic molecule.

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# The electron-nucleus problem in molecular structures: Born-Oppenheimer (Adiabatic) Approximation

It is, in principle, an extremely complex problem,

$$\hat{H}_{mol}(r, R)\Psi(r, R) = E\Psi(r, R)$$

Therefore one has to make approximations; the most important one is the separation of electronic and nuclear degrees of freedom

based on the fact that $\mathrm{M}_n \gg m_e \Rightarrow v_n \ll v_e$

So, nuclear dynamics is put aside for the electronic dynamics.

Start by treating the nuclear momenta (P) and coordinates (R) as classical variables. The electronic problem becomes

$$\begin{aligned}\left(\hat{T}_e(r) + V_{ee}(r) + V_{eN}(r, R) + V_{NN}(R)\right)\psi_a(r; R) &= \varepsilon_a\psi_a(r; R) \\ \left(\hat{T}_e(r) + V_{ee}(r) + V_{eN}(r, R)\right)\psi_a(r; R) &= \left(\varepsilon_a - V_{NN}\right)\psi_a(r; R)\end{aligned}$$

Potential Energy Surface (PES): $U_a(R) \equiv \varepsilon_a(R) - V_{NN}(R)$

Potential energy landscape for the electrons in the approximation that nuclear dynamics is "decoupled" from electronic dynamics.

$\psi_a(r, R) = \langle r, R|\psi_a\rangle$ is called the adiabatic electronic wavefunction

# Dynamics on the Potential Energy Surfaces (PES)

A general state of the combined (electronic+nuclei) system can be expanded in terms of the instantaneous (adiabatic) states of $\hat{H}_{el}(r,R)$ as

$$\Psi(r;R) = \textstyle\sum_a \chi_a(R)\psi_a(r,R)$$

In the Born-Oppenheimer Approximation:

$$\Psi(r;R) \approx \chi_a(R,t)\psi_a(r;R)$$

Substitute the BO product state into the TDSE, multiply from left by $\psi_a^*(r;R)$ and integrate over $r$

$$i\hbar\frac{\partial}{\partial t}\chi_a(R,t) = \langle\psi_a|\hat{H}_{el}|\psi_a\rangle\chi_a(R,t) - \sum_n \frac{\hbar^2}{2M_n}\langle\psi_a(r;R)|\nabla_n^2\psi_a(r;R)\chi_a(R,t)\rangle$$

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\chi_a(R,t) &= \varepsilon_a(R)\chi_a(R,t) \\ &- \sum_n \frac{\hbar^2}{2M_n}\left[\langle\psi_a|\psi_a\rangle\nabla_n^2 + 2\langle\psi_a|\nabla_n\psi_a\rangle\nabla_n + \langle\psi_a|\nabla_n^2\psi_a\rangle\right]\chi_a(R,t)\end{aligned}$$

# Dynamics on the Potential Energy Surfaces (PES)

Born-Oppenheimer Approximation:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\chi_a(R,t) &= \varepsilon_a(R)\chi_a(R,t) \\ &- \sum_n \frac{\hbar^2}{2M_n}\left[\langle\psi_a|\psi_a\rangle\nabla_n^2 + 2\langle\psi_a|\nabla_n\psi_a\rangle\nabla_n + \langle\psi_a|\nabla_n^2\psi_a\rangle\right]\chi_a(R,t) \end{aligned}$$

For systems in stationary state without magnetic fields $\psi_a(r;R) \in \mathbb{R}$ ;

and $\nabla_n\langle\psi_a|\psi_a\rangle = \langle\nabla_n\psi_a|\psi_a\rangle + \langle\psi_a|\nabla_n\psi_a\rangle = 0$ .

Therefore $\langle\nabla_n\psi_a|\psi_a\rangle = -\langle\psi_a|\nabla_n\psi_a\rangle = 0$ .

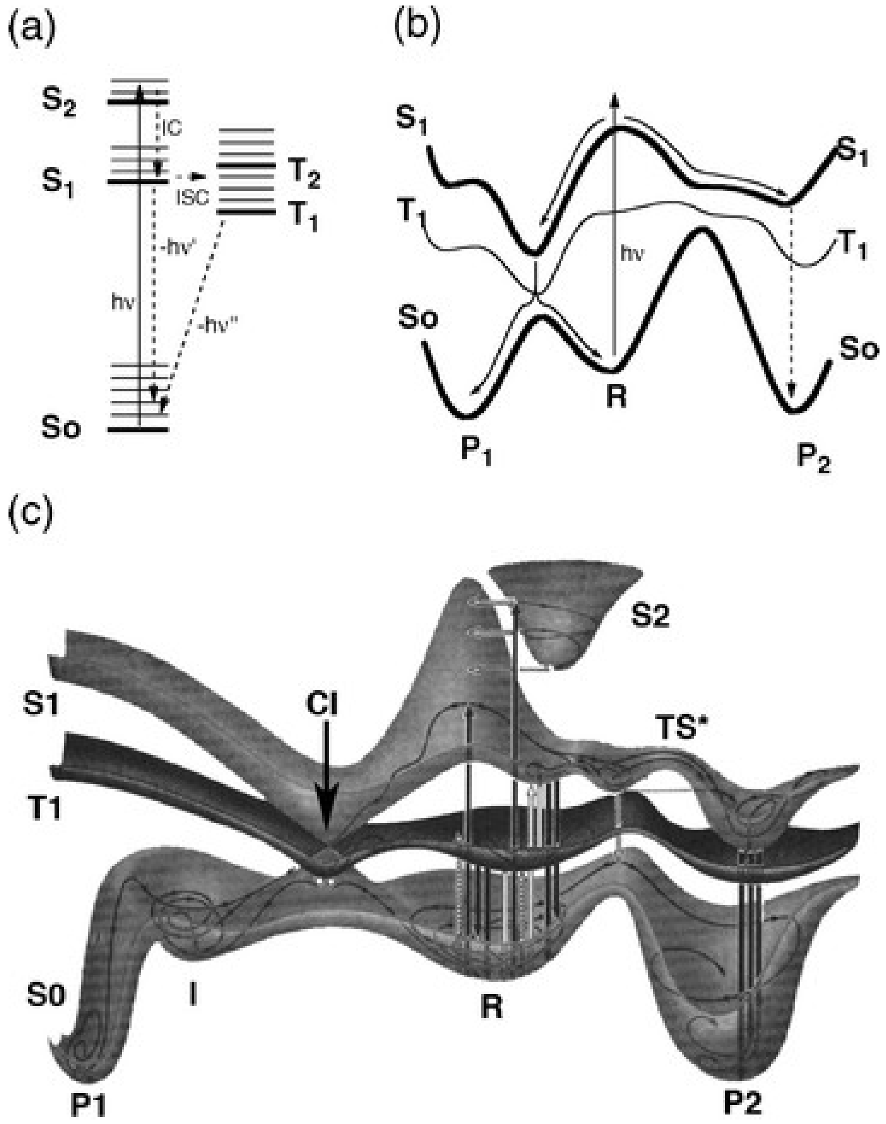
$\langle\psi_a|\nabla_n^2\psi_a\rangle\chi(R,t)$ is generally disregarded for being a small term.

Thus we end up with the following TDSE for the nuclei in the PSE given by

$$i\hbar\frac{\partial}{\partial t}\chi_a(R,t) = -\sum_n \frac{\hbar^2}{2M_n}\nabla_n^2\chi_a(R,t) + \varepsilon_a(R)\chi_a(R,t)$$

with $\varepsilon_a(R) = \langle\psi_\alpha|\hat{H}_{el}(r,R)|\psi_\alpha\rangle$

# Potential Energy Surfaces (PES)
# photoinduced dynamics



(a) Jablonski diagram,

(b) reaction coordinate,

(c) Potential Energy Surface (PES)

Sn = singlet states

S0 = ground state

Tn = triplet states

L1 = lowest triplet

R = reactant state

Pn = product states

I = intermediary state (metastable)

hν = photon energy

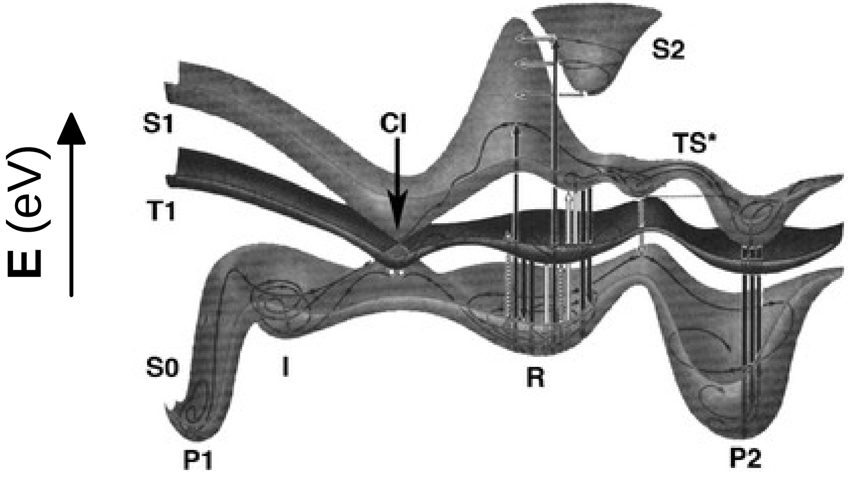
TS = transition state

CI = conical intersection (*diabolic intersection*)

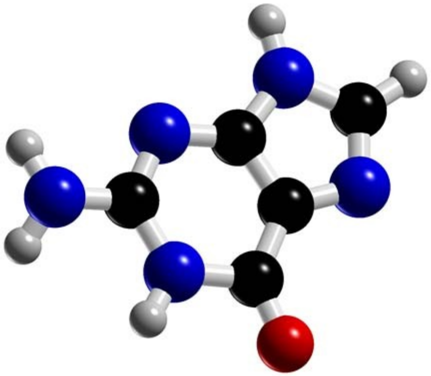
ISC – inter-system crossing

Photochem. Photobiol. Sci., 2010, 9, 1574.

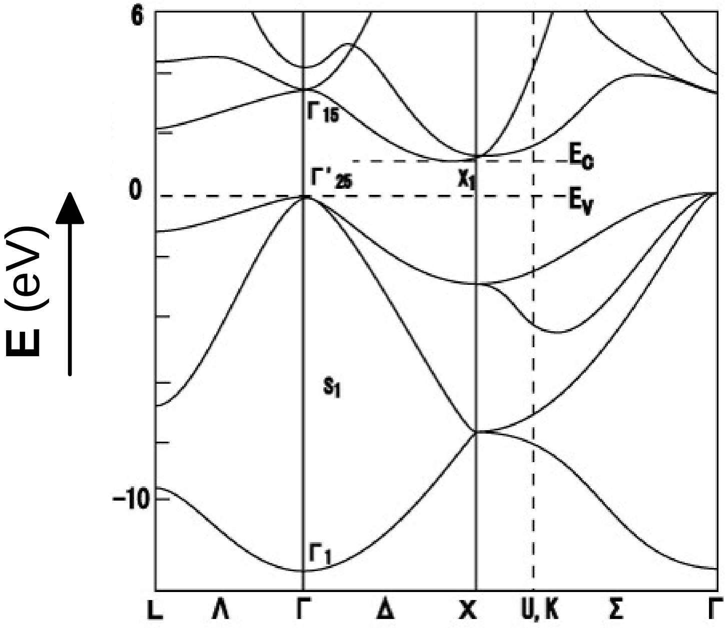
# Potential Energy Surface (PES) *vs* Electronic Band Structure



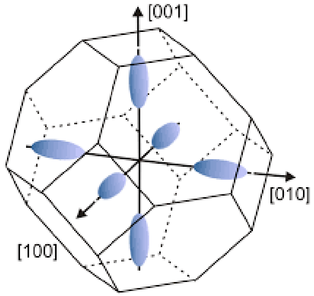
Reaction Coordinate, ***Q***



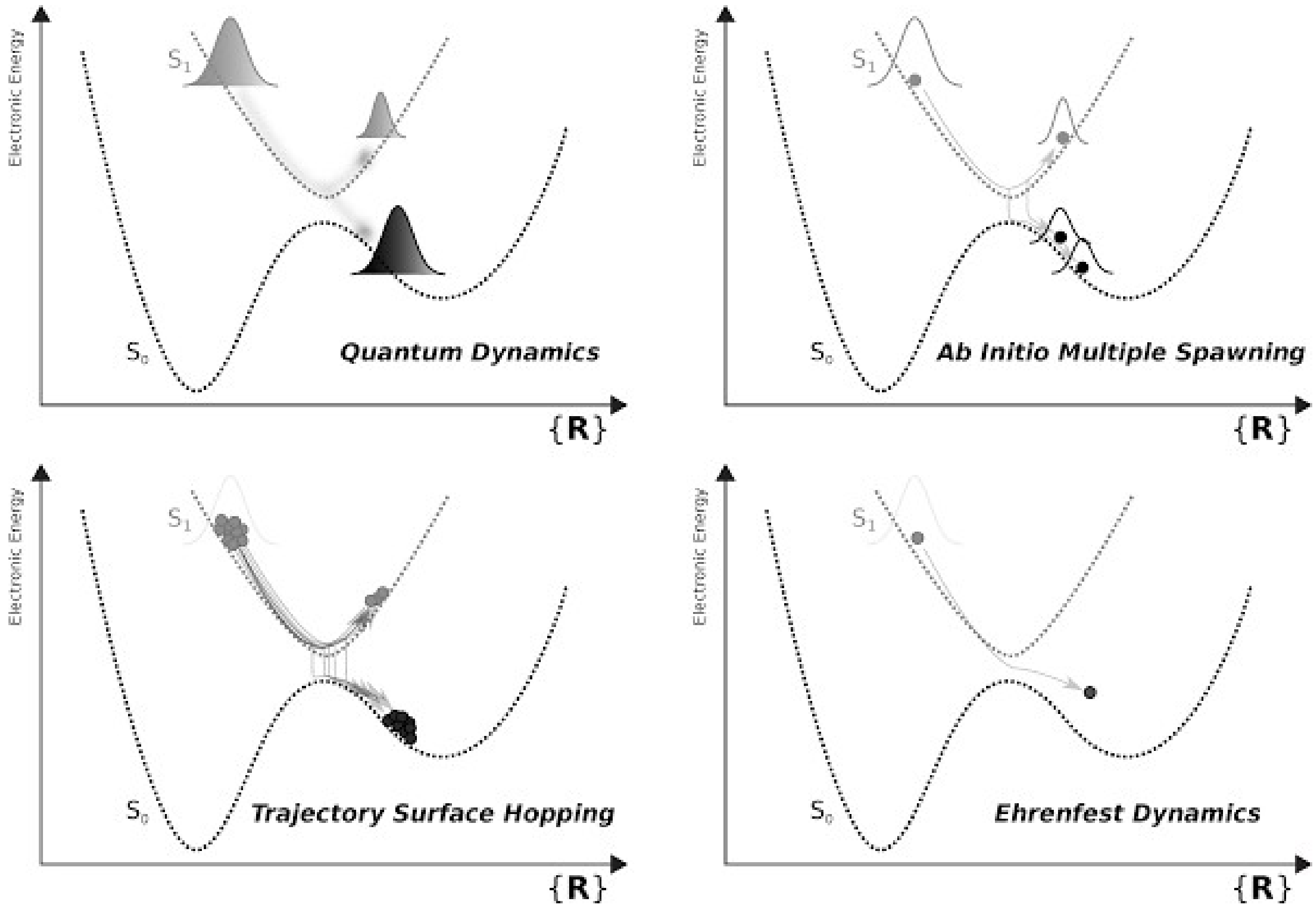
Si electronic band structure



Wavevector, ***k***



# Methodologies of Non-adiabatic Molecular Dynamics



B. F. E. Curchod, U. Rothlisberger, and I. Tavernelli. ChemPhysChem 2013, 14, 1314-1340

# Trajectory based Quantum-Classical Hybrid Methods

Assume two particles:

- the light particle with mass ***m*** and coordinates ***r***
- the heavy particle with mass ***M*** and coordinate ***R***

The Schrödinger equation for these particles is:

$$i\hbar\frac{\partial}{\partial t}\Psi = \left(-\frac{\hbar^2}{2m}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_R^2 + V(r,R)\right)\Psi$$

The ***Ehrenfest Theorem*** yields operator R and P of the heavy particle :

$$\begin{aligned} \frac{d}{dt}\langle R\rangle &= \langle P\rangle/M\ , \qquad \hat{P} = -i\hbar\nabla_R \\ \frac{d}{dt}\langle P\rangle &= -\langle\nabla_R V\rangle \end{aligned}$$

with $\langle\nabla_R V\rangle = \int (\nabla_R V(r,R))\,|\Psi(r,R,t)|^2\ dr dR$

$\langle R\rangle$ and $\langle P\rangle$ are the position and momentum of the heavy particle wavepacket.

Derivation of Quantum-Classical MD equations of motion for R and P

$$\langle\nabla_R V\rangle \cong \langle\psi, \nabla_R V(r,\langle R\rangle)\psi\rangle$$

# Trajectory based Quantum-Classical Hybrid Methods

Derivation of Quantum-Classical MD equations of motion for R and P.

- F.A. Bornemann, P. Nettesheim, C. Schütte. J. Chem. Phys. 105, 1074 (1996)

Two approximation steps:

1) separation of electronic and nuclear wavefunctions $\Longrightarrow \mathcal{O}(\epsilon/L)$
2) short wavelength limit for the nuclei dynamics $\Longrightarrow \mathcal{O}(\sqrt{m/M})$

Assuming the separable wavefunction $\Psi(r,R,t)_{\otimes} = \psi(r,t)\chi(R,t)$

$\rightarrow$ $\psi(r,t)$ is the electronic (light particle) wavefunction

$\rightarrow$ $\chi(r,t)$ is the nuclear (heavy particle) wavefunction

We get the TDSCF system of equations

$$\begin{aligned} i\hbar\dot{\psi} &= \left(-\tfrac{\hbar^2}{2m}\nabla_r^2 + \langle\chi, V(r,\cdot)\chi\rangle\right)\psi \\ i\hbar\dot{\chi} &= \left(-\tfrac{\hbar^2}{2M}\nabla_R^2 + \langle\psi, V(\cdot,R)\psi\rangle\right)\chi \end{aligned}$$

so that

$$i\hbar\frac{\partial}{\partial t}\Psi_{\otimes} = \left(-\frac{\hbar^2}{2m}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_R^2 + V_{\otimes}(r,R)\right)\Psi_{\otimes}$$

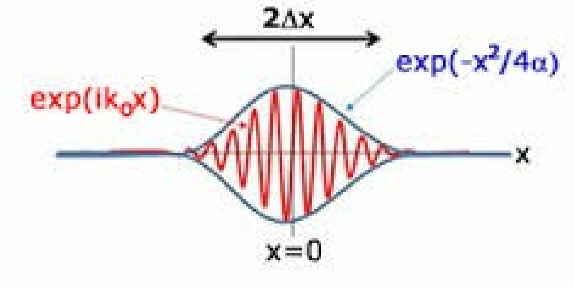
with

$$\mathrm{V}_{\otimes}(r,R) = \langle\chi, V(r,\cdot)\chi\rangle + \langle\psi, V(\cdot,R)\psi\rangle$$

# Trajectory based Quantum-Classical Hybrid Methods

Assume that $\mathrm{m} \ll M$, so that $\chi$ is an approximate $\delta$ function:

$$\chi(R,t)\,|_{t=t_0} = \frac{1}{\left(\epsilon(t)\sqrt{2\pi}\right)^{2d}} \exp\left(-\frac{|R-\langle R\rangle|^2}{4\epsilon(t)^2}\right) \exp\left(i\frac{\langle P\rangle}{\hbar}R\right)$$



Short wavelength asymptotics dynamics via WKB

$$\chi(R,t) = a(R,t)\exp\left(i\frac{S(R,t)}{\hbar}\right) + \mathcal{O}(\sqrt{m/M})$$

Hamilton-Jacobi equations render the canonical equations

$$\begin{aligned} \frac{d}{dt}\langle R\rangle &= \langle P\rangle/M \\ \frac{d}{dt}\langle P\rangle &= -\langle\psi, \nabla_R V(r,R)\psi\rangle\ , \qquad\qquad P = \nabla_R S[R(t),t] \end{aligned}$$

Thus, we get

$$\langle\nabla_R V\rangle \longrightarrow \nabla_R\langle V(r,\langle R\rangle)\rangle_r$$

$$\int (\nabla_R V(r,R))\,|\Psi(r,R,t)|^2\; dr dR \longrightarrow \int \nabla_R V(r,\langle R\rangle)|\psi(r,t;R)|^2\; dr$$

Hellmann-Feynman force if $\psi$ is an eigenstate of $H_{el}$ .

# Trajectory based Quantum-Classical Hybrid Methods

## Conservation of Energy:

The total energy of the full quantum system in the $\Psi$ state is conserved

$$E(\Psi) = \left\langle \Psi(r,R) \left| -\frac{\hbar^2}{2m}\nabla_r^2 \; - \frac{\hbar^2}{2M}\nabla_R^2 + V(r,R) \right| \Psi(r,R) \right\rangle = const$$

The Quantum-Classical separation yields:

$$E(\Psi) = \langle \psi(r;R,t) | \hat{H}_{el}(t) | \psi(r;R,t) \rangle + \frac{P(t)^2}{2M} + \Delta E_0 + \mathcal{O}(\epsilon/L + \sqrt{m/M})$$

where *L* is a typical length and

$$\hat{H}_{el}(t) = -\frac{\hbar^2}{2m}\nabla_r^2 + V(\hat{r}; R(t))$$

become a time-dependent hamiltonian for the quantum system.

$$\Delta E_0 = \frac{d\hbar^2}{8M\epsilon^2} \text{ is the self-energy of the “classical” particle.}$$

**The energy of the Quantum-Classical system conserved:**

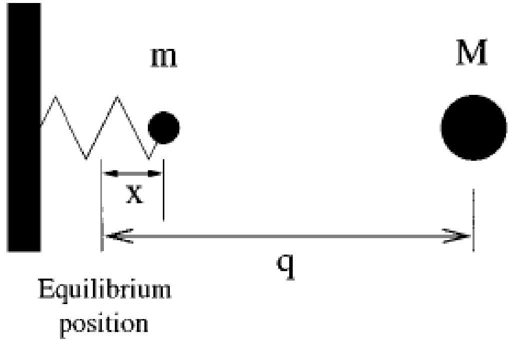
$$E_{QC} = \langle \psi(r;R,t) | \hat{H}_{el}(t) | \psi(r;R,t) \rangle + \frac{P(t)^2}{2M}$$

with the canonical equations: $\dot{R} = \frac{\partial}{\partial P} E_{QC}$ and $\dot{P} = -\frac{\partial}{\partial R} E_{QC}$

# Quantum-Classical MD: Example

F.A. Bornemann, P. Nettesheim, C. Schütte. J. Chem. Phys. 105, 1074 (1996)

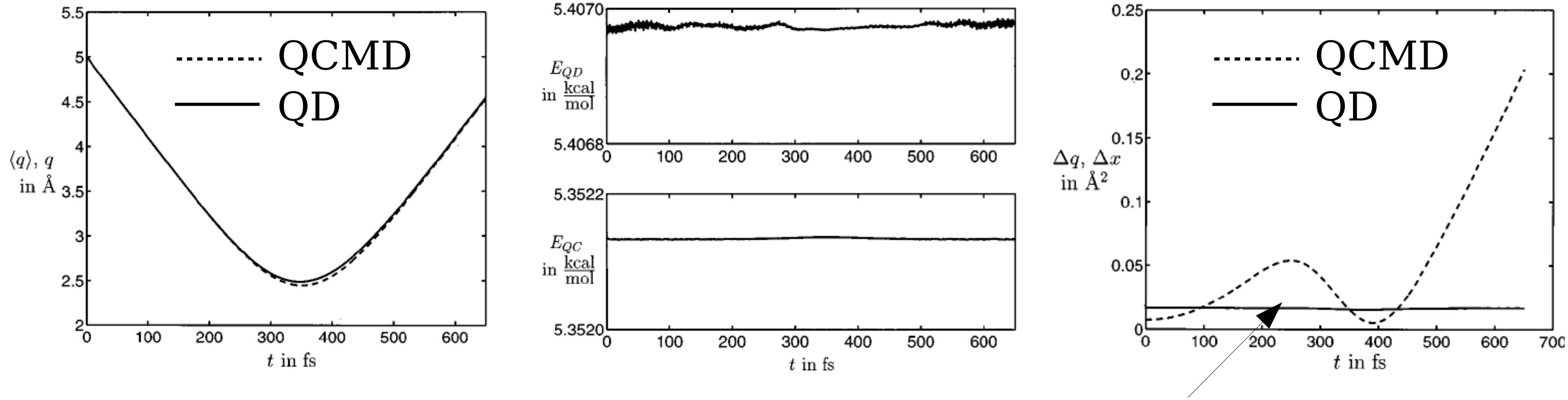
Model system



$$H = -\frac{\hbar^2}{2m}\nabla_x^2 - \frac{\hbar^2}{2M}\nabla_q^2 + \underbrace{\frac{m}{2}\omega^2 x^2 + U(|x-q|)}_{=V(x,q)}$$

Model parameters:

$$\mathrm{M/m} = 40 \qquad \mathrm{U(r)} = \mathrm{A}\,\exp(-br) \quad \epsilon = 0.0075\text{Å} \quad x/\text{Å} \in [-1, 0.5] \quad q/\text{Å} \in [1, 12]$$



For t > $t_{max}$ the the nuclear wavepacket will diffuse.

# Trajectory based Quantum-Classical Hybrid Methods

The equations for the Quantum-Classical Molecular Dynamics become

$$i\hbar\frac{\partial}{\partial t}\psi(r;R,t) = \left(-\frac{\hbar^2}{2m}\nabla_r^2 + V(r;R)\right)\psi(r;R,t) \ ,$$

Schrödinger Equation
light particle

$$\begin{aligned} \dot{R} &= P/M \ , \\ \dot{P} &= -\nabla_R \langle \psi(r;R,t)|V(r,R)|\psi(r;R,t)\rangle_r \ , \end{aligned}$$

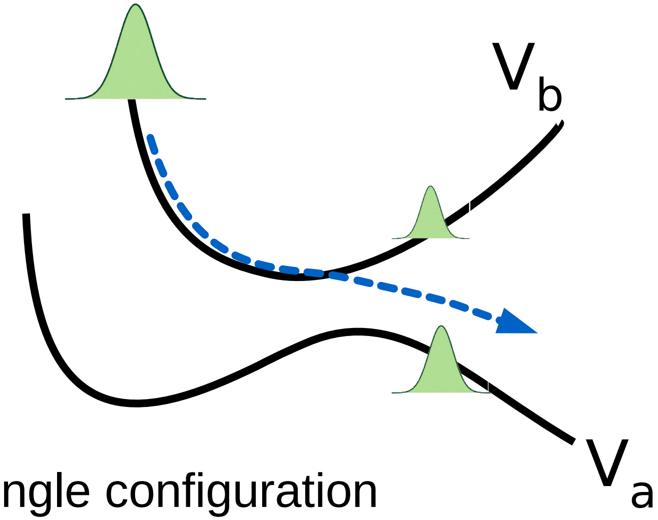
Classical Equations
heavy particle

$\psi(r,t)$ can be a linear combination of adiabatic orbitals:

$$\psi(r,t;R) = \sum_a c_a(t;R)\phi_a(r,t;R)$$

$\Longrightarrow$ Hellmann-Feynman forces
with Pulay corrections

Ehrenfest Dynamics



Problem: average path for single configuration

# Trajectory based Quantum-Classical Hybrid Methods

The equations for the Quantum-Classical Molecular Dynamics become

$$i\hbar\frac{\partial}{\partial t}\psi(r;R,t) = \left(-\frac{\hbar^2}{2m}\nabla_r^2 + V(r;R)\right)\psi(r;R,t) \ ,$$

Schrödinger Equation

$$\begin{aligned} \dot{R} &= P/M \ , \\ \dot{P} &= -\nabla_R \langle \psi(r;R,t)|V(r,R)|\psi(r;R,t)\rangle_r \ , \end{aligned}$$

Canonical Equations

The Schrödinger equation describes the dynamics of the quantum particle, whereas the canonical equations describe the dynamics of the “classical” particle.

The approximation fails:

- if the mass M is small;
- if the initial variance Є of the heavy wavepacket is not small enough, allowing for dispersion of the wavepacket (like wavepacket in dispersive medium);
- for long time simulations ($t>t_{max}$), the wavepacket diffuses;
- if the equation gets multivalued after passing a focal point (conical intersections).

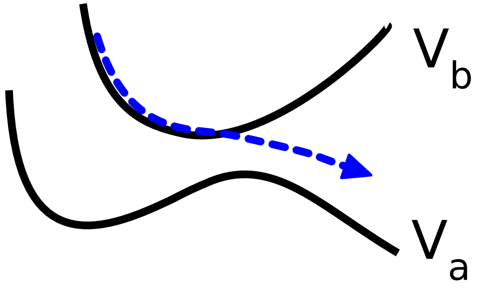
# Trajectory based Quantum-Classical Hybrid Methods

Ehrenfest Dynamics:

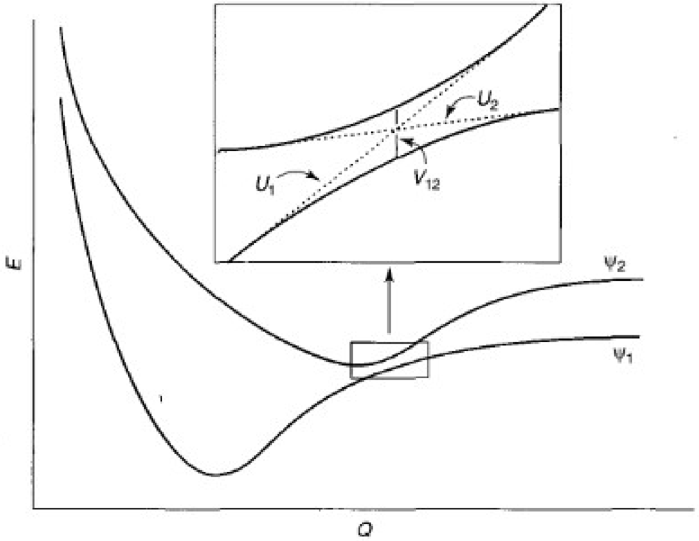
$$M\ddot{R} \quad = \quad -\nabla_R \langle \psi(r;R,t)|V(r,R)|\psi(r;R,t)\rangle_r$$

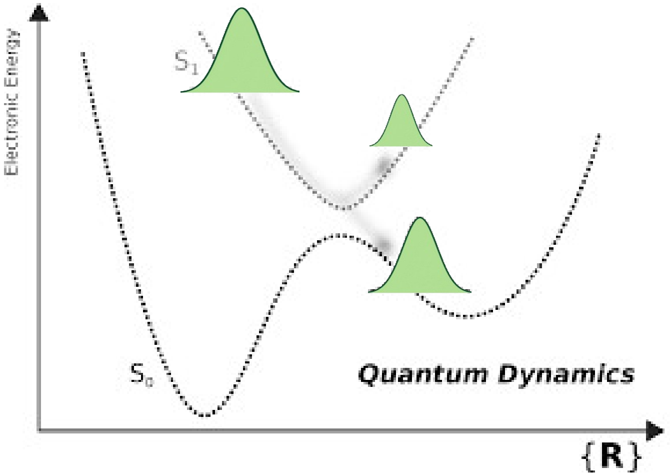
$\psi(r,t)$ can be a linear combination of adiabatic orbitals $\psi = \sum_a c_a(R,t)\phi_a(r;R,t)$

Ehrenfest classical ionic trajectory



But the real quantum system splits at the PES intersection





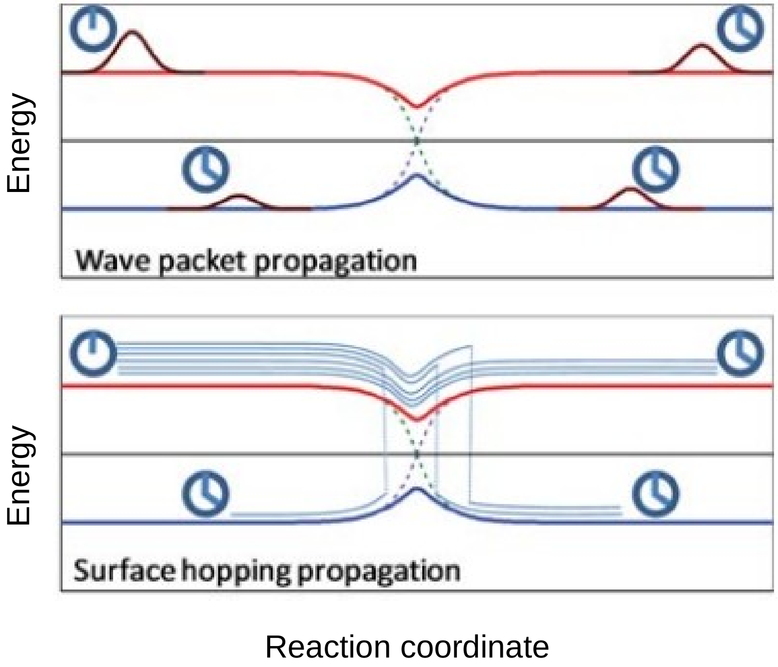
# Trajectory based Quantum-Classical Hybrid Methods

Surface Hopping (SH) approach:

- *“Molecular dynamics with electronic transitions”*
  John C. Tully, J. Chem. Phys. 93(2), 1061, 15 July 1990.

> “The TDSE is solved self-consistently with the classical mechanical equations of motion of the atoms. At each integration time step a decision is made whether to switch electronic states, according to the probalistic fewest switches algorithm ( aka “FSSH”).”

FSSH atomic trajectories aim to simulate the wave packet propagation



Barbatti, WIRES Comput. Mol Sci 2011, 1, 620

$$H = T_N + H_{el}(r,R) \quad ; \quad H_{el}(r,R)\phi_j = \varepsilon_j \phi_j$$

$$\begin{cases} \psi(r,R,t) = \sum_j c_j(t)\phi_j(r;R) & \Longleftarrow \text{from TDSE} \\ M\ddot{R} = -\nabla_k \varepsilon_k & \Longleftarrow \text{motion on a single PES} \end{cases}$$

$$\begin{cases} g_{kj} = \dfrac{-\left(2\mathbb{R}[\rho_{jk}]\mathbf{R}\cdot\mathbf{d}_{jk}\right)dt}{\rho_{kk}} & \Longleftarrow \text{switching prob.} \\ g_{k,j} < \xi < g_{k,j+1} \end{cases}$$

$$\begin{cases} \text{“large” ensemble of trajectories} \\ \text{conserve energy for each trajectory} \end{cases}$$

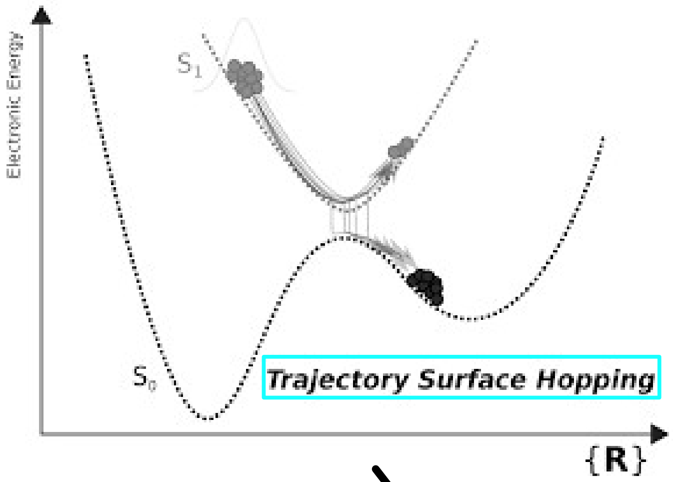
# Trajectory based Quantum-Classical Hybrid Methods

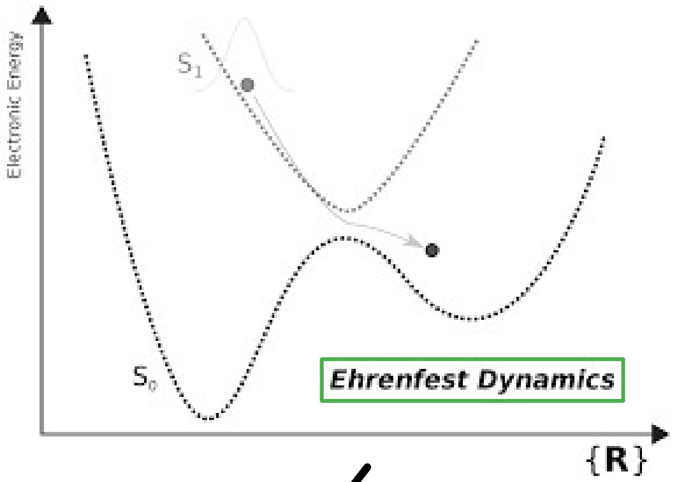
## Correcting Shortcomings of Surface Hopping

- Overcoherence problem
- Forbiden hops (or frustrated hops)
- Velocity-reversal
- Quantum mechanical coherence neglected

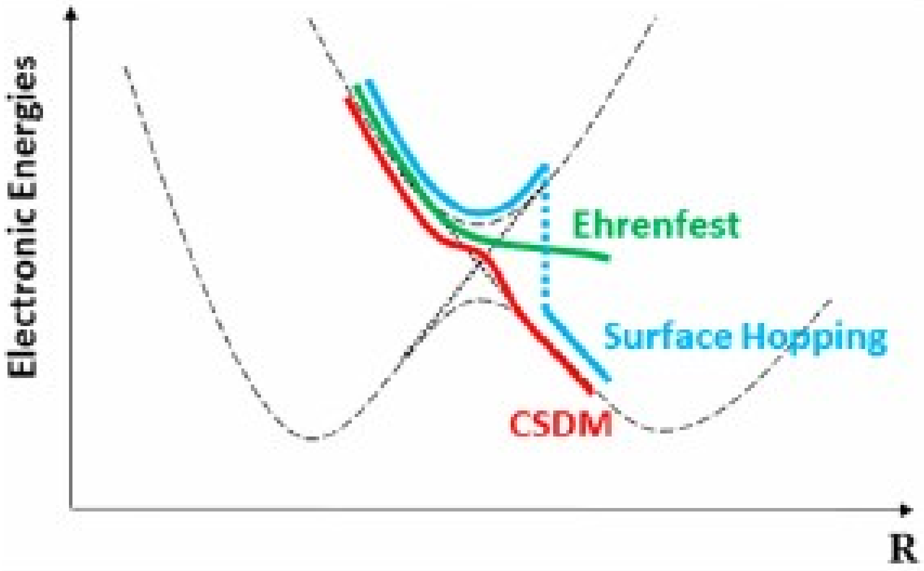
## Surface Hopping (SH) based approaches

- *ODC-FSSH (overlap decoherence correction-FSSH)*
  Granucci, Persico, et al.
- *FSTU (fewest-switches with time uncertainty)*
  Truhlar et al.
- *DISH (Dicoherence-Induced Surface Hopping)*
  Prezhdo, Akimov, et al.
- *A-FSSH (augmented-FSSH)*
  Subotnik, Shevin, et al.
- *Surface Hopping by consensus*
  C. Martens
- many more





## CSDM = Coherent Switches with Decay of Mixing



J. Chem. Theory Comput. 2020, 16, 3464−3475

JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 16 22 OCTOBER 2004

**Coherent switching with decay of mixing: An improved treatment of electronic coherence for non-Born–Oppenheimer trajectories**

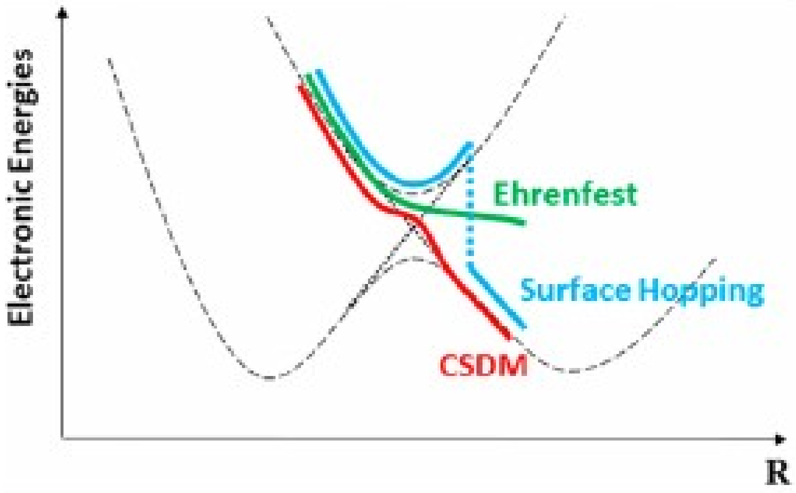
Chaoyuan Zhu, Shikha Nangia, Ahren W. Jasper, and Donald G. Truhlar
*Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431*

**Implementation of Coherent Switching with Decay of Mixing into the SHARC Program**

Yinan Shu,[⊥] Linyao Zhang,[⊥] Sebastian Mai, Shaozeng Sun,[*] Leticia González,[*] and Donald G. Truhlar[*]

*J. Chem. Theory Comput.* 2020, 16, 3464–3475

CSDM = Coherent Switches with Decay of Mixing



# Trajectory-Based Methods

## Hybrid Quantum-Classical Dynamics:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(r,R,t)=\left[\frac{\hbar^2}{2m}\nabla_r^2+\frac{\hbar^2}{2M}\nabla_R^2+V(r,R)\right]\Psi(r,R,t)$$

## ➔ Coherent quantum dynamics for the electrons:

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(r;R,t)\right\rangle=\hat{H}_{el}(R(t))\left|\Psi(r;R,t)\right\rangle \quad , \quad \Psi(r;R,t)=\text{electronic wavepacket}$$

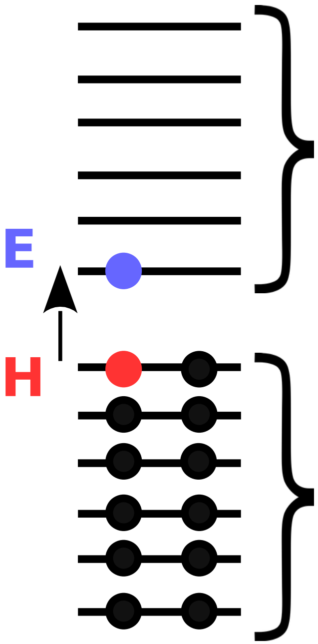
$$\Downarrow$$

$$\frac{d}{dt}C_n+\sum_m C_m\langle\phi_n|\frac{d}{dt}\phi_m\rangle+\frac{i}{\hbar}\mathcal{E}_n C_n=0 \qquad \langle\phi_n|\tfrac{d}{dt}\phi_m\rangle=\dot{\mathbf{R}}\cdot\mathbf{d}_{nm}$$

## ➔ Classical dynamics for the nuclei:

$$\begin{aligned}\dot{R}_{\scriptscriptstyle N} &= P_{\scriptscriptstyle N}/M_{\scriptscriptstyle N}\ ,\\ \dot{P}_{\scriptscriptstyle N} &= -\nabla_{\scriptscriptstyle N}U[R,\Psi(r)]\end{aligned}$$

# Dynemol QM-MM method



unoccupied

occupied

$$\langle \Psi(\mathbf{r};\mathbf{R},t)|V(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r};\mathbf{R},t)\rangle_{\mathbf{r}} \approx V^{GS} + V^{QM}_{eh}\left[\Psi^{el}(t), \Psi^{hl}(t)\right]$$

$$\begin{aligned} V^{GS} &= \sum_{bonds} K_b(R-R_o)^2 + \sum_{angles} K_\theta(\theta-\theta_o)^2 + \sum_{torsions}\sum_{n=0}^{5} C_n(cos\phi)^n \\ &+ \sum_{i,j\neq i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right] + \sum_{i,j\neq i}\frac{q_j q_i}{4\pi\epsilon_o R_{ij}} \end{aligned}$$

# Coherent Switches with Decay of Mixing (CSDM)

- Hybrid quantum-classical hamiltonian:

$$\mathrm{H} = \mathrm{T} + \left\{ V^{GS} + \langle\Psi|\mathbf{H}^{eh}|\Psi\rangle \right\} = T + V^{GS} + V^{QM}$$

- Adiabatic representation: $\mathbf{H}^{eh}|\phi\rangle = \varepsilon|\phi\rangle$ , $|\Psi\rangle = \sum_i C_i|\phi_i\rangle$ , $\mathrm{V}^{QM} = Tr\left[\rho\mathbf{H}^{eh}\right]$

- Electronic density matrix: $\rho = |\Psi\rangle\langle\Psi|$

$$\boxed{\dot{\rho} = \dot{\rho}\Big|_{\mathrm{Coh}} + \dot{\rho}\Big|_{\mathrm{Decoh}}}$$

- Conservation of energy for the hybrid hamiltonian: $\dot{H} = \dot{T} + \dot{V} = 0$

$$T = \sum_N \frac{\vec{P}_N \cdot \vec{P}_N}{2M_N} \Longrightarrow \dot{T} = \sum_N \frac{\vec{P}_N}{M_N} \cdot \dot{\vec{P}}_N = \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N$$

$$V = V^{GS} + Tr\left[\rho\mathbf{H}^{eh}\right] \Longrightarrow \dot{V} = \dot{V}^{GS} + \dot{V}\Big|_{Coh} + \dot{V}\Big|_{Dech}$$

# Coherent Switches with Decay of Mixing (CSDM)

$$
\begin{aligned}
\dot{V}^{QM} = \dot{V}\big|_{\text{Coh}} + \dot{V}\big|_{\text{Dech}} &= \sum_i \dot{\rho}_{ii} E_i + \sum_i \rho_{ii} \dot{E}_i \\
&= \sum_i \left\{ \dot{\rho}_{ii}\big|_{\text{Coh}} + \dot{\rho}_{ii}\big|_{\text{Dech}} \right\} E_i + \sum_i \rho_{ii} \dot{E}_i \\
&= \underbrace{\sum_i \dot{\rho}_{ii}\big|_{\text{Coh}} E_i + \sum_i \rho_{ii} \dot{E}_i}_{\dot{V}\big|_{\text{Coh}}} + \underbrace{\sum_i \dot{\rho}_{ii}\big|_{\text{Dech}} E_i}_{\dot{V}\big|_{\text{Dech}}}
\end{aligned}
$$

- Conservation of energy for the hybrid hamiltonian: $\dot{H} = \dot{T} + \dot{V} = 0$

$$
\begin{aligned}
\dot{\mathbf{H}} &= \sum_N \vec{v}_N \cdot \left( \dot{\vec{P}}_N\big|_{\text{Coh}} + \dot{\vec{P}}_N\big|_{\text{Dech}} \right) + \dot{V}^{GS} + \dot{V}\big|_{\text{Coh}} + \dot{V}\big|_{\text{Dech}} = 0 \\
&= \left\{ \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Coh}} + \dot{V}^{GS} + \dot{V}\big|_{\text{Coh}} \right\} + \left\{ \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Dech}} + \dot{V}\big|_{\text{Dech}} \right\} = 0
\end{aligned}
$$

# Mean-Field Ehrenfest Method

- Coherent electronic dynamics:

$$\dot{V}\big|_{\text{Coh}} = \sum_i \rho_{ii}\dot{E}_i + \sum_i \dot{\rho}_{ii}\big|_{\text{Coh}} E_i$$

$$= \sum_N \vec{v}_N \cdot \left\{ \rho_{ii}\nabla_N E_i - \sum_{i\neq j} 2\mathbb{R}\left[\rho_{ij}\right] E_i \vec{d}^{N}_{ij} \right\}$$

$$\boxed{\dot{U} = \sum_N \vec{v}_N \cdot \nabla_N U}$$

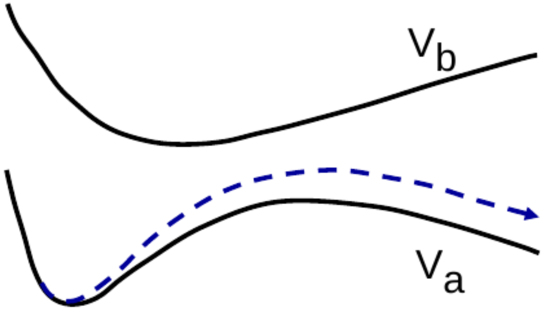
- Ehrenfest Mean-Field Force

$$\boxed{\vec{F}_N^{\text{Ehrenfest}} = -\nabla_N V^{QM} = -\rho_{ii}\nabla_N E_i + \sum_{i\neq j} 2\mathbb{R}\left[\rho_{ij}\right] E_i \vec{d}^{N}_{ij}}$$

- Energy conservation:

$$\sum_N \vec{v}_N \cdot \left\{ \vec{F}_N\big|_{\text{Coh}} + \nabla_N V^{GS} + \nabla_N V^{QM} \right\} = 0$$

$$\vec{F}_N\big|_{\text{Coh}} = -\nabla_N V^{\text{GS}} - \nabla_N V^{QM}$$

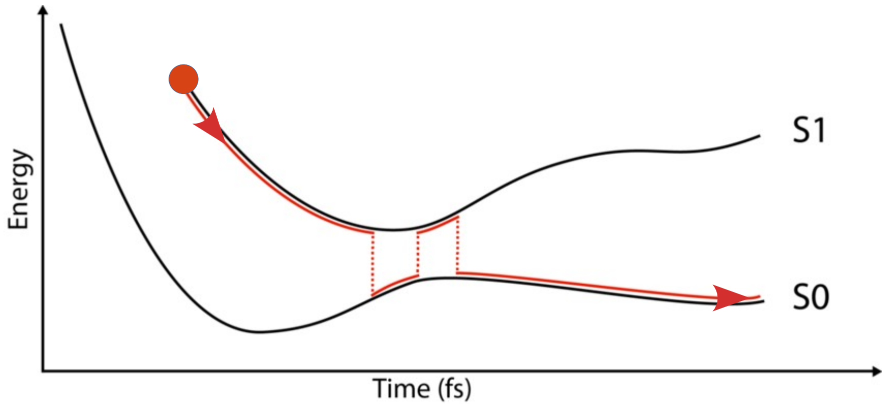


# Fewest Switches Surface Hopping (FSSH)

- Surface Hopping Force

$$\boxed{\vec{F}_N^{FSSH} = -\nabla_{R_N}\langle\phi_k|\hat{H}|\phi_k\rangle = -\nabla_{R_N} E_k(\{\vec{R}\})}$$

$$\vec{F}_N = -\nabla_N V^{\mathrm{GS}} - \nabla_N E_k(R)$$



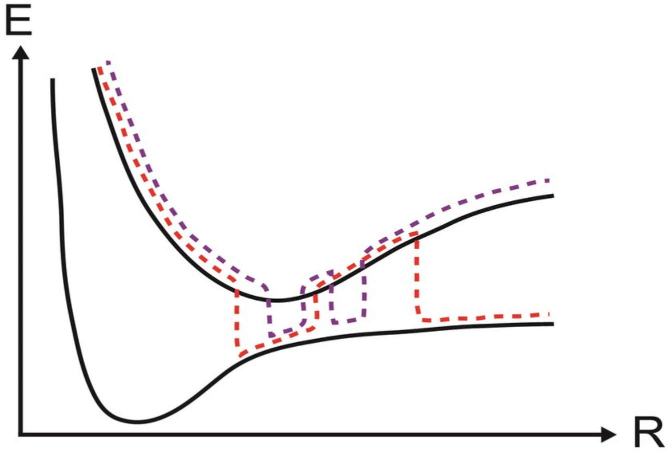
- Fewest Switches transition probability:

$$\frac{d\rho_{kk}}{dt} = -\sum_{i\neq k} 2\mathbb{R}\left[\rho_{ik}\right]\left(\sum_N \vec{v}_N\cdot\vec{d}_{ik}^{N}\right) = \sum_{i\neq k}\dot{\rho}_{ik}$$

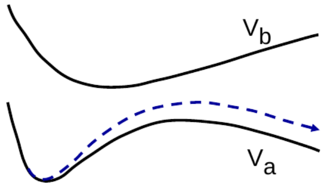
$$\boxed{P_{k\to i} = \max\left(0, -\frac{\dot{\rho}_{ik}dt}{\rho_{kk}}\right)}$$

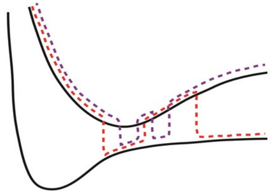
- Nuclear velocity rescaling due to transition $k \to i$

$$\sum_N \frac{\vec{P}_N^2}{2M_N} + E(\phi_k) = \sum_N \frac{\vec{P'}_N^2}{2M_N} + E(\phi_i)$$



# Mean Field Ehrenfest VS Surface Hopping (FSSH)





| Mean Field Ehrenfest | Surface Hopping (FSSH) |
|---|---|
| • Adiabatic or diabatic representation | • only adiabatic representation |
| • Good in strong coupling regions<br>Bad in the asymptotics<br>(does not satisfy detailed balance) | • Not so good in strong coupling regions<br>good in the asymptotics<br>(satisfies detailed balance) |
| • Clear physical demonstration | • Several ad-hoc steps, motivated by computational simplicity |
| • $F_N$ is given by mean-field approach<br>(time-dependent Hartree method) | • $F_N$ is given by single Pot. Energy Surface |
| • Single continuous trajectory | • Ensemble of discontinuous trajectories |
| • Electronic overcoherence | • Electronic overcoherence |

# Coherent Switches with Decay of Mixing (CSDM)

$$
\begin{aligned}
\dot{V}^{QM} = \dot{V}\big|_{\text{Coh}} + \dot{V}\big|_{\text{Dech}} &= \sum_i \dot{\rho}_{ii} E_i + \sum_i \rho_{ii} \dot{E}_i \\
&= \sum_i \left\{ \dot{\rho}_{ii}\big|_{\text{Coh}} + \dot{\rho}_{ii}\big|_{\text{Dech}} \right\} E_i + \sum_i \rho_{ii} \dot{E}_i \\
&= \underbrace{\sum_i \dot{\rho}_{ii}\big|_{\text{Coh}} E_i + \sum_i \rho_{ii} \dot{E}_i}_{\dot{V}|_{\text{Coh}}} + \underbrace{\sum_i \dot{\rho}_{ii}\big|_{\text{Dech}} E_i}_{\dot{V}|_{\text{Dech}}}
\end{aligned}
$$

- Conservation of energy for the hybrid hamiltonian: $\dot{H} = \dot{T} + \dot{V} = 0$

$$
\begin{aligned}
\dot{\mathbf{H}} &= \sum_N \vec{v}_N \cdot \left( \dot{\vec{P}}_N\big|_{\text{Coh}} + \dot{\vec{P}}_N\big|_{\text{Dech}} \right) + \dot{V}^{GS} + \dot{V}\big|_{\text{Coh}} + \dot{V}\big|_{\text{Dech}} = 0 \\
&= \left\{ \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Coh}} + \dot{V}^{GS} + \dot{V}\big|_{\text{Coh}} \right\} + \left\{ \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Dech}} + \dot{V}\big|_{\text{Dech}} \right\} = 0
\end{aligned}
$$

# Coherent Switches with Decay of Mixing (CSDM)

- Decoherence effect on the electronic dynamics:

$$\sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\Big|_{\mathrm{Dech}} + \dot{V}\Big|_{\mathrm{Dech}} = 0$$

$$\tau_{ik} = \frac{\hbar}{|E_i - E_k|}\left(1 + \frac{C}{E_{kin}}\right)$$

- Define *__Pointer State__* “k” , so that

$$C_i \longrightarrow C_i e^{-\Delta t/(2\tau_{ik})}, \qquad i \neq k$$

$$C_k \longrightarrow \frac{C_k}{|C_k|}\left[1 - \sum_{i\neq k} |C_k|^2\right]^{1/2}$$

$\Rightarrow$

$$\begin{aligned} \dot{\rho}_{ii}\Big|_{\mathrm{Dech}} &= -\frac{\rho_{ii}}{\tau_{ik}} < 0 \;, \qquad i \neq k \\ \dot{\rho}_{kk}\Big|_{\mathrm{Dech}} &= \sum_{j\neq k} \frac{\rho_{jj}}{\tau_{jk}} > 0 \;, \end{aligned}$$

Decay of Mixing

- *__Pointer State__* switch (analogous to FSSH):

$$P_{ik} = \max\left(0, -\frac{\dot{\rho}_{ik} dt}{\rho_{ii}}\right)$$

$$\dot{\rho}_{ik} = 2\mathbb{R}\left[\rho_{ik}\right]\left(\sum_N \vec{v}_N \cdot \vec{d}_{ik}^{N}\right)$$

# Coherent Switches with Decay of Mixing (CSDM)

- Decoherence effect on the electronic dynamics:

$$\sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\Big|_{\text{Dech}} + \dot{V}\Big|_{\text{Dech}} = 0$$

⇒

$$\sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\Big|_{\text{Dech}} = \sum_{i \neq k} \frac{\rho_{ii}}{\tau_{ik}} \left(E_i - E_k\right)$$

$$\begin{aligned}
\dot{V}\Big|_{\text{Dech}} &= \sum_i \dot{\rho}_{ii}\Big|_{\text{Dech}} E_i \\
&= \sum_{i \neq k} \dot{\rho}_{ii}\Big|_{\text{Dech}} E_i + \dot{\rho}_{kk}\Big|_{\text{Dech}} E_k \\
&= -\sum_{i \neq k} \frac{\rho_{ii}}{\tau_{ik}} \left(E_i - E_k\right)
\end{aligned}$$

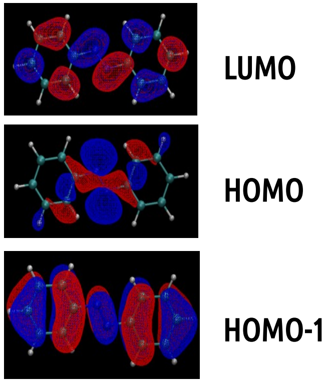
- Decoherent force:

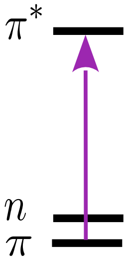
$$\vec{F}_N\Big|_{\text{Dech}} = \sum_{i \neq k} \frac{\rho_{ii}}{\tau_{ik}} \frac{\left(E_i - E_k\right)}{\left(\sum_N \vec{v}_N \cdot \hat{s}_{ik}^N\right)} \hat{s}_{ik}^N$$

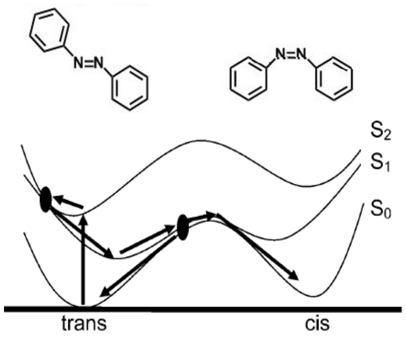
- Total force on atom N:

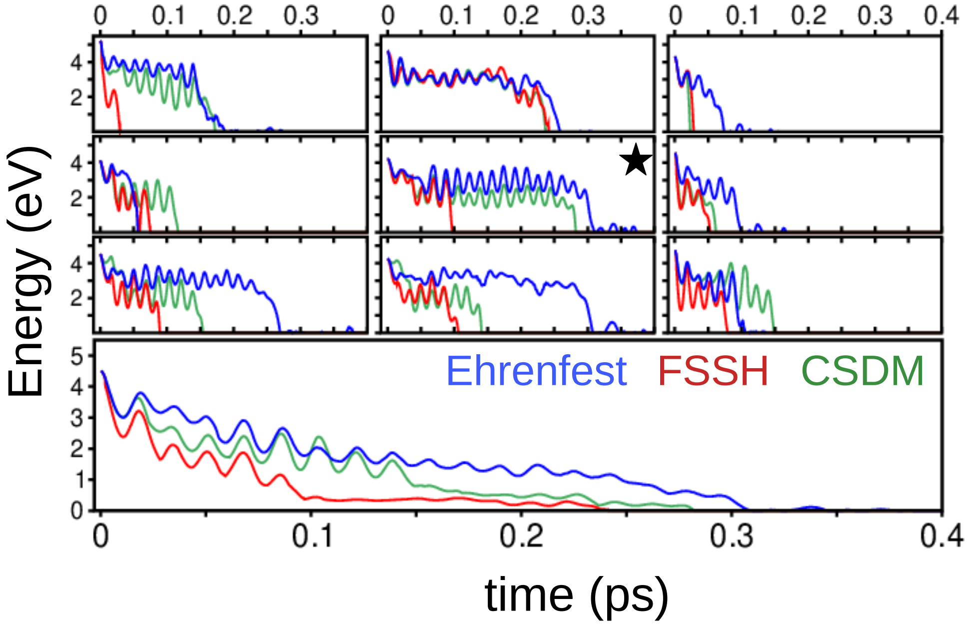
$$\boxed{\vec{F}_N = \vec{F}_N\Big|_{\text{Coh}} + \vec{F}_N\Big|_{\text{Dech}} = \vec{F}_N^{\text{Ehrenfest}} + \vec{F}_N\Big|_{\text{Dech}}}$$

# Azobenzene

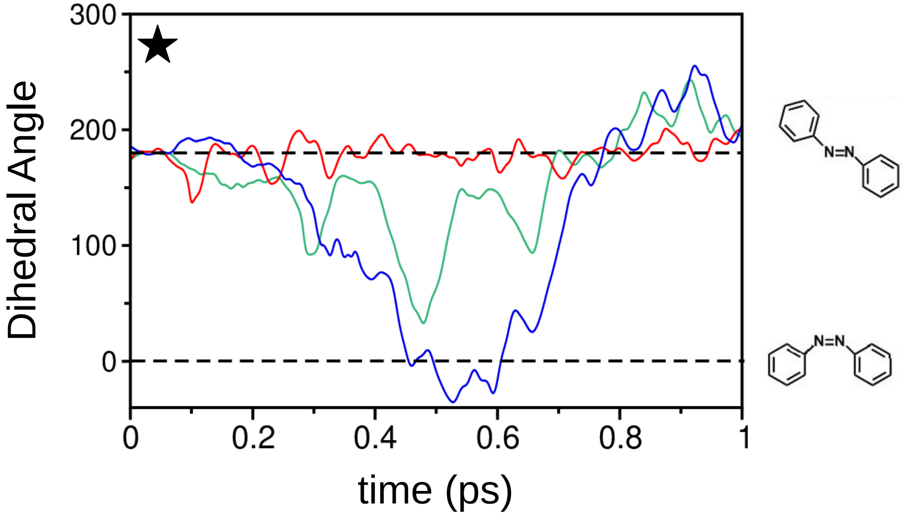


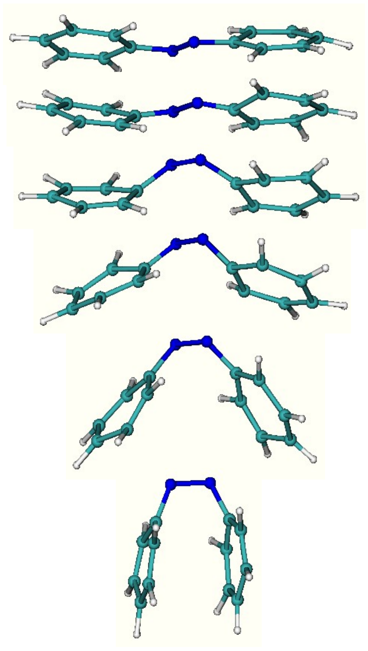




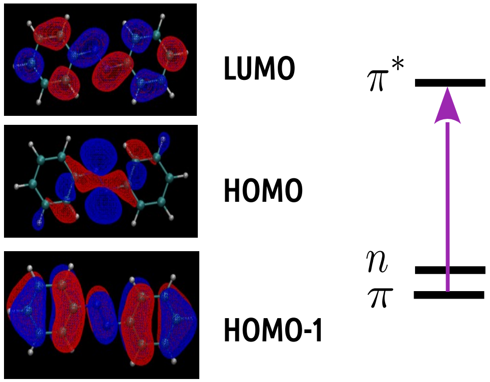


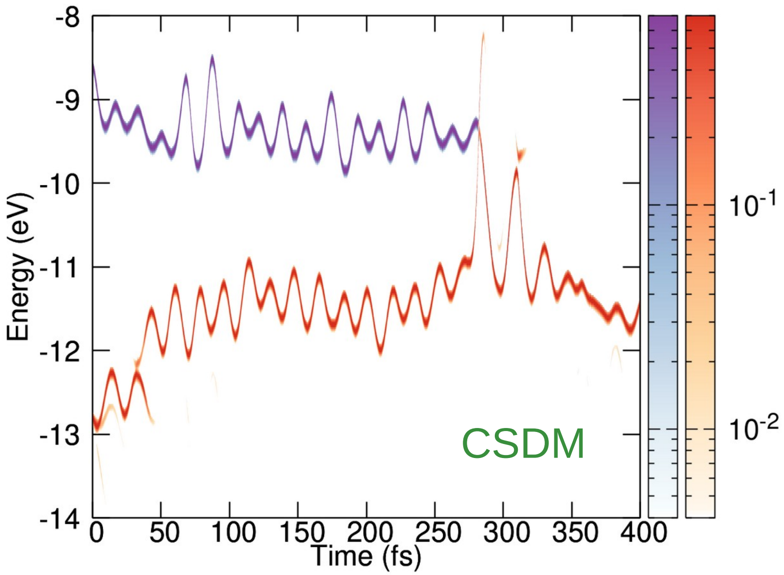
- Photo induced isomerization of Azobenzene:



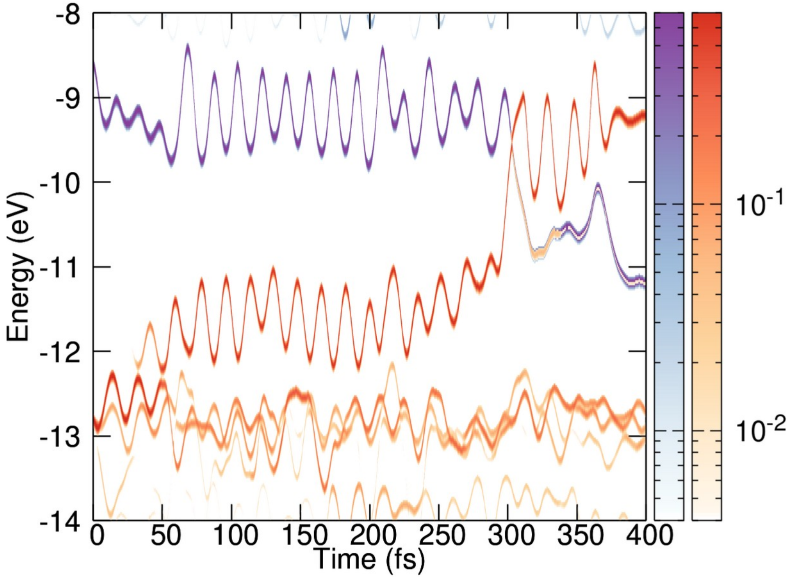


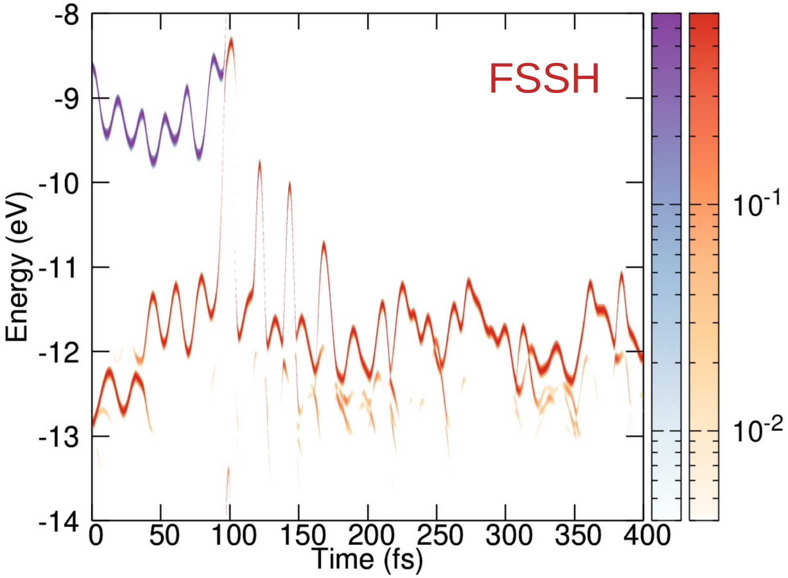
# Azobenzene





Ehrenfest





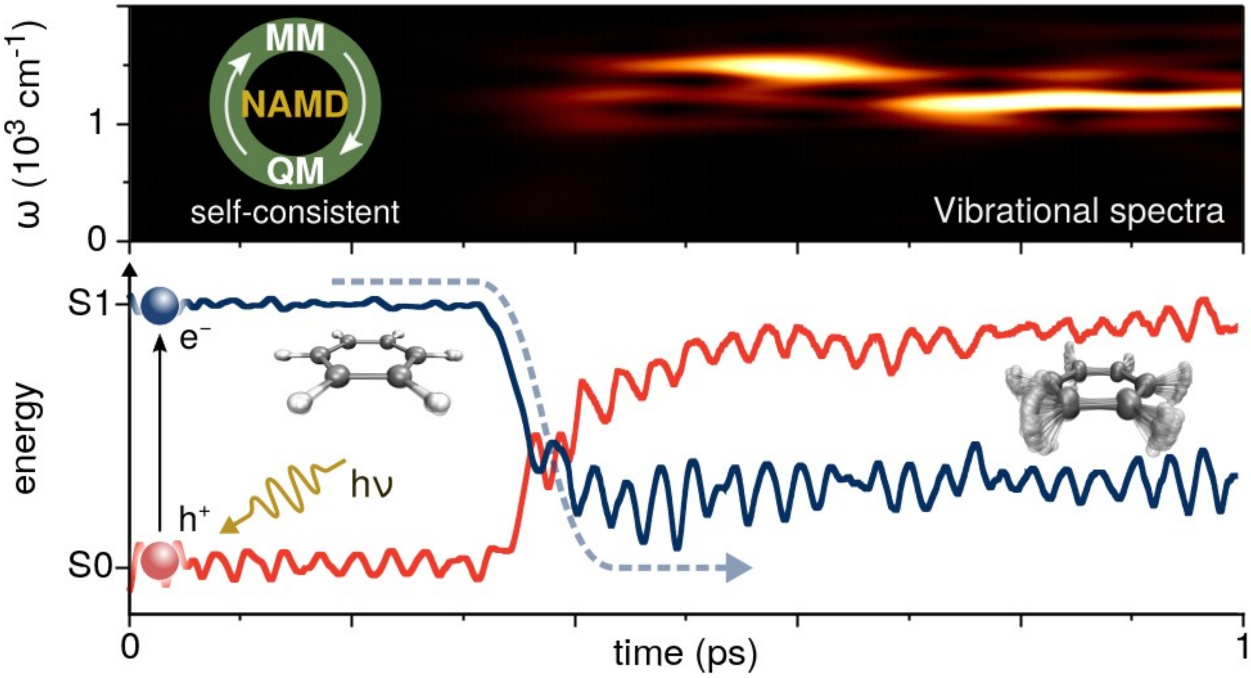
# Summary: Coherent Switches with Decay of Mixing (CSDM)

Advantages of the CSDM method:

- CSDM combines Mean-Field Ehrenfest and Fewest Switches Surface Hopping;
- No discontinuities in nuclear momentum (due to non-adiabatic hops);
- Total energy is naturally conserved;
- Includes electronic decoherence effects in Mean-Field Ehrenfest;
- Decoherence is weaker at strong coupling regions, allowing for vibronic effects.

# DynEMol Method

## Dynamics of Electrons in Molecules
## A Semi-empirical MO method for Large Scale Electronic Quantum Dynamics



**DynEMol: tools for studying Dynamics of Electrons in Molecules. https://github.com/lgcrego/Dynemol**

# Extended Hückel Tight-binding

Extended Hückel theory to ***account for the chemical bonding***:

$$H_{ab}^{EHT} = K_{ab}\ S_{ab}\ \frac{h_a + h_b}{2}$$

Atomic Orbitals: Slater-type orbitals (STO)

$$f_a^{STO}(\vec{r} - \mathbf{R}_A(t)) = (\zeta_a)^{n+1/2} \sqrt{\frac{1}{(2n)!}}\ r^{n-1}\ \ \exp\left[-\zeta_a r\right]\ Y_{lm}(\theta, \varphi)$$

$$\text{Overlap Matrix:} \begin{cases} S_{ab} = \delta_{ab}\ , & A = B \\ \\ S_{ab}(t) = \langle\ f_a(\mathbf{R}_A(t))\ |\ f_b(\mathbf{R}_B(t))\ \rangle\ , & A \neq B \end{cases}$$

***Sensitive to molecular geometry, short range couplings***: cutoff = 12 Å.

$Y_{ml}$ = Spherical Harmonics;

$K_{ab}$ = Wolfsberg-Helmholz coupling parameter

$h_a, h_b \approx$ Valence State Ionization Potentials (VSIPs)

$\zeta$ = constant related to the effective charge of the nucleus

$^*$Optimize EHT semiempirical parameters

# Extended Hückel Tight-binding

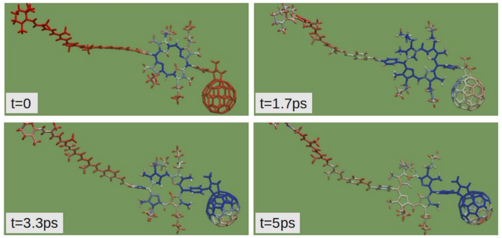
Electronic hamiltonian can include short range (SR) and long range (LR) interactions:

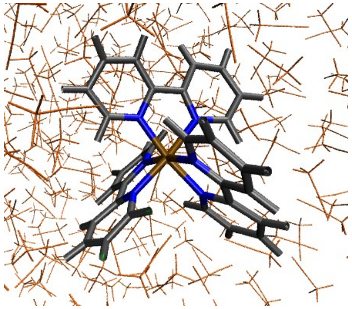
short range (***SR***: EHT) + long range (***LR***: ElHl, Polarization, Solvent) interactions:

$$\hat{H}_{el}(R(t)) = \hat{H}^{SR} + \hat{H}^{LR}$$

$$\hat{H}_{el}(R(t)) = \hat{H}^{EHT} + \hat{H}^{El/Hl} + \hat{H}^{Pol} + \hat{H}^{Solvent}$$

$$\begin{aligned} \hat{H}^{EHT} &\equiv \text{extended Hückel theory} \\ \hat{H}^{El/Hl} &\equiv \text{electron-hole coupling} \\ \hat{H}^{Pol} &\equiv \text{intramolecular polarization} \\ \hat{H}^{Solvent} &\equiv \text{Solvent} \end{aligned}$$





# Quantum Dynamics

The time-dependent Schrödinger Equation (TDSE) in the Adiabatic (MO) basis:

$$i\hbar\frac{\partial}{\partial t}\Psi(r;R,t) = \hat{H}_{el}\Psi(r;R,t)\ ,$$

$$\hat{H}_{el}(\mathbf{R}_t)\phi_n(t) = \mathcal{E}_n(t)\phi_n(t)$$

$$\text{with}\quad |\Psi(t)\rangle = \sum_n C_n(t)\,|\phi_n(t)\rangle$$

⬇

$$\frac{d}{dt}C_n + \sum_m C_m\langle\phi_n|\frac{d}{dt}\phi_m\rangle + \frac{i}{\hbar}\mathcal{E}_n C_n = 0\ .$$

Time evolution operator

$$\mathcal{U}(\tau) = \mathcal{T}\exp\left[-i\int_0^\tau \mathcal{H}(\mathbf{R}_t)dt/\hbar\right]$$

$\mathcal{T}$ is the time ordering operator

# Quantum Dynamics

Time evolution operator

$$\mathcal{U}(\tau) = \mathcal{T} \exp\left[-i \int_0^{\tau} \mathcal{H}(\mathbf{R}_t) dt/\hbar\right]$$

$\mathcal{T}$ is the time ordering operator

Apply the split time-step method for quantum propagation

$$t_j = j\delta t \longrightarrow \mathcal{H}^{(j)}|\phi_n^{(j)}\rangle = \mathcal{E}_n^{(j)}|\phi_n^{(j)}\rangle$$

$$|\Psi(t_{j+1})\rangle = [\, \boxed{\mathcal{U}(t_{j+1}, t_j)} \ldots \mathcal{U}(t_2, t_1)\, \mathcal{U}(t_1, t_0)\, ]|\Psi(t_0)\rangle$$

$$\boxed{\mathcal{U}(t_{j+1}, t_j) = \mathcal{U}_{NA}(t_{j+1}, t_j)\, \mathcal{U}_{AD}(t_j)}$$

# Quantum Dynamics

$$\mathcal{U}_{AD}|\Psi(t_j)\rangle = \sum_n C_n(t_j)\ exp\left\{\frac{-i\mathcal{E}_n^{(j)}\delta t}{\hbar}\right\}\ |\phi_n^{(j)}\rangle \qquad \Leftarrow \text{Schrödinger pict. contribution}$$

$$\mathcal{U}_{NA}|\Psi(t_j)\rangle = \sum_{n,m} \Omega_{mn}\ \left\{\langle\phi_n^{(j)}|\Psi(t_j)\rangle\right\}\ |\phi_m^{(j+1)}\rangle \qquad \Leftarrow \text{Interaction pict. contribution}$$

The nonadiabatic coupling term $\Omega_{mn}$

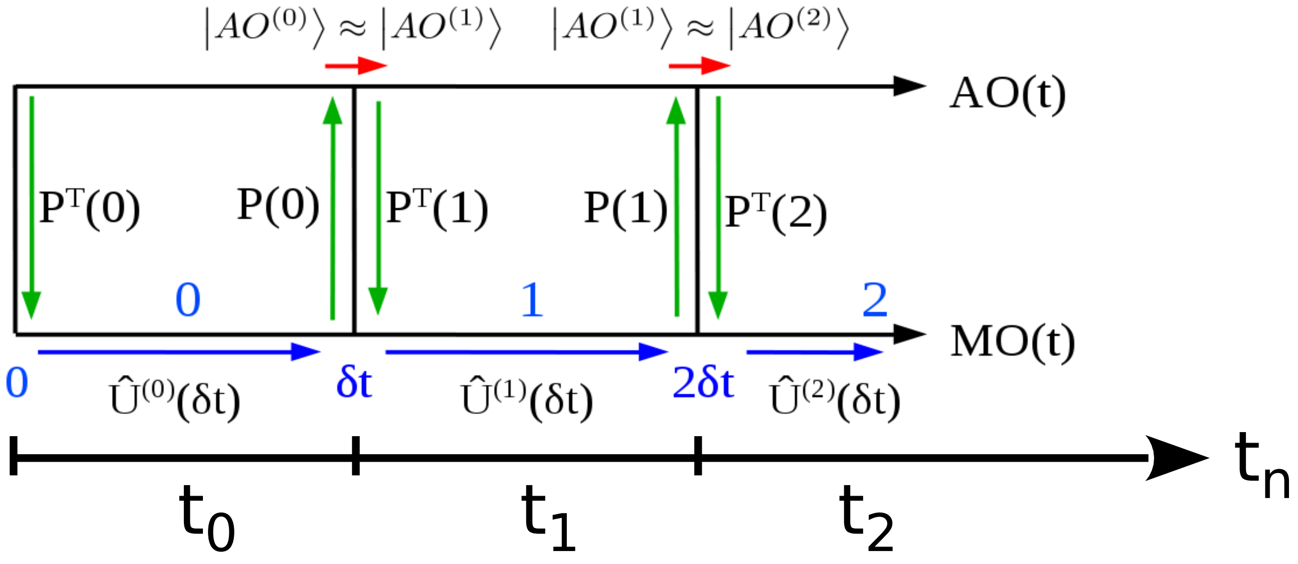
$$\Omega_{mn} = \langle\phi_m^{(j+1)}|\phi_n^{(j)}\rangle \approx \delta_{n,m} + \langle\dot{\phi}_m^{(j)}|\phi_n^{(j)}\rangle\delta t$$

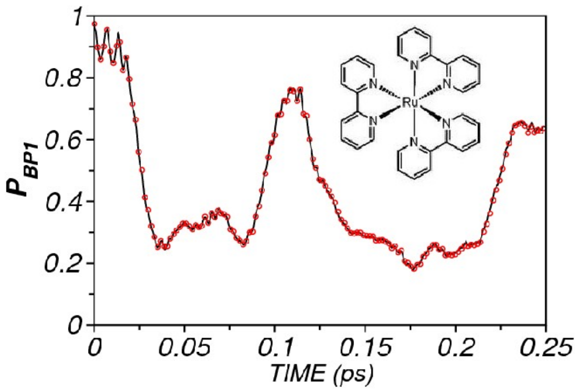
The unitary quantum propagator is solution of the TDSE

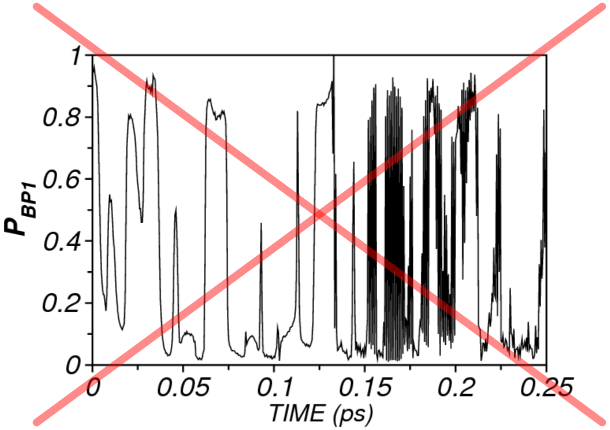
$$|\Psi(t)\rangle = \mathcal{U}(t,0)\ |\Psi(t_0)\rangle \qquad \Leftrightarrow \qquad \dot{C}_n + \sum_m C_m\langle\phi_n|\dot{\phi}_m\rangle = -\frac{i}{\hbar}\mathcal{E}_n C_n$$

*JPCL* 2015, **6**, 4927.

# State Tracking: Dynemol method







The unitary quantum propagator is solution of the TDSE

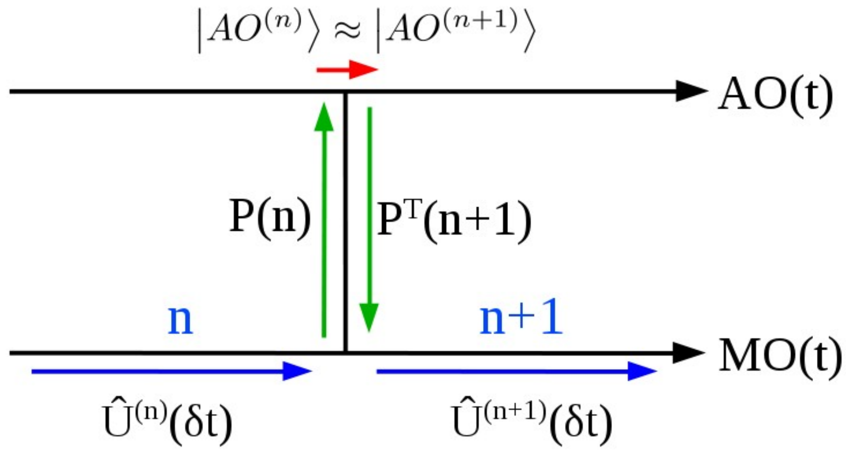
$$|\Psi(t)\rangle = \mathcal{U}(t,0)\ |\Psi(t_0)\rangle \quad \Longleftrightarrow \quad \dot{C}_n + \sum_m C_m \langle \phi_n | \dot{\phi}_m \rangle = -\frac{i}{\hbar}\mathcal{E}_n C_n$$

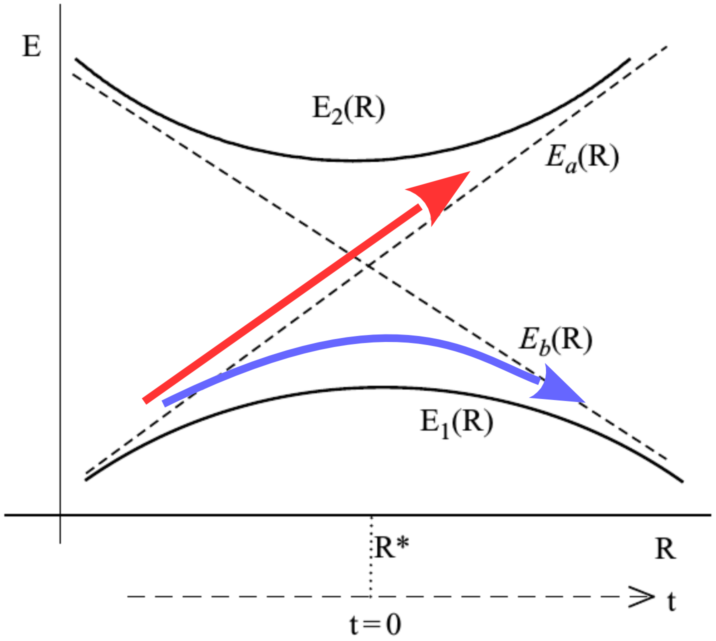
*JPCL* 2015, **6**, 4927.

http://luisrego.sites.ufsc.br/wp-content/uploads/2015/12/dynemol.pdf

# State Tracking: Dynemol method

## The nonadiabatic passage

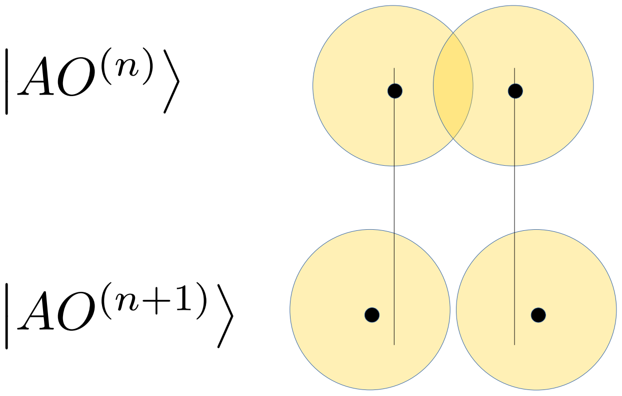


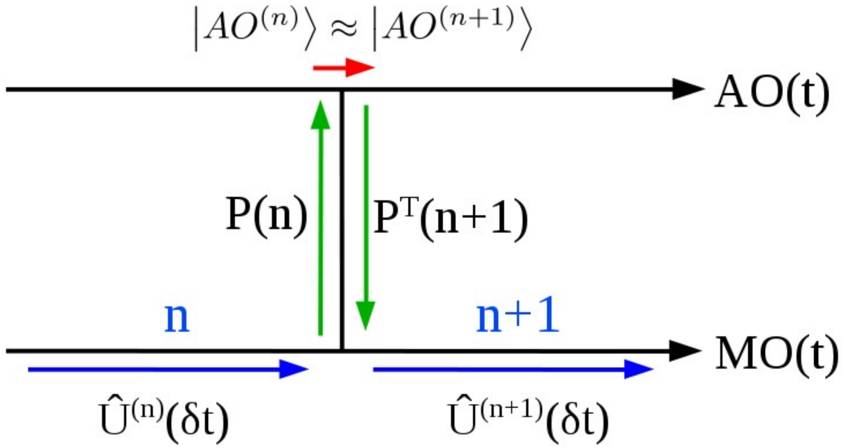


$$
\begin{aligned}
|\Psi(t+2\delta t)\rangle &= \hat{U}_{AD}^{(n+1)}(\delta t)\ \hat{U}_{NA}(\delta t)\ \hat{U}_{AD}^{(n)}(\delta t)\ |\Psi(t)\rangle \\
&= \exp\left[-\frac{i}{\hbar}\hat{H}_{n+1}\delta t\right]\ [Q_{n+1}]^T \cdot Q_n\ \exp\left[-\frac{i}{\hbar}\hat{H}_n\delta t\right]\ |\Psi(t)\rangle
\end{aligned}
$$

# State Tracking: Dynemol method

The **quasi-static** approx. in the Diabatic basis: $\left|AO^{(n)}\right\rangle \approx \left|AO^{(n+1)}\right\rangle$





$$\begin{aligned} |i^{(n+1)}\rangle &\approx |i^{(n)}\rangle + \frac{d\vec{R}}{dt} \cdot \nabla_R |i^{(n)}\rangle \delta t \\ &\approx |i^{(n)}\rangle + (\vec{v}\delta t) \cdot \nabla_R |i^{(n)}\rangle \end{aligned}$$

Consider a spherical STO, $f_i^{(n)}(\vec{r} - \vec{R}) = N e^{-\zeta|\vec{r}-\vec{R}|}$

$$|i^{(n+1)}\rangle \approx |i^{(n)}\rangle + \left( \vec{l} \cdot \zeta \frac{(\vec{r} - \vec{R})}{|\vec{r} - \vec{R}|} \right) |i^{(n)}\rangle = (1 + l\zeta)\, |i^{(n)}\rangle \ ,$$

$\vec{l} = \vec{v}\delta t$ is the nuclei displacement in the time-slice $\delta t \approx 0.05\ fs \quad \Longrightarrow \quad l \ll 1$ Å

$\zeta \approx\ 1$ Å$^{-1} \quad \Longrightarrow \quad l\zeta \ll 1 \quad \Longrightarrow \quad |i^{(n+1)}\rangle \approx |i^{(n)}\rangle$

# Classical Nuclear Dynamics in the GS

## Molecular Mechanics

$$M\ddot{\vec{R}} = -\nabla_{\vec{R}}\, V_{gs}^{FF}$$

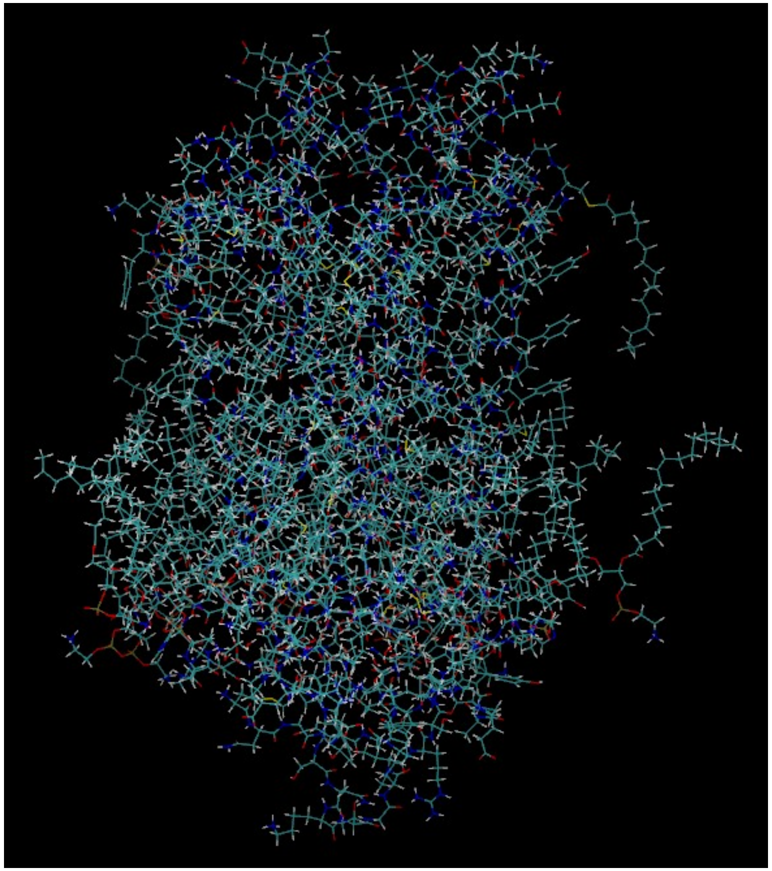
$$\begin{aligned} V_{gs}^{FF} \quad &= \quad \sum_{bonds} K_b (R - R_o)^2 + \sum_{angles} K_\theta (\theta - \theta_o)^2 + \sum_{torsions} \sum_{n=0}^{5} C_n (cos\phi)^n \\ &+ \quad \sum_{i,j \neq i} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{6} \right] + \sum_{i,j \neq i} \frac{q_j q_i}{4\pi\epsilon_o R_{ij}} \end{aligned}$$

$^*$In this case we keep the charges $q_i$ and $q_j$ fixed.

# Benchmarking Dynemol MM

benchmarking the force field: NAMD *vs* DynEMol

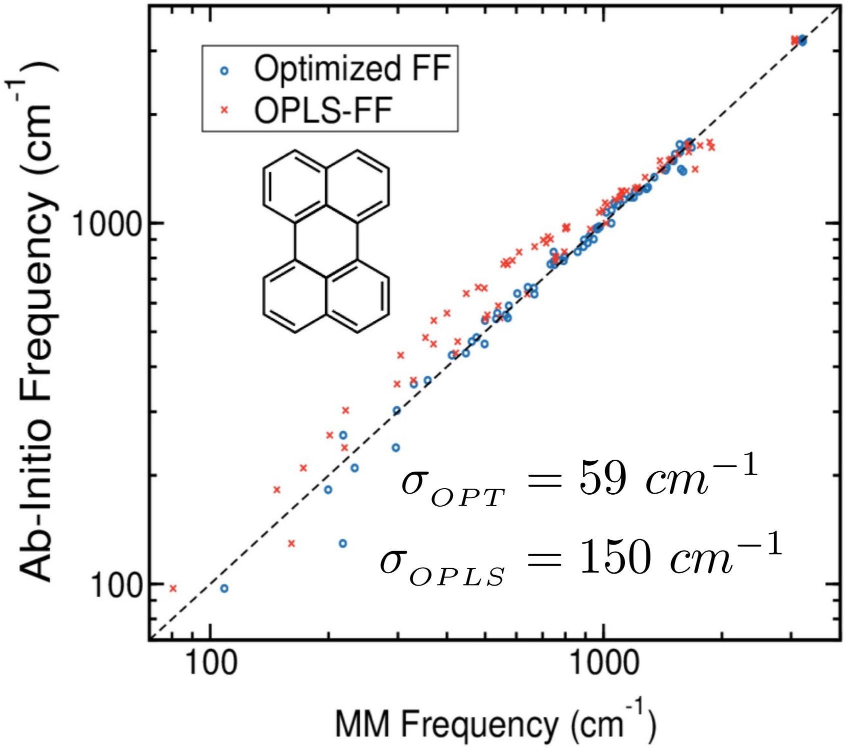
## Rhodopsin Protein

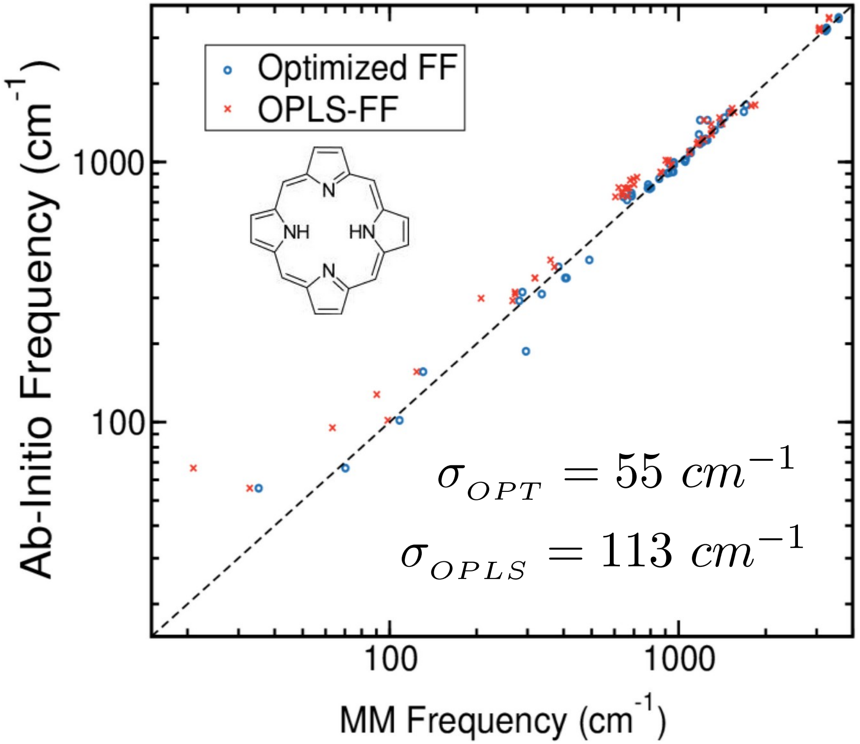


| | NAMD | DynEMol |
|---|---|---|
| | kJ/mol | kJ/mol |
| **bond** | 1522.6902 | 1522.7247 |
| **angle** | 4720.2675 | 4720.3785 |
| **Proper dih** | 13101.2090 | 13101.4409 |
| **improper** | 175.1565 | 175.1605 |
| **LJ (intra)** | -11033.9398 | -11034.2266 |
| **LJ 1-4** | 5138.1135 | 5138.0629 |
| **Elect (intra)** | -93274.7639 | -93276.0724 |
| **Elect 1-4** | 77352.7657 | 77353.9860 |

# Classical Nuclear Dynamics

We can **optimize the Force Field** (FF).

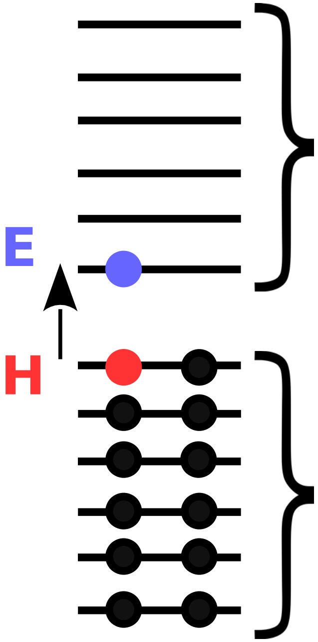




$$\sigma = \sqrt{\sum_{\gamma} \frac{(\omega_{\gamma}^{2} - \omega_{\gamma 0}^{2})^{2}}{3N - 6}}\ .$$

# Classical Nuclear Dynamics in the ES

Ehrenfest Method: $M\ddot{\mathbf{R}} = -\nabla_{\mathbf{R}}\langle\Psi(\mathbf{r};\mathbf{R},t)|V(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r};\mathbf{R},t)\rangle_{\mathbf{r}}$



unoccupied

$$\langle\Psi(\mathbf{r};\mathbf{R},t)|V(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r};\mathbf{R},t)\rangle_{\mathbf{r}} \approx V_{gs}^{FF} \boxed{+ V_{eh}^{QM}\left[\Psi^{el}(t), \Psi^{hl}(t)\right]}$$

occupied

$$\begin{aligned} V_{gs}^{FF} &= \sum_{bonds} K_b(R-R_o)^2 + \sum_{angles} K_\theta(\theta-\theta_o)^2 + \sum_{torsions}\sum_{n=0}^{5} C_n(cos\phi)^n \\ &+ \sum_{i,j\neq i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right] + \sum_{i,j\neq i}\frac{q_j q_i}{4\pi\epsilon_o R_{ij}} \end{aligned}$$

*In this case we keep the charges $q_i$ and $q_j$ fixed.

# Quantum-Classical Coupling

Quantum energy $(E_{QM})$ :

$$V_{eh}^{QM}\left[\Psi^{el}(t),\Psi^{hl}(t)\right] = Tr\left[\rho^{eh}\mathbf{H}\right] = \sum_n \mathcal{E}_n \rho_{nn}^{eh}$$

with, $\rho_{nm}^{eh} = \rho_{nm}^{el} - \rho_{nm}^{hl}$

Force on atom A due to the quantum perturbation $V_{eh}^{QM}$

$$\mathbf{F}_A^{eh} = -\nabla_{R_A} V_{eh}^{QM}$$

Hellmann-Feynman Theorem

$$\frac{dE_{QM}}{d\mathbf{R}_A} = \sum_n |C_n(t)|^2 \frac{d\mathcal{E}_n(t)}{d\mathbf{R}_A} + \sum_n \mathcal{E}_n(t)\left(\frac{dC_n^*(t)}{d\mathbf{R}_A}C_n(t) + C_n^*(t)\frac{dC_n(t)}{d\mathbf{R}_A}\right)$$

# Quantum-Classical Coupling

From

$$\frac{dE_{QM}}{d\mathbf{R}_A} = \sum_n |C_n(t)|^2 \frac{d\mathcal{E}_n(t)}{d\mathbf{R}_A} + \sum_n \mathcal{E}_n(t) \left( \frac{dC_n^*(t)}{d\mathbf{R}_A} C_n(t) + C_n^*(t) \frac{dC_n(t)}{d\mathbf{R}_A} \right)$$

Total force (AD + NA) between atom pair A and B,

in the **Extended Hückel formalism**, is

$$\mathbf{F}_{AB} = -2 \sum_{a \in A} \sum_{b \in B} \langle f_b | \nabla f_a \rangle \quad \times \quad \left\{ \sum_n \rho_{nn}^{eh} \left( \chi_{ab} - \mathcal{E}_n \right) Q_b^n Q_a^n \right.$$
$$\left. + \quad \sum_{m>n} \mathbb{R} \left( \rho_{nm}^{eh} \right) \left[ \left( \chi_{ab} - \mathcal{E}_m \right) Q_a^n Q_b^m + \left( \chi_{ba} - \mathcal{E}_n \right) Q_b^n Q_a^m \right] \right\}$$

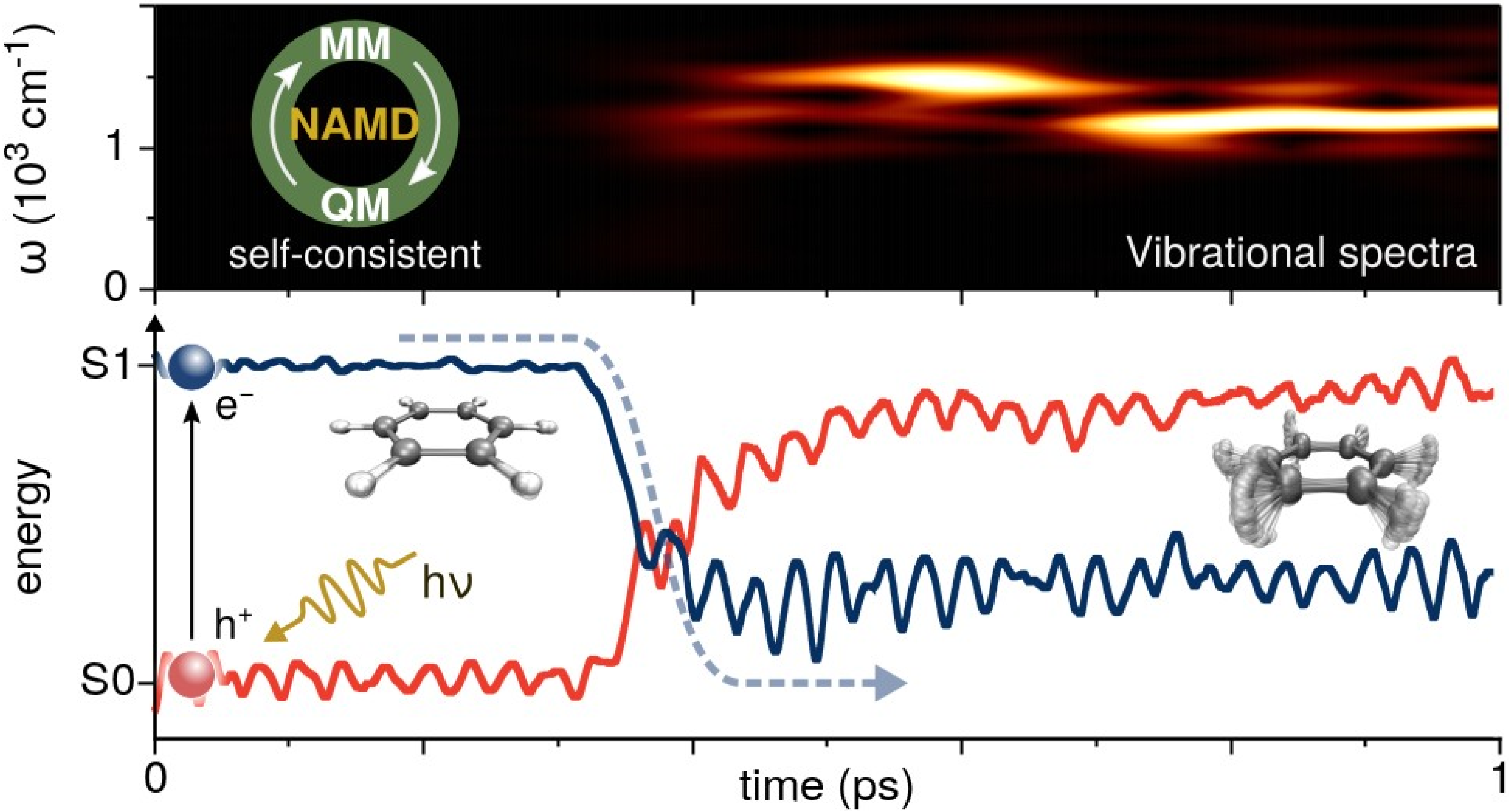
the extended Hückel hamiltonian is given by $H_{ab} = \chi_{ab} S_{ab}$ ,

with $\chi_{ab} \equiv K_{ab} \frac{h_a + h_b}{2}$.

Adiabatic states: $H Q_n = \mathcal{E}_n S Q_n$

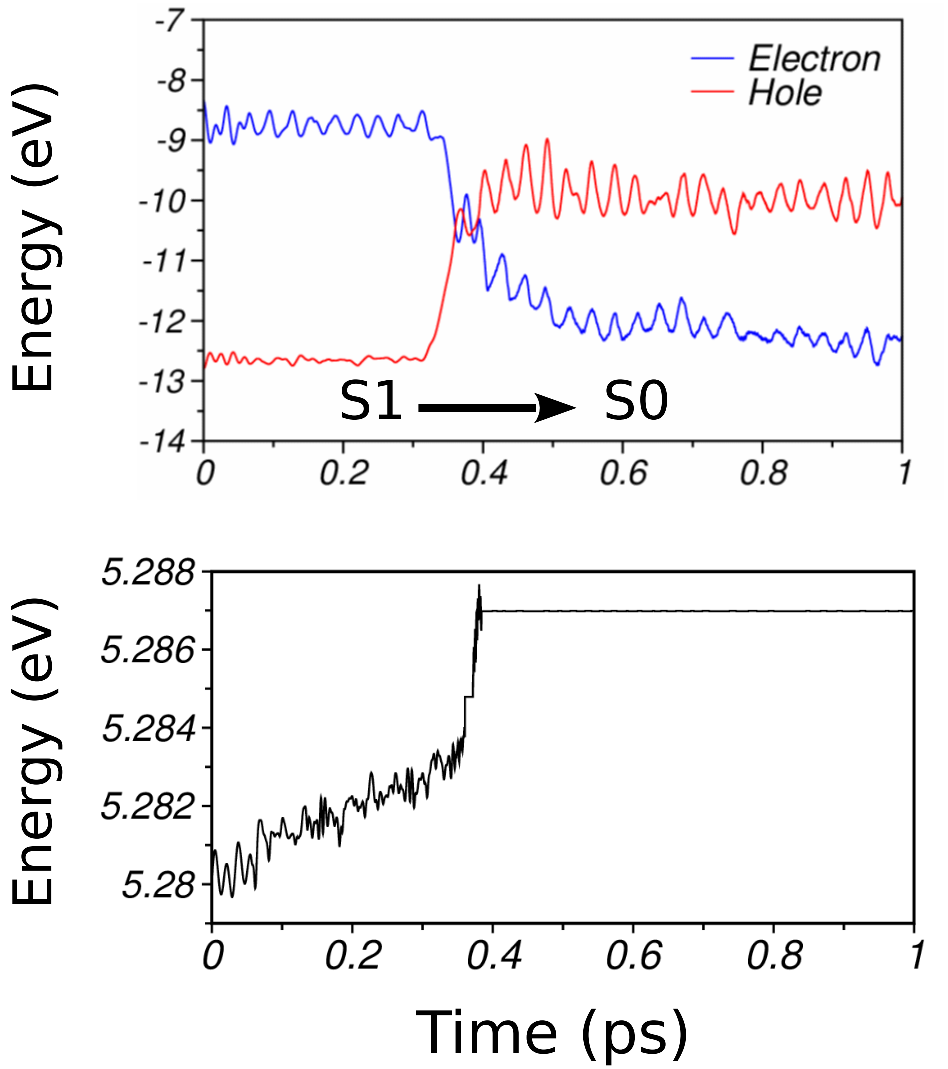
*JPCC* 2016, **120**, 27688.

# Benzene – Intramolecular Vibrational Relaxation (IVR)



J. Phys. Chem. C 2016, 120, 27688

# Benzene: Energy balance in Vibrational Relaxation



Excitation Energy

$$E^{el} = \sum_n \mathcal{E}_n(t)|C_n^{el}(t)|^2$$

$$E^{hl} = \sum_n \mathcal{E}_n(t)|C_n^{hl}(t)|^2$$

Total Quantum-Classical Energy

$$\delta t = 0.005\text{fs}$$

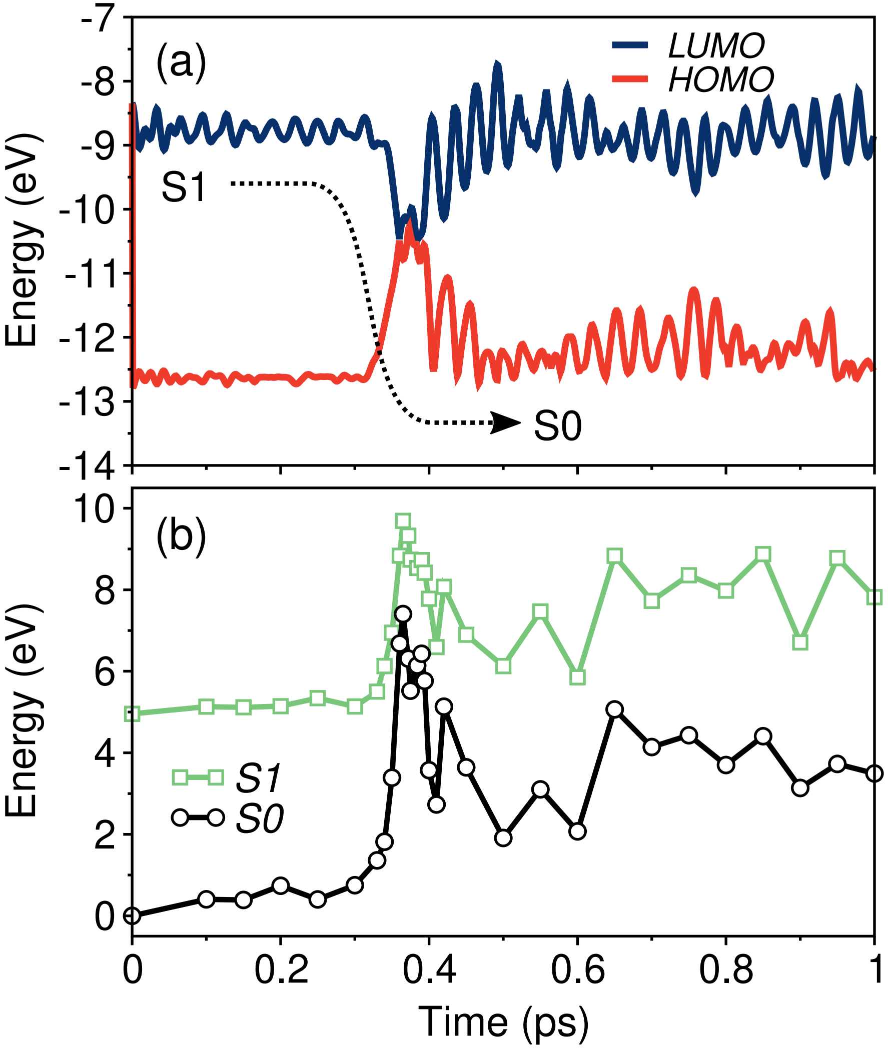
$$E_{S1} \longrightarrow E_{S0}$$

$$E_{MM} + E_{QM} = K + V_{gs}^{FF} + Tr\left[\rho^{eh}\mathbf{H}\right]$$

$$E_{MM} = K + V_{gs}^{FF}$$

# Benzene – Intramolecular Vibrational Relaxation (IVR)

## Check: comparisson with high-level theory



→ EHT-MM-Ehrenfest

→ CASSCF(6,6)/6-31G*

(performed with Gaussian-09)

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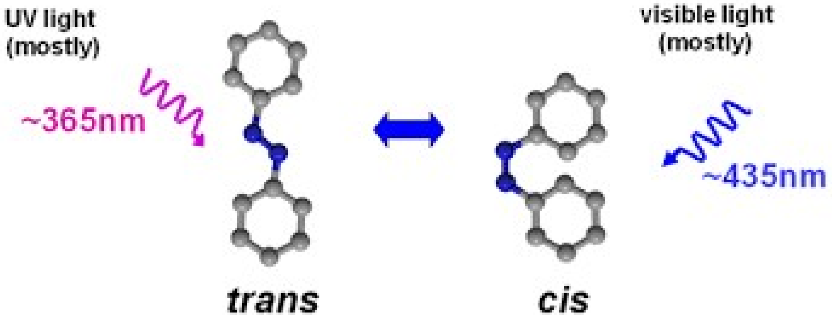
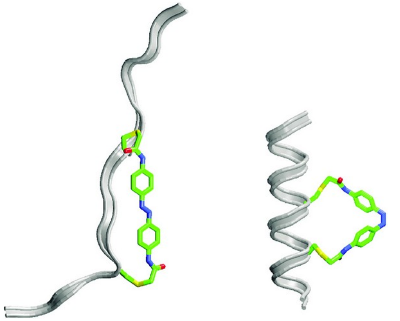
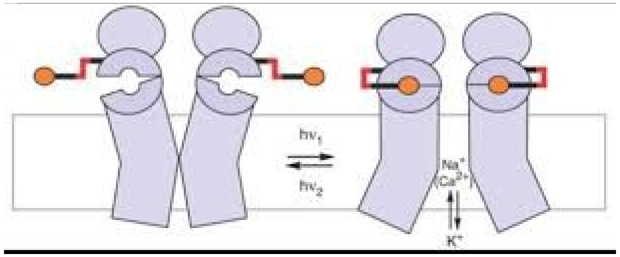
# Azobenzene – Photoinduced Isomerization



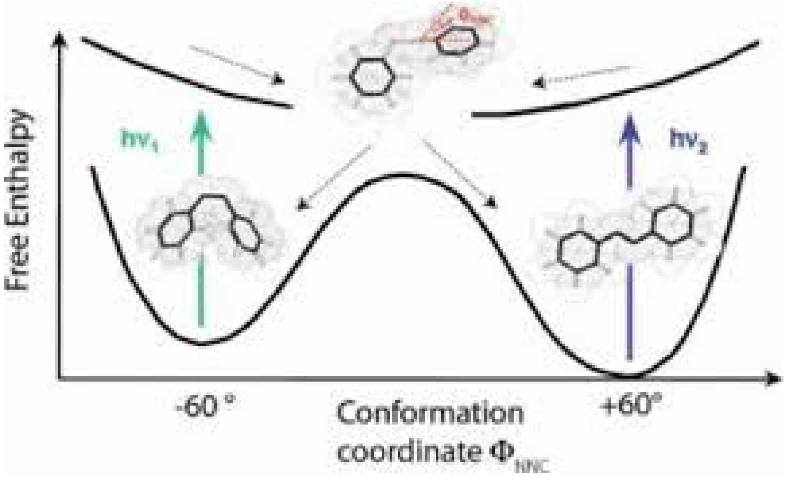
## Applications: molecular photoswitch



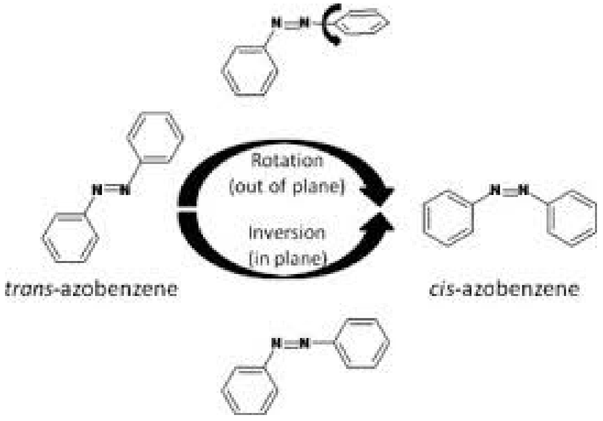
light activated Shaker K+ channel

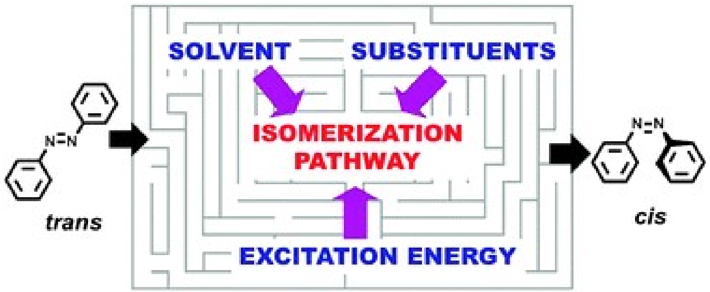


Bandara & Burdette, Chem.Soc. Rev. 2012,1809



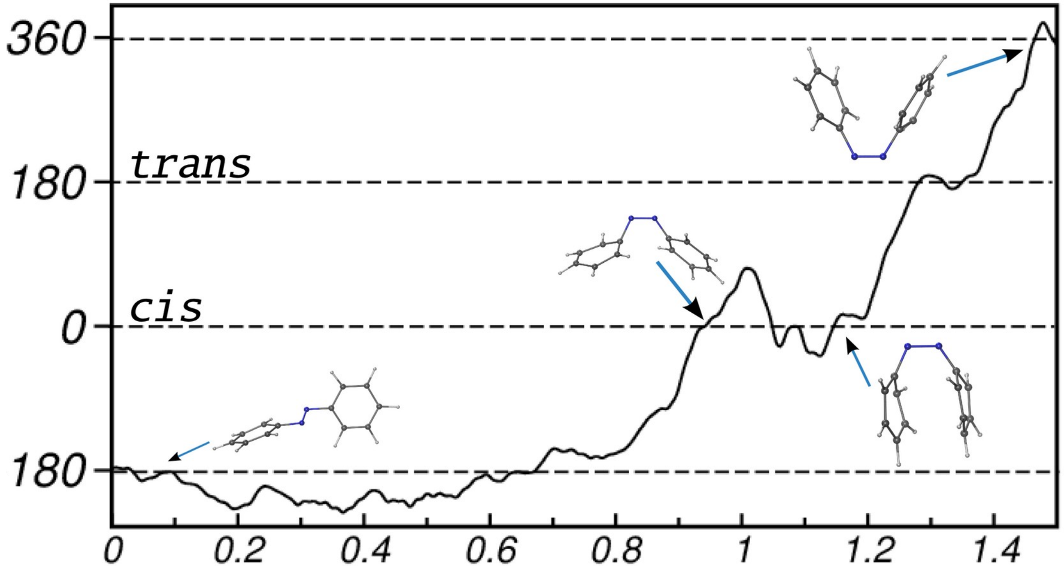
## Photoisomerization mechanism

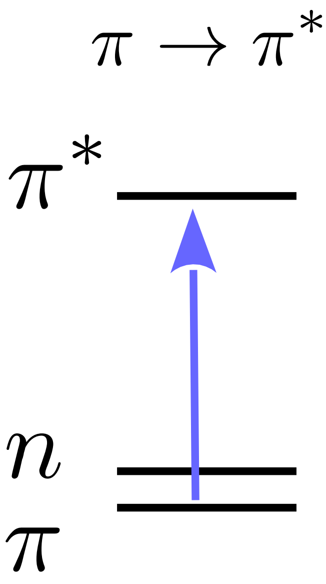




# Azobenzene – Photoinduced Isomerization

CNNC dihedral angle



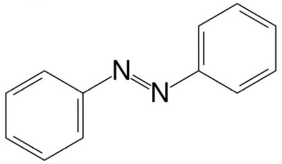


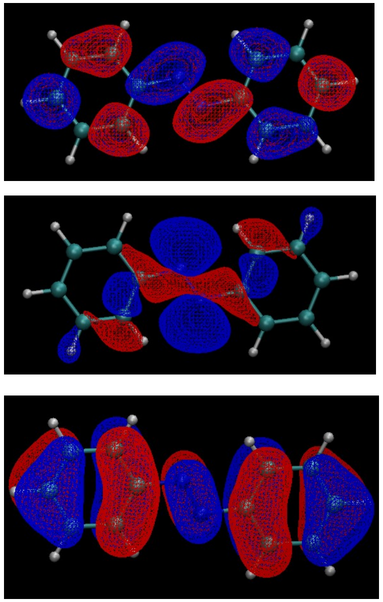
$\pi \rightarrow \pi^*$

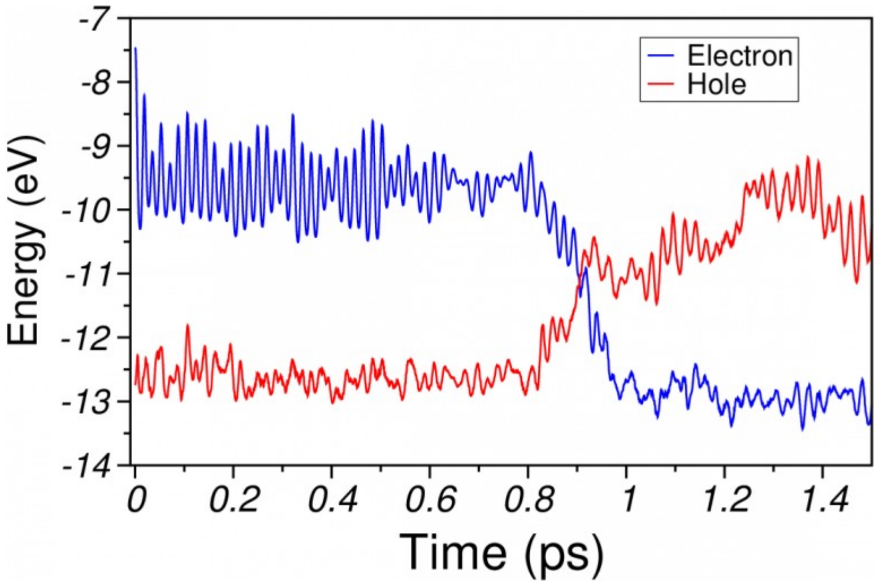
$\pi^*$

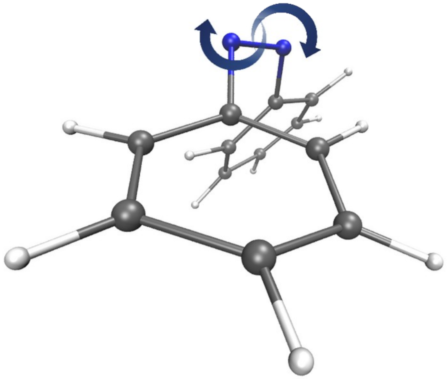
$n$

$\pi$









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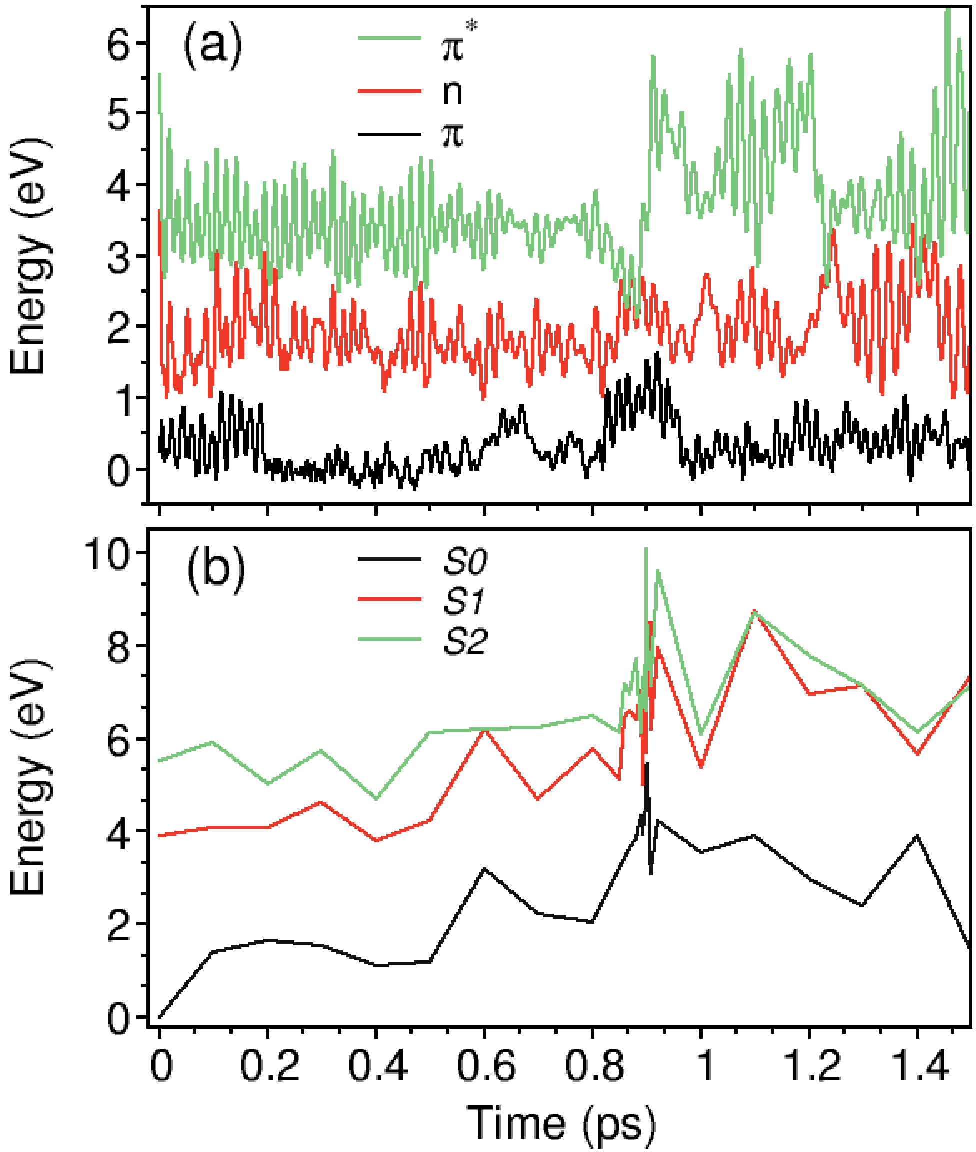
# Azobenzene – Photoinduced Isomerization

Check: comparisson with high-level theory



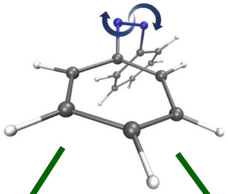
→ EHT-MM-Ehrenfest

$$\delta t = 0.005 \text{fs}$$

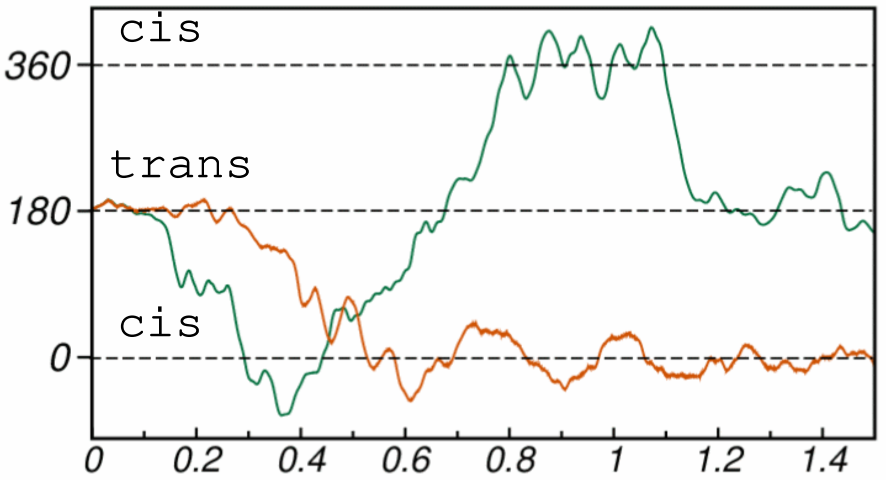
$$\text{run time} \sim \text{12h on a 16 core CPU}$$

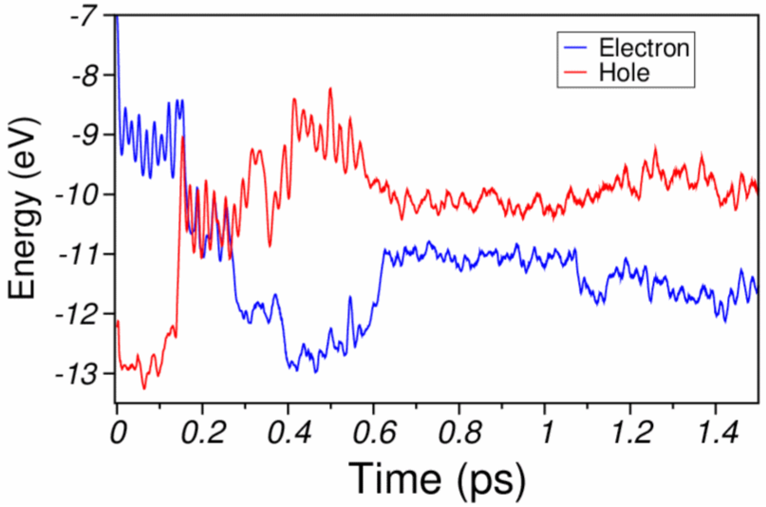
→ CASSCF(14,12)/6-31G*

# Azobenzene in Methanol solution

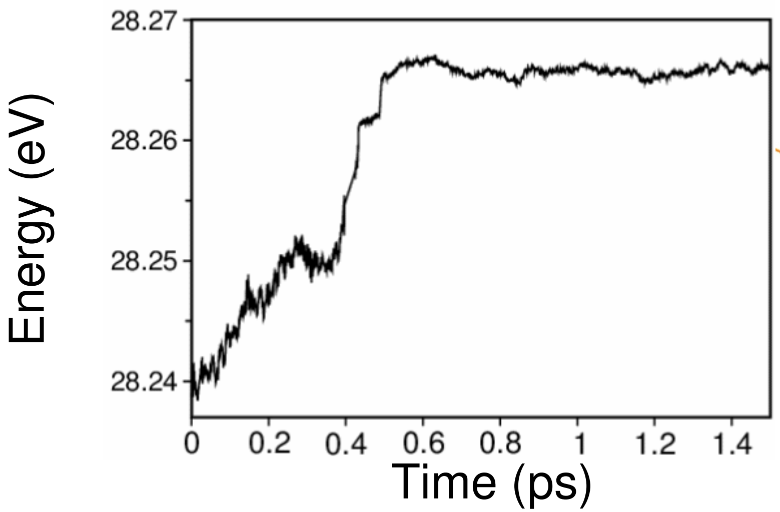


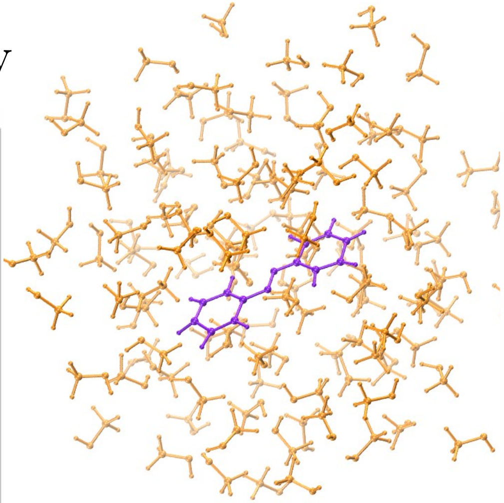
CNNC dihedral angle



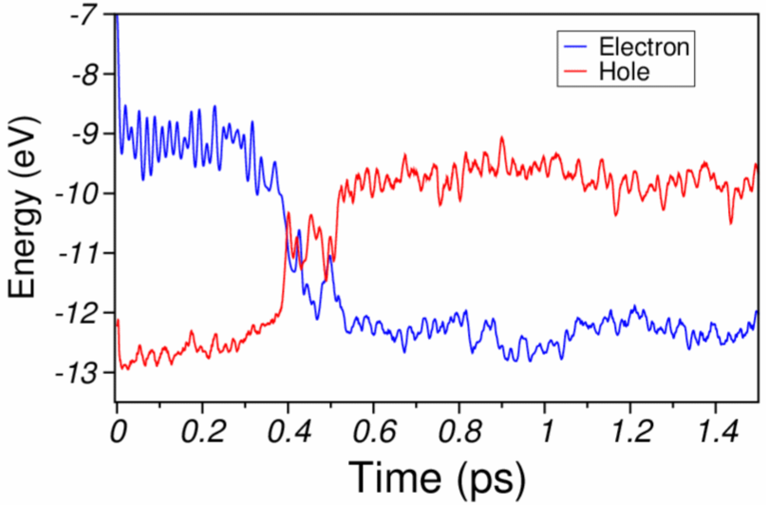


Total Quantum-Classical Energy





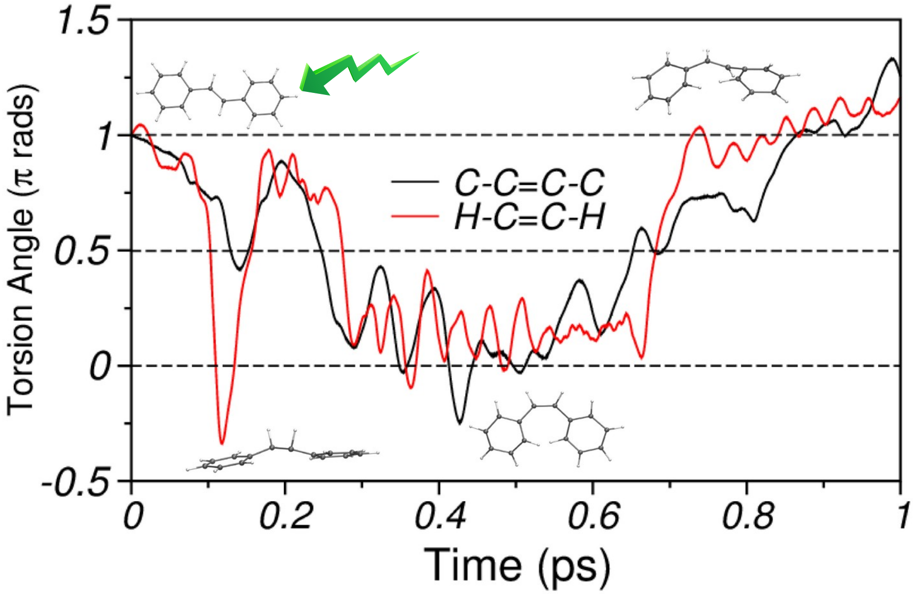
QM-MM simulation



# Concerted Photoisomerization of Stilbene

the *trans*→*cis* torsion

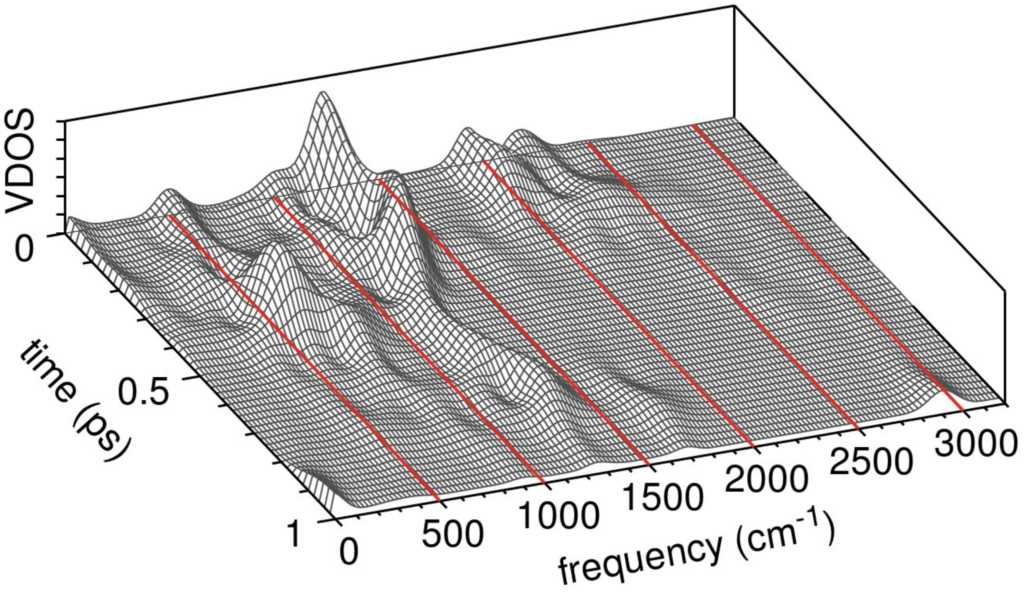
H-C=C-H dihedral drives the C-C=C-C isomerization



Time-dependent Vibrational Spectra

$$C_v(t) = \frac{\sum_i m_n \vec{v}_n(0) \cdot \vec{v}_n(t)}{\sum_i m_n \vec{v}_n(0) \cdot \vec{v}_n(0)}$$

$$g_\tau(\omega, t) = \left| \int_{t_0}^{t_f} C_v(t') \exp\left[-\frac{(t'-t)^2}{2\tau^2}\right] e^{-i\omega t'}\, dt' \right|$$



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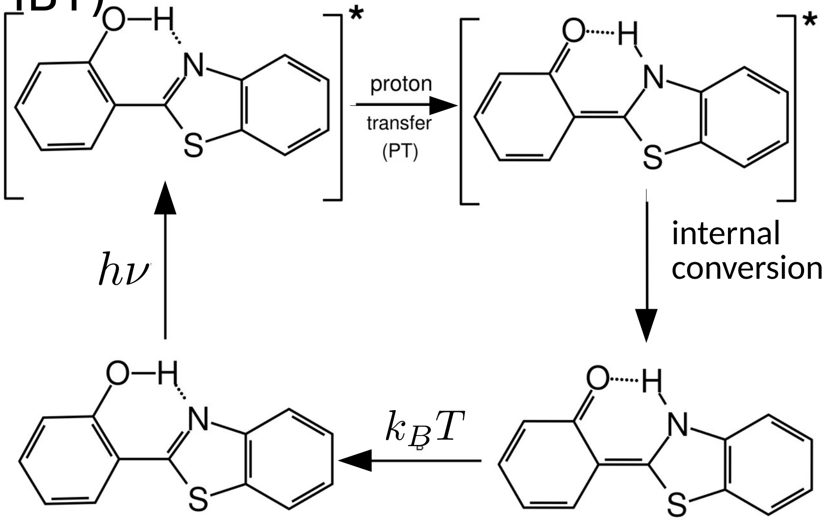
# Excited State Intramolecular Proton Transfer

2-(2'-hydroxyphenyl) benzothiazole (HBT)



- Morse potential for the O-H and N-H bonds

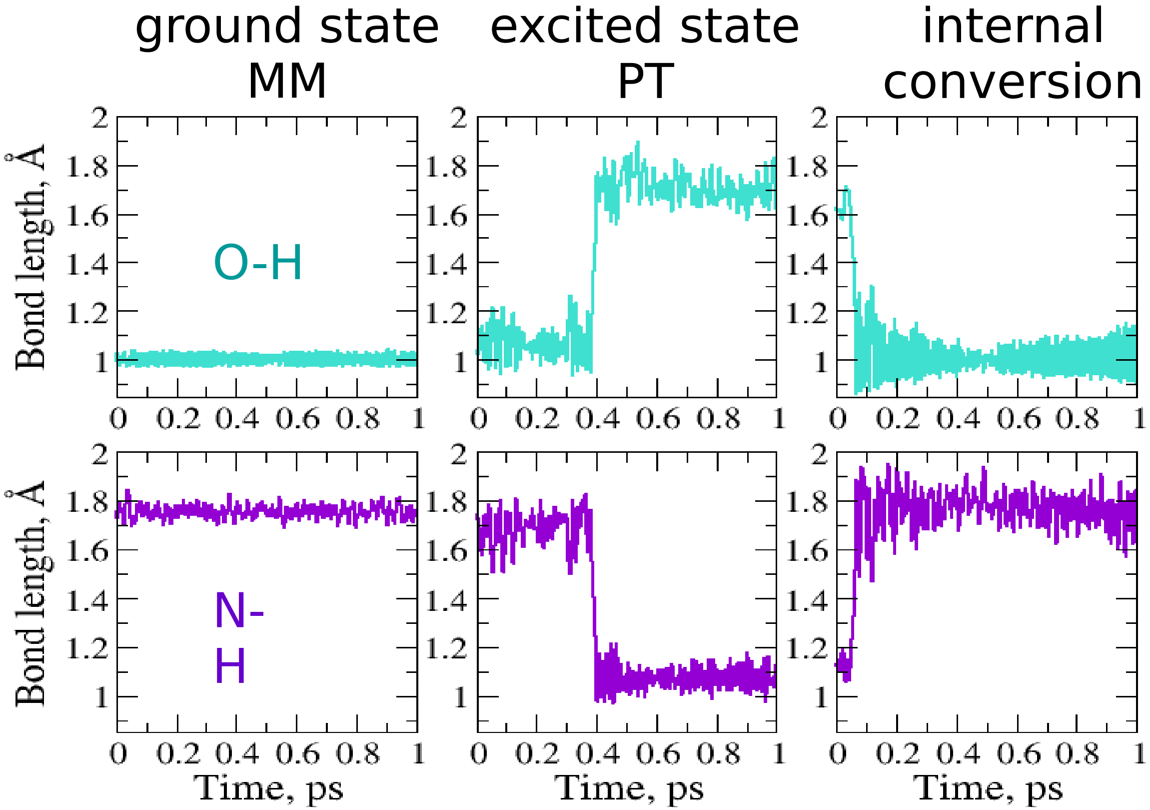
$$V_{ij} = D_{ij}\left[1 - e^{(-\beta_{ij}(R_{ij}-R_0))}\right] .$$

- O-N distance is constrained by harmonic bond potential.
- all other bonds by standard MM-FF.

✓ proton is transferred in the excited-state.

✓ proton returns as soon as excited-state decays.

✖ theoretical PT efficiency is not as high as experimental one.



# Excited State MD in the ***Diabatic Representation***

The time-dependent Schrödinger Equation (TDSE) in the Diabatic (atomic) basis:

$$i\hbar\frac{\partial}{\partial t}\Psi(r;R,t) = \hat{H}_{el}\Psi(r;R,t)\ , \qquad \text{with} \quad |\Psi(t)\rangle = \sum_{\alpha} A_{\alpha}(t)\,|f_{\alpha}\rangle$$

Expand the quantum propagator in Recursive Taylor Expansion:

$$\Psi(t_{j+1}) = \prod_{j=0}\mathcal{U}(t_{j+1},t_j)\Psi(t_0)\ ,$$

$$\Psi(t+\delta t) \approx \Psi(t) + \sum_{k=1}^{K}\left(\frac{-i\delta t}{\hbar k}\right)\mathcal{H}^{(j)}\Psi_{k-1}$$

$$\mathcal{H}^{(j)} \equiv \mathcal{H}(j\delta t) \qquad \Psi_0 \equiv \Psi(t) \quad \text{and} \quad \Psi_k = -i\delta t/(\hbar k)\mathcal{H}^{(j)}\Psi_{k-1}$$

D. Hoff and LGCR, *Chemical Modelling*: v.10, chapter 14 (2014).

# Excited State MD in the ***Diabatic Representation***

Expand the quantum propagator in Recursive Taylor Expansion:

$$\Psi(t+\delta t) \approx \Psi(t) + \sum_{k=1}^{K} \left( \frac{-i\delta t}{\hbar k} \right) \mathcal{H}^{(j)} \Psi_{k-1}$$

For the nonorthogonal Slater-type orbitals (STO): $HQ_n = \mathcal{E}_n S Q_n$

## Left Hand Side

$$\begin{aligned} \mathbf{Q}^T S S^{-1} \mathcal{H} &= \mathbf{E}\,\mathbf{Q} S \\ \mathbf{Q}' \mathcal{H}' &= \mathbf{E}\,\mathbf{Q}' \ , \end{aligned}$$

$$\begin{aligned} &\langle \Psi(t+\delta t)| \\ \approx\ & \sum_{\alpha} \left\langle \alpha^{(j)} \right| \left\{ c_{\alpha}^{\mathcal{L}}(t) - i \frac{\delta t}{\hbar} \sum_{k=1}^{K} \frac{1}{k} \left[ c_{k-1}^{\mathcal{L}}(t)\, \mathcal{H}'(t) \right]_{\alpha} \right\} \\ \approx\ & \sum_{\alpha} \left\langle \alpha^{(j)} \right| c_{\alpha}^{\mathcal{L}}(t+\delta t) \ , \end{aligned}$$

## Right Hand Side

$$\begin{aligned} S^{-1} \mathcal{H} \mathbf{Q} &= S^{-1} S \mathbf{Q}\,\mathbf{E} \\ \mathcal{H}' \mathbf{Q} &= \mathbf{Q}\,\mathbf{E} \end{aligned}$$

$$\begin{aligned} &|\Psi(t+\delta t)\rangle \\ \approx\ & \sum_{\alpha} \left\{ c_{\alpha}^{\mathcal{R}}(t) - i \frac{\delta t}{\hbar} \sum_{k=1}^{K} \frac{1}{k} \left[ \mathcal{H}'(t)\, c_{k-1}^{\mathcal{R}}(t) \right]_{\alpha} \right\} |\alpha^{(j)}\rangle \\ \approx\ & \sum_{\alpha} c_{\alpha}^{\mathcal{R}}(t+\delta t)\, |\alpha^{(j)}\rangle \ . \end{aligned}$$

# Interfacial Electron Transfer (IET)

Hellmann-Feynman forces become a **bottleneck**

$$\mathbf{F}_{AB} = -2 {\sum_{\alpha,\beta}}' \langle \alpha | \nabla \beta \rangle$$

$$\times \quad \left\{ \sum_{n} \rho^{eh}_{nn} \left( \chi_{ab} - \mathcal{E}_n \right) Q^n_b Q^n_a + \sum_{m>n} \mathbb{R} \left( \rho^{eh}_{nm} \right) \left[ \left( \chi_{ab} - \mathcal{E}_m \right) Q^n_a Q^m_b + \left( \chi_{ba} - \mathcal{E}_n \right) Q^n_b Q^m_a \right] \right\}$$

The Hellman-Feynman forces in diabatic representation become

$$\mathbf{F}_{\mathrm{AB}} = -2 {\sum_{\alpha,\beta}}' \langle \alpha | \nabla \beta \rangle \left\{ \chi \circ \rho_{\mathbb{R}} + \mathcal{H}' \rho_{\mathbb{R}} \right\}_{\beta\alpha} \ ,$$

with $(A \circ B)_{\beta\alpha} = A_{\beta\alpha} B_{\beta\alpha}$ and $\rho_{\mathbb{R}} \equiv \rho^{AO}_{\mathbb{R}}$

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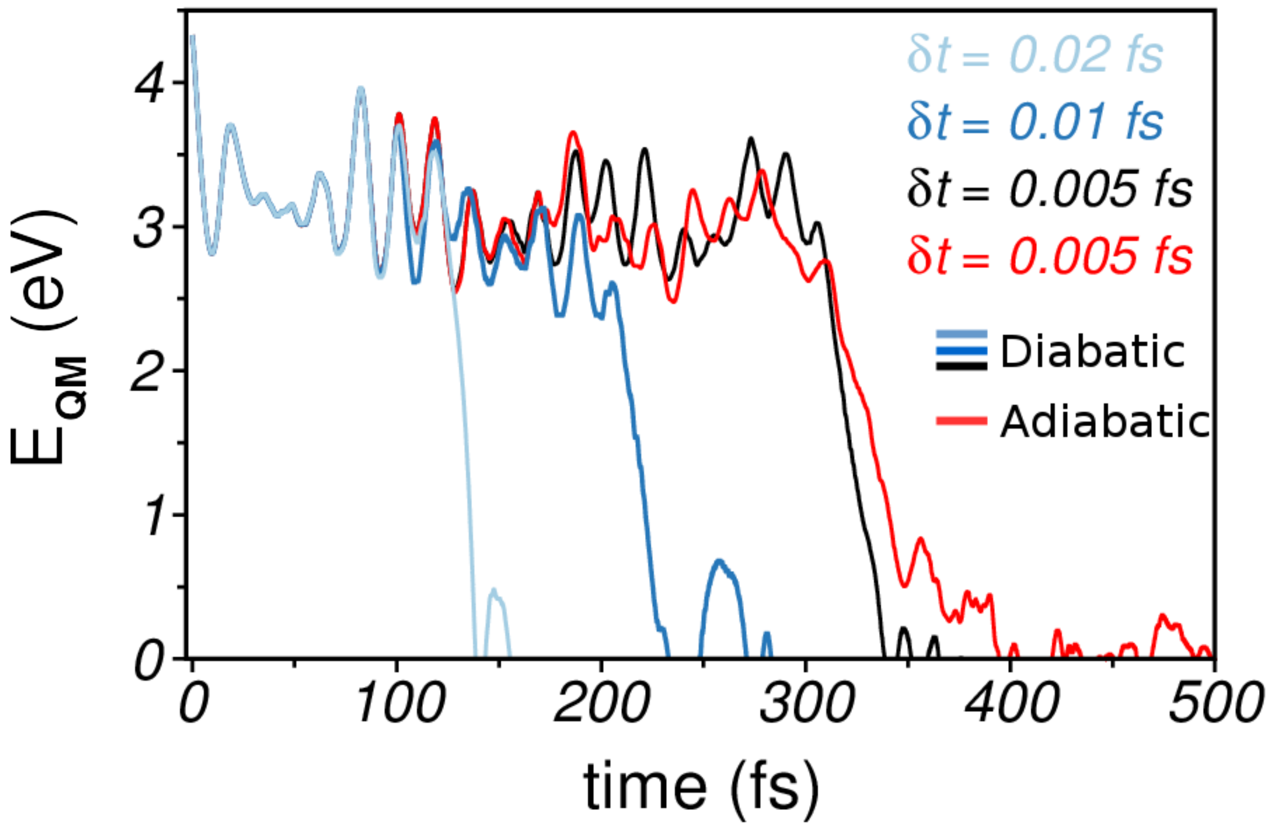
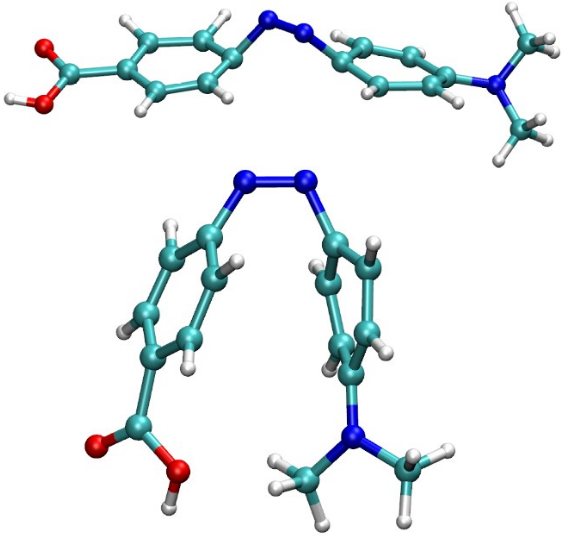
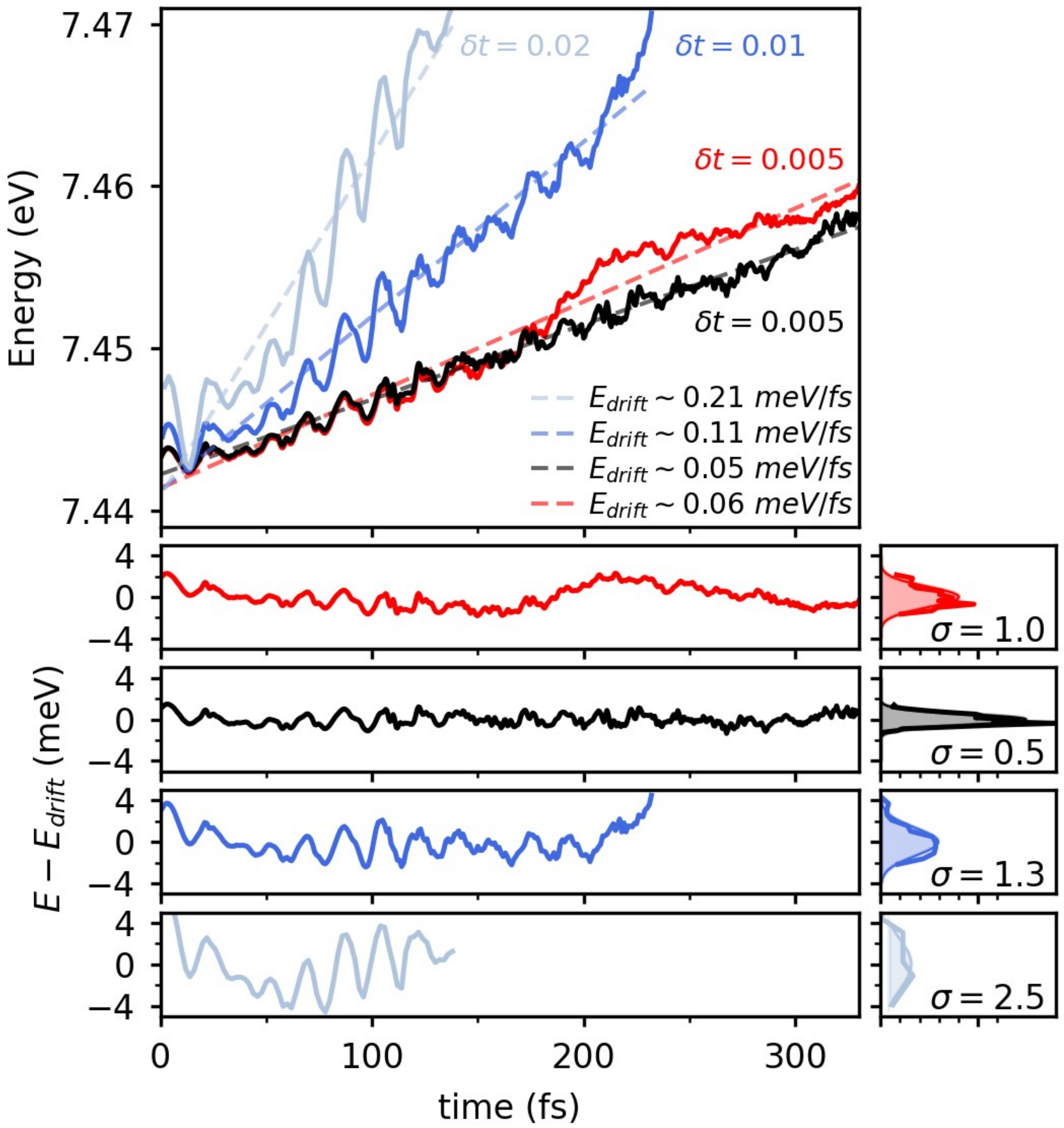
in the GPU
$\sim 20 \times$ faster
than propagation in
Adiabatic basis with
identical results

# NAMD through Conical Intersection





# Energy Conservation

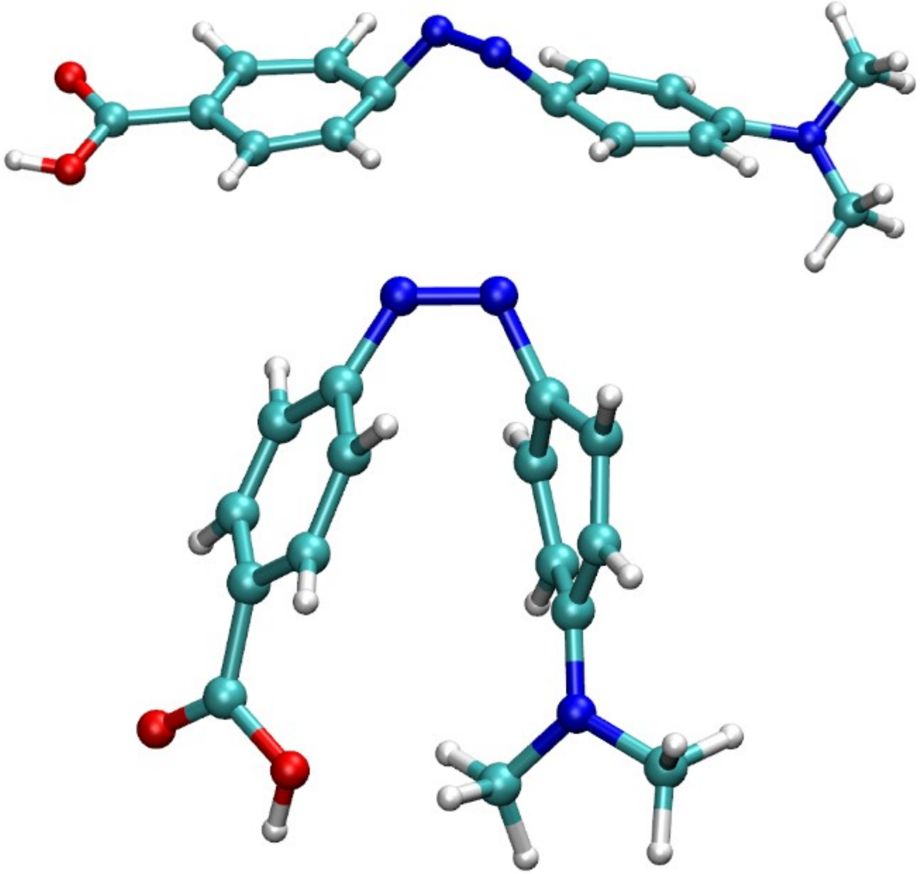


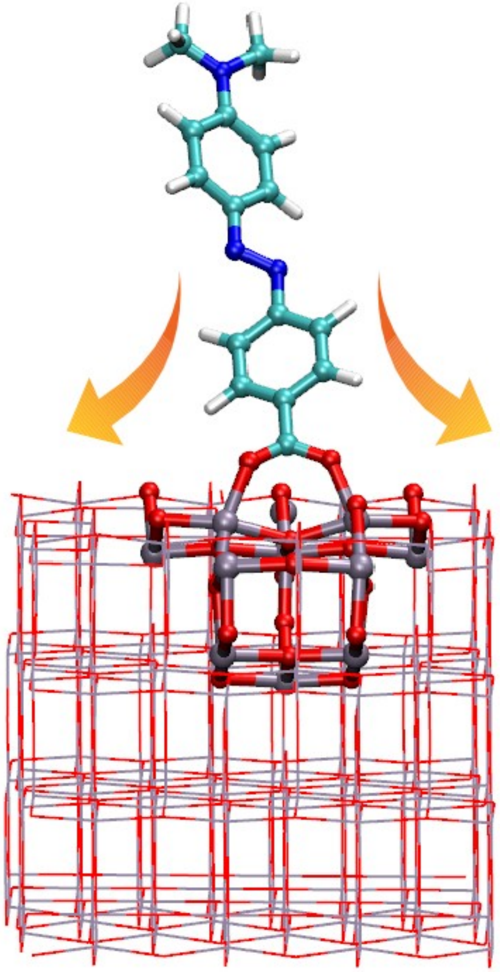
Diabatic

Adiabatic

# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

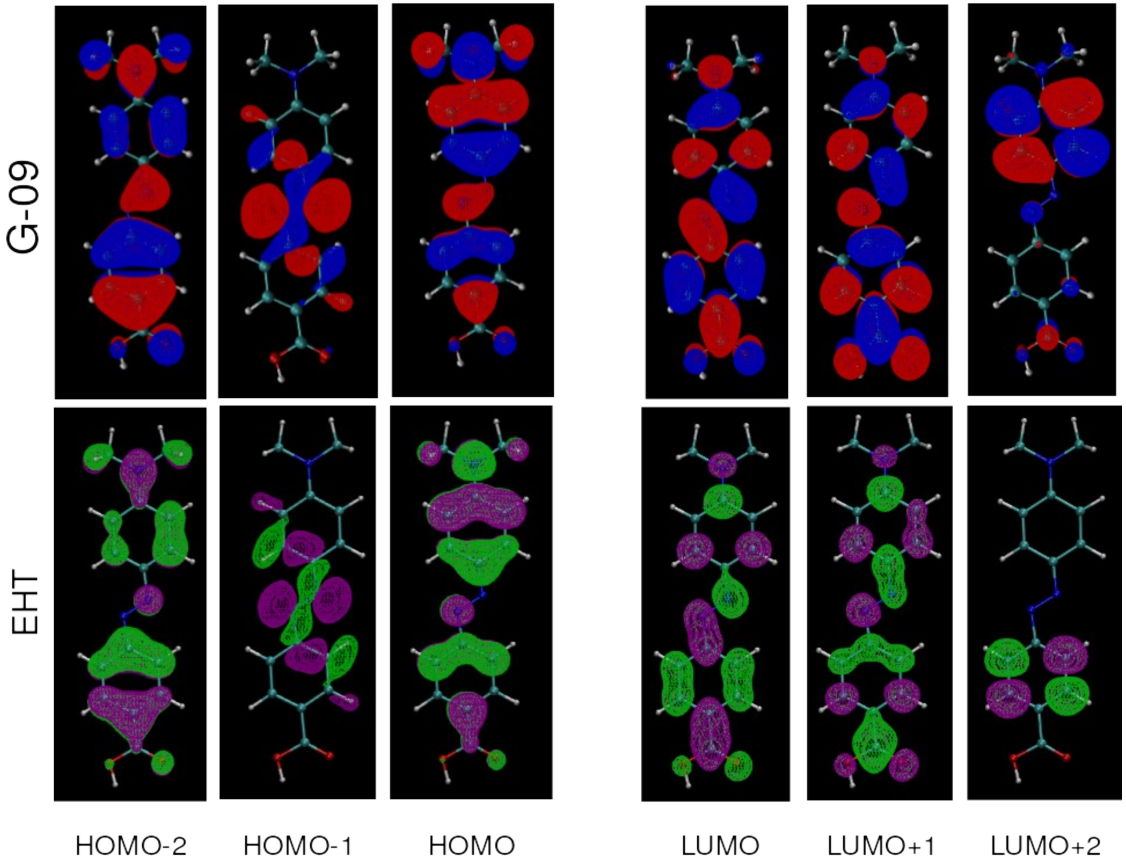
## Push-Pull AZO compounds and Dye Sensitizers



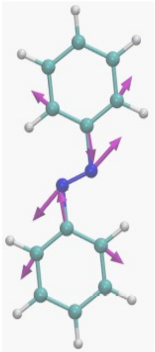


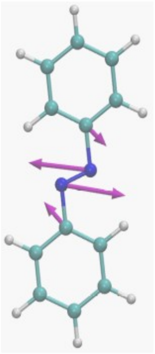
JPC Lett., 2018, **9**, 5926.

# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

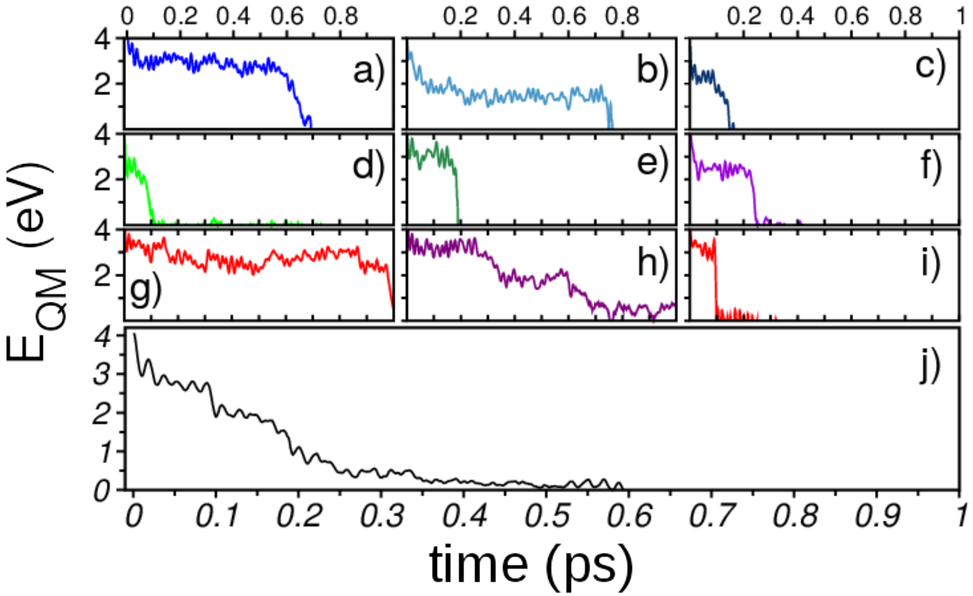


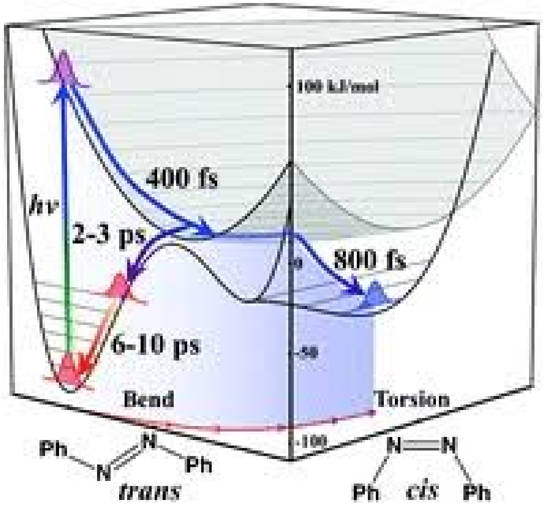
| Frontier Orbitals | DFT/B3LYP/6-31G(d) | DynEMol-EHT |
|---|---|---|
| LUMO - HOMO | 3.14 | 2.97 |
| HOMO - [HOMO-1] | 0.81 | 0.67 |
| LUMO - [HOMO-1] | 3.78 | 3.63 |
| [LUMO+1] - LUMO | 1.70 | 1.81 |


$\mathbf{F}(\pi,\pi^*)$

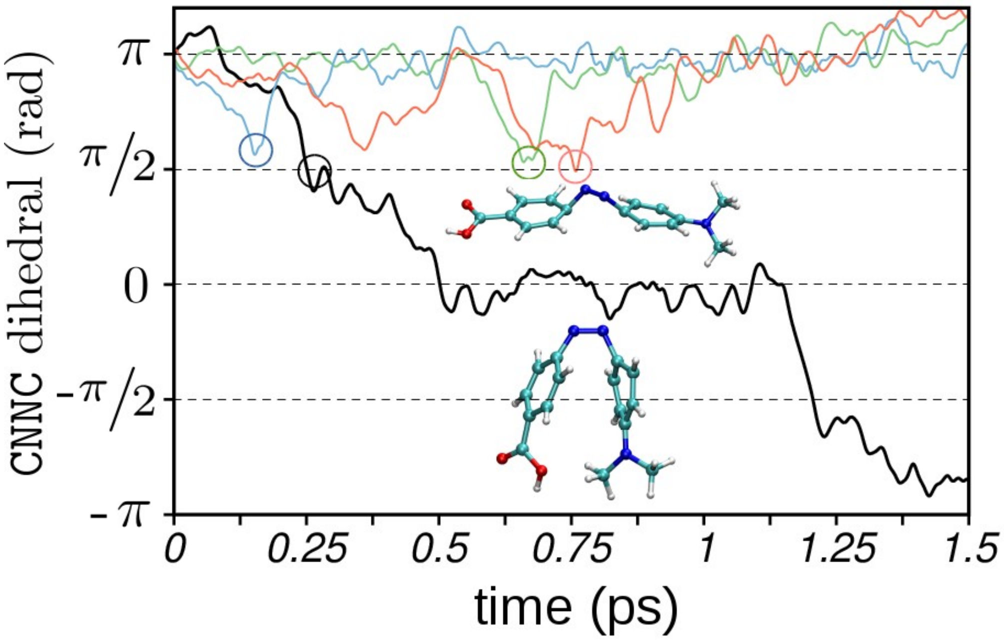

$\mathbf{F}(n,\pi^*)$

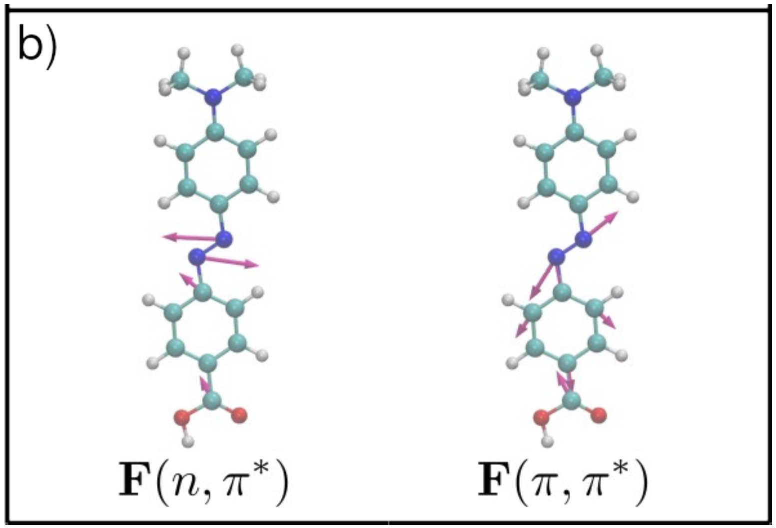
# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



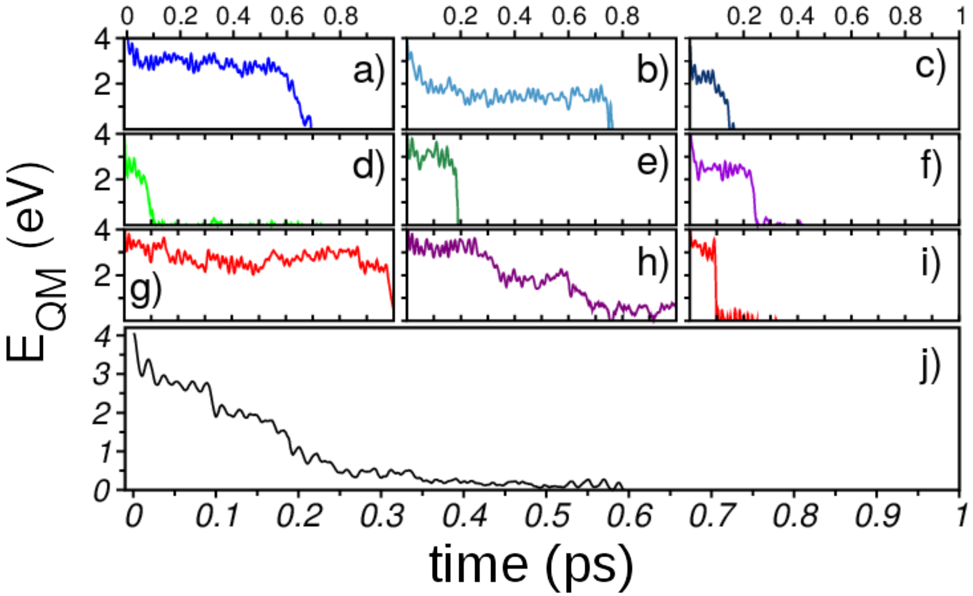


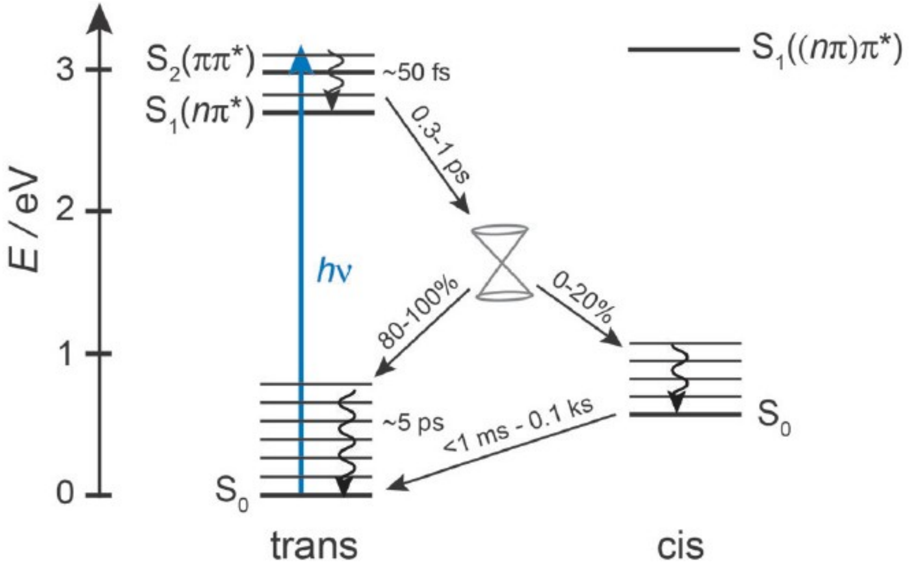
D.P.Hoffman& R.A.Mathies PCCP, 2012,6298



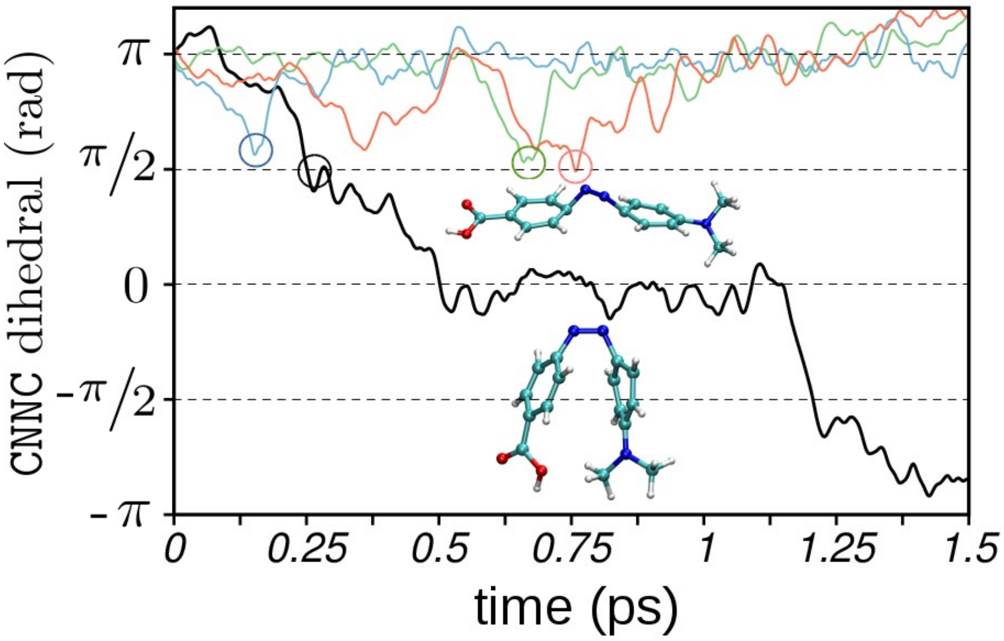


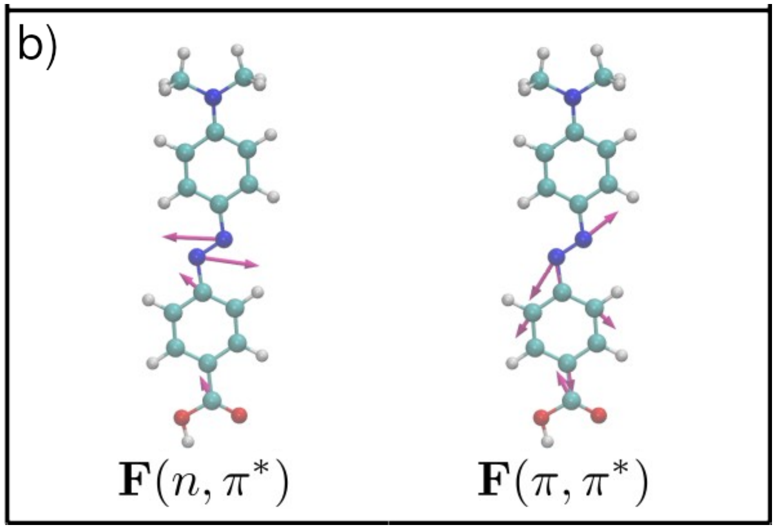
# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



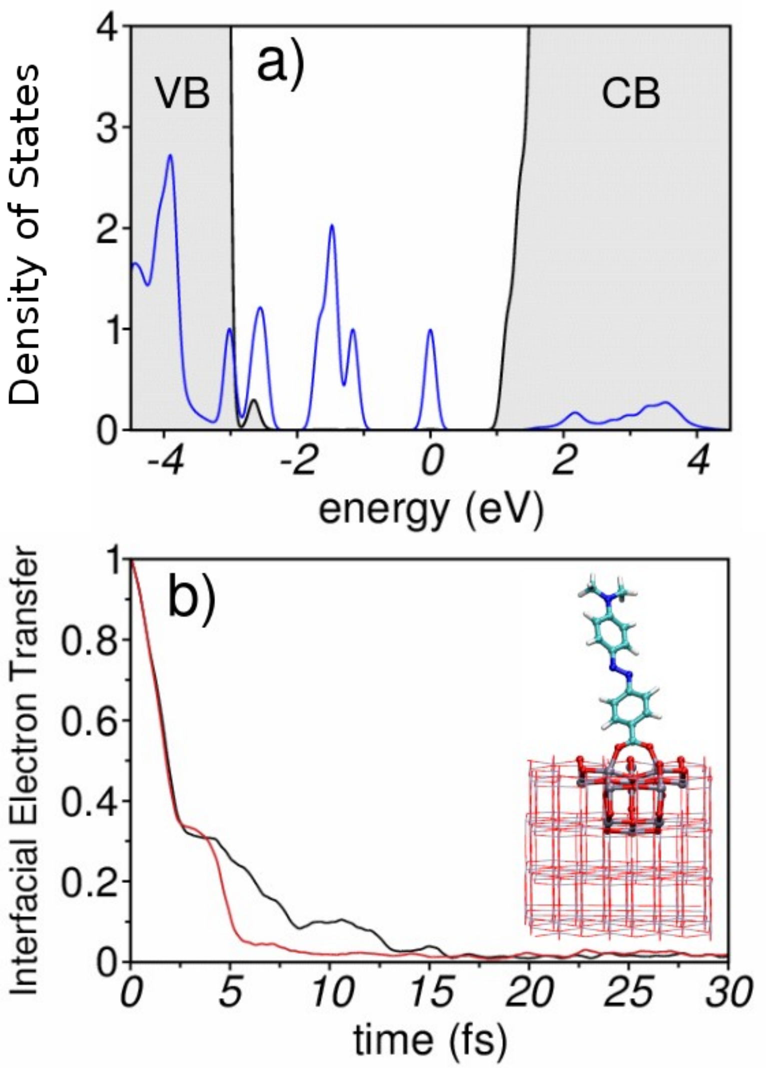


Vauthey et al.,PCCP, 2018,7254

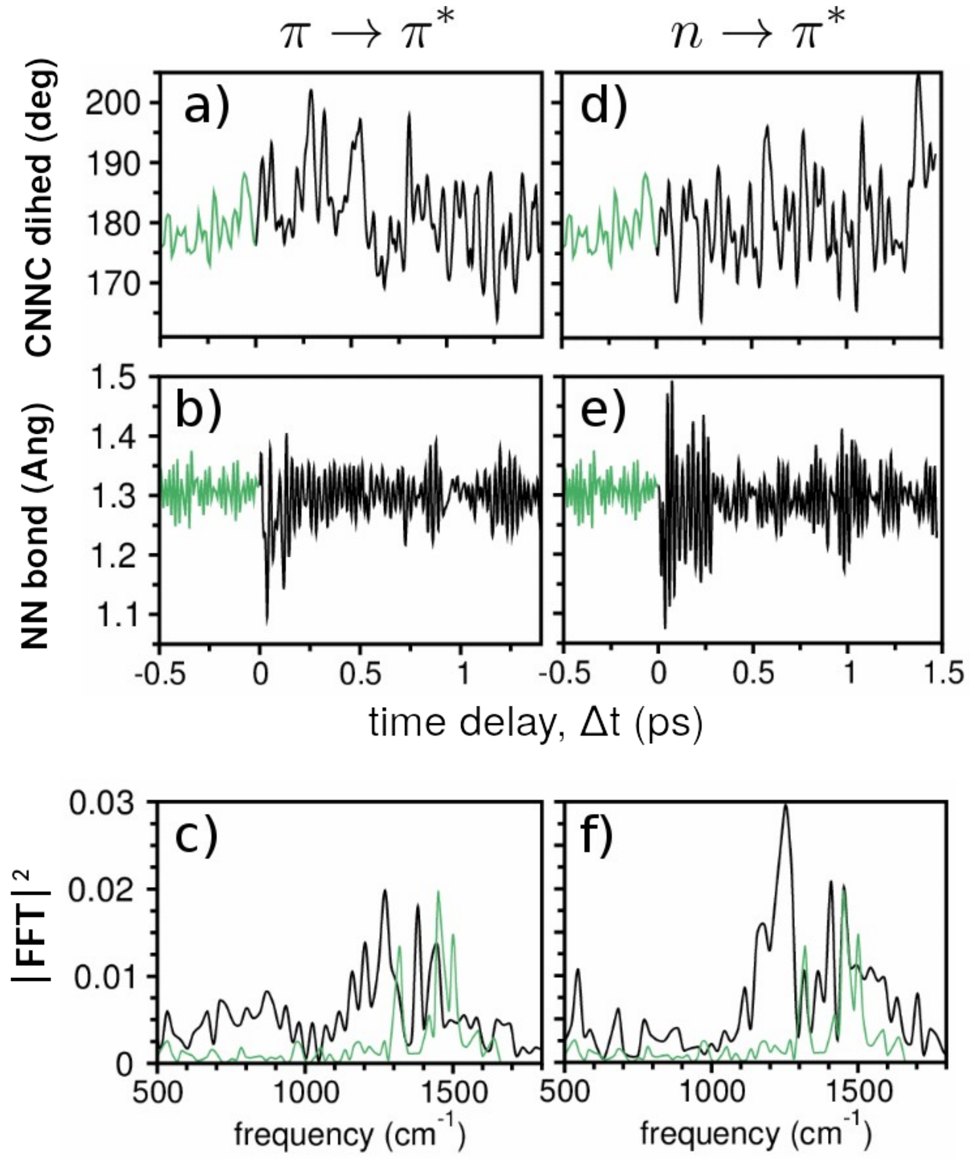


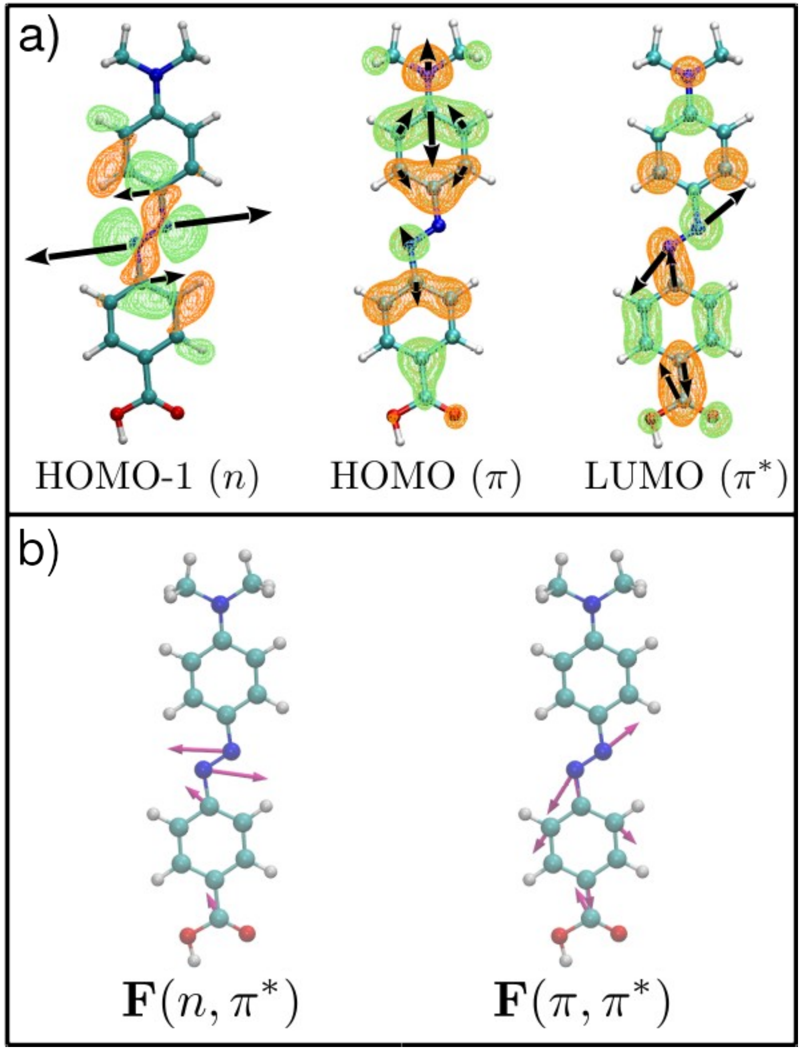


# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



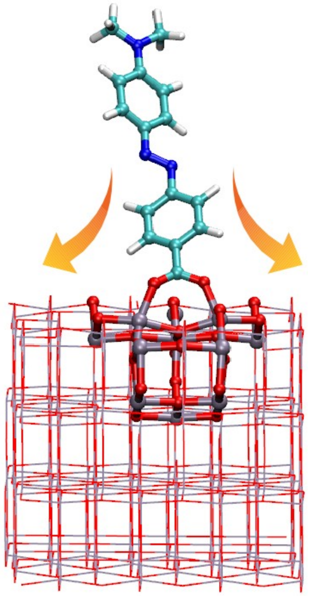
# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

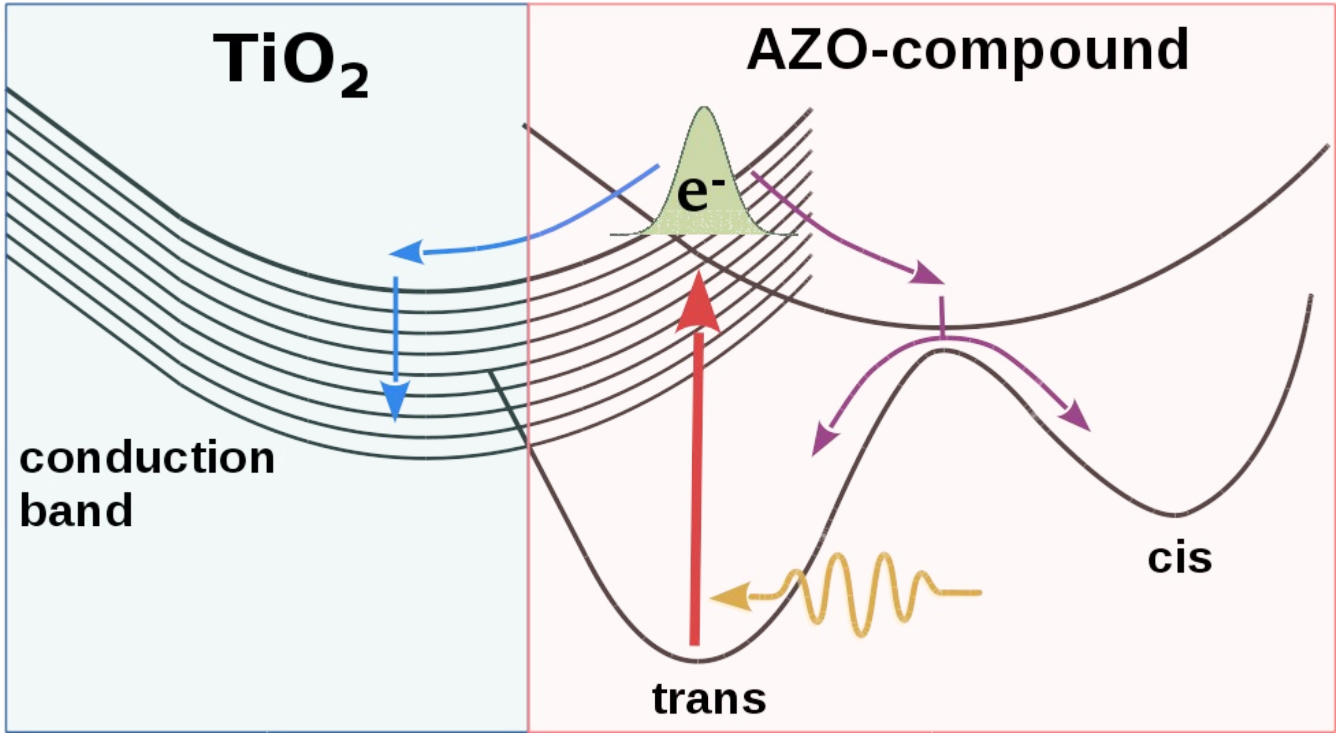


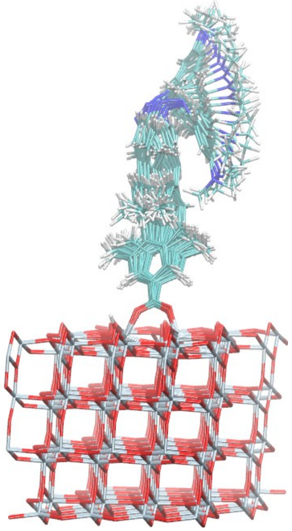


# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

## Push-Pull AZO compounds and Dye Sensitizers

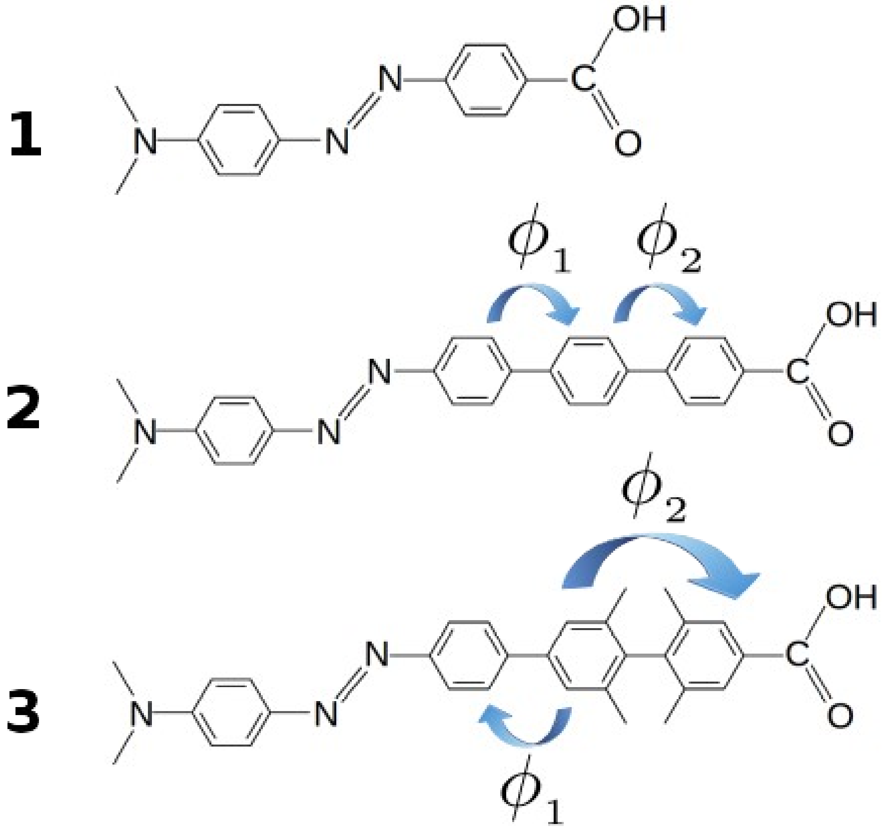


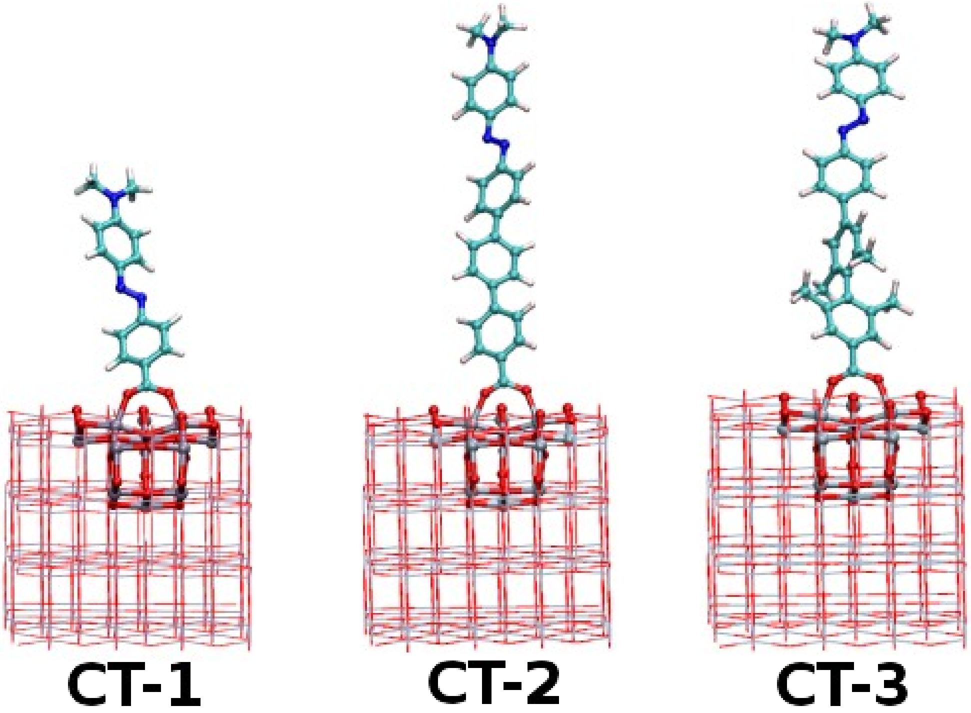




J. Phys. Chem. C, 2019

# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



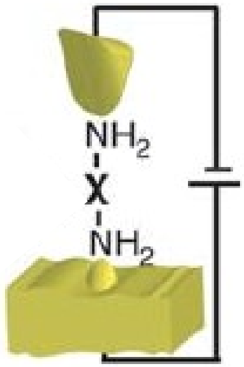


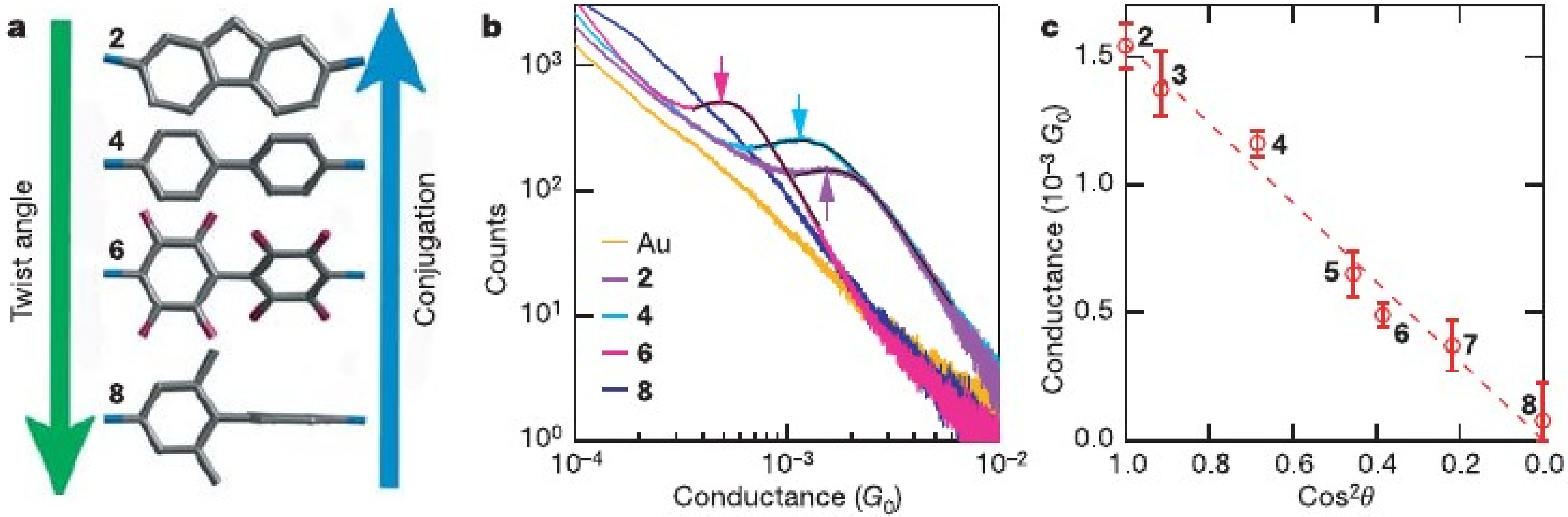
J. Phys. Chem. C, 2019

nature Vol 442|24 August 2006|doi:10.1038/nature05037

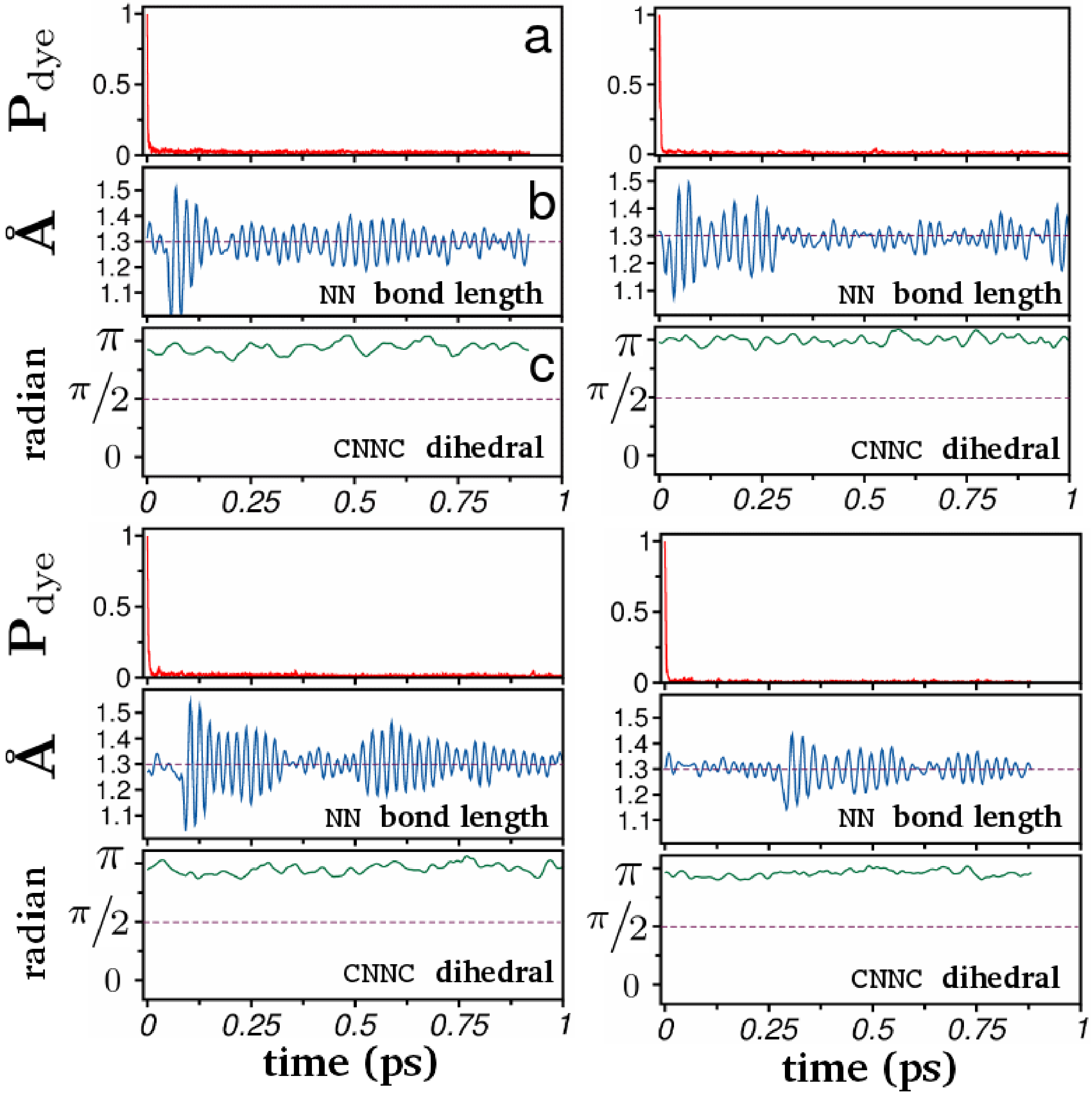
# Dependence of single-molecule junction conductance on molecular conformation

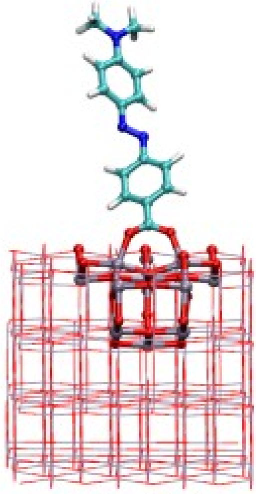
Latha Venkataraman[1,4], Jennifer E. Klare[2,4], Colin Nuckolls[2,4], Mark S. Hybertsen[3,4] & Michael L. Steigerwald[2]





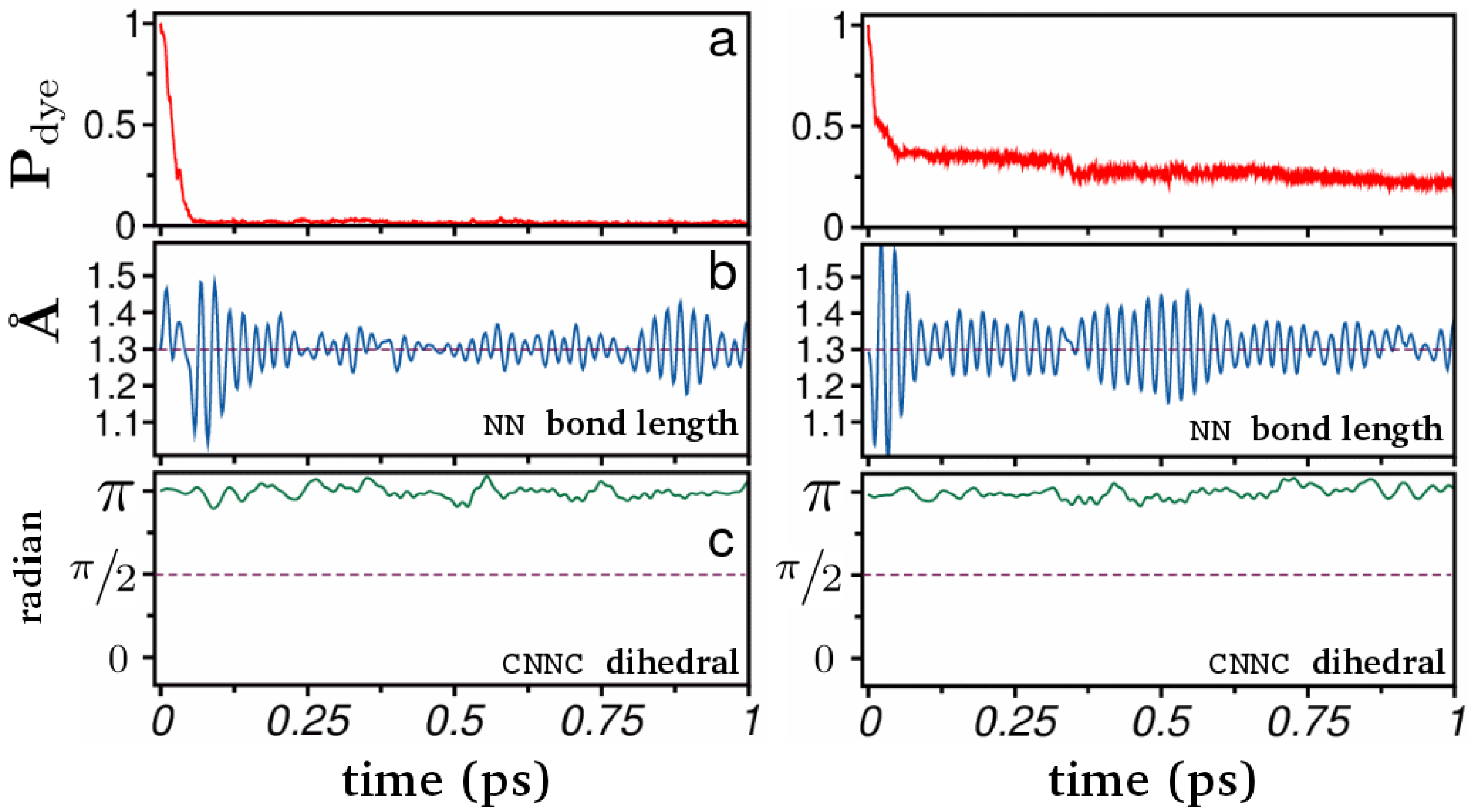
# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

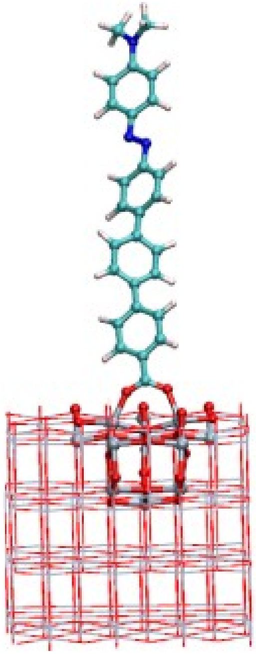




**CT-1**

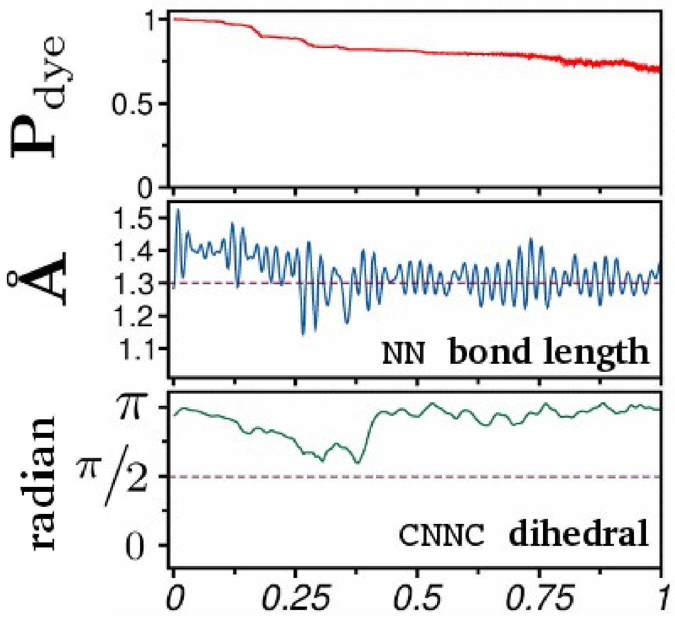
# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

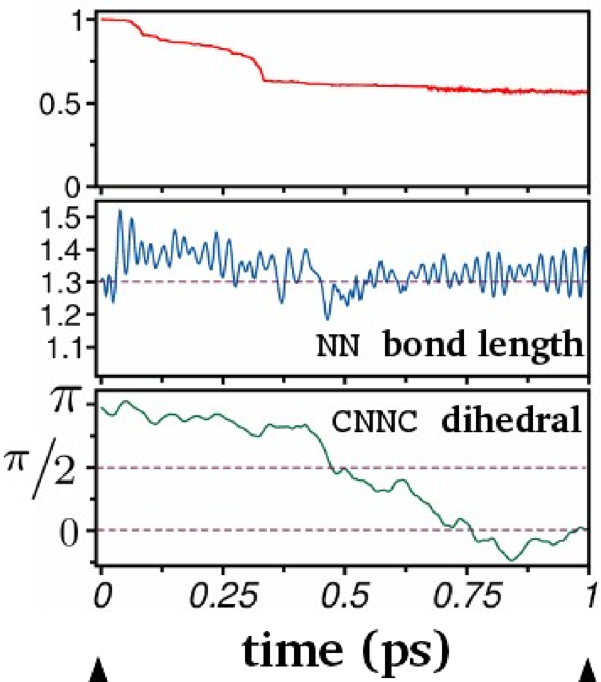


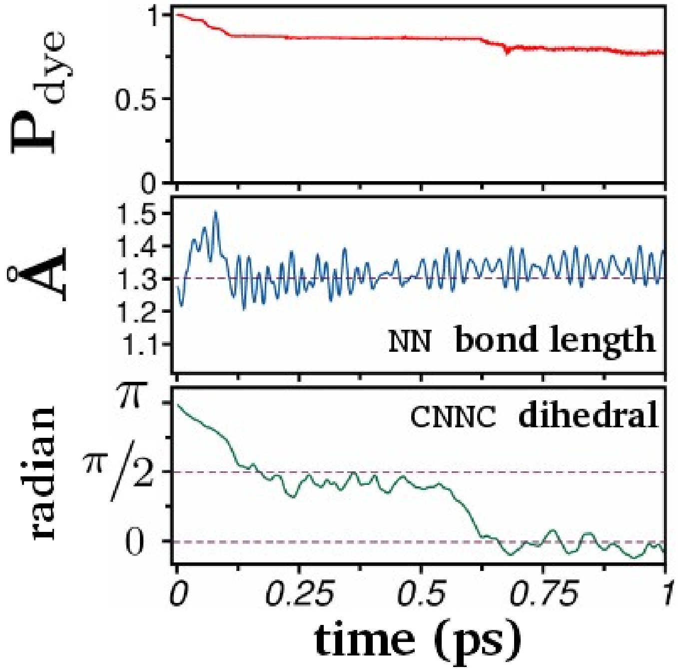


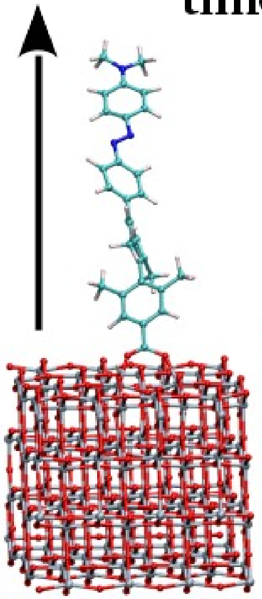
**CT-2**

# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

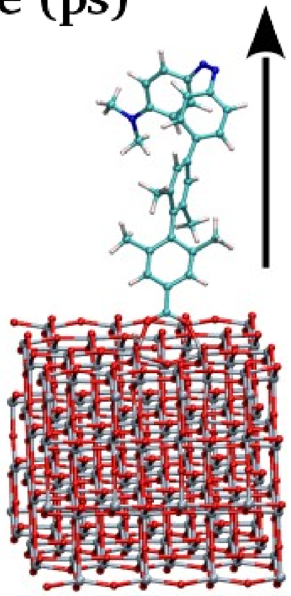




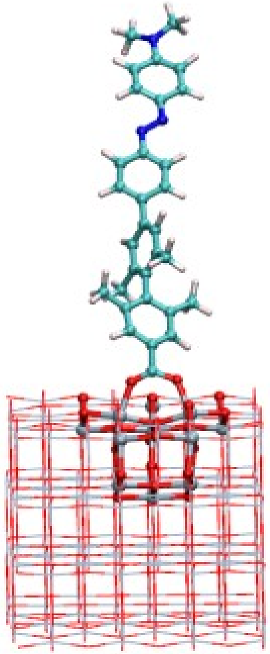




**CT-3**

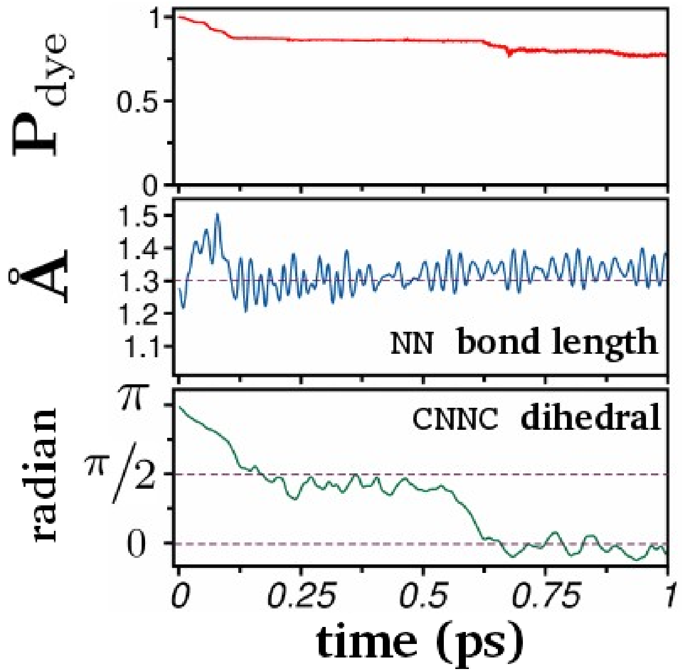


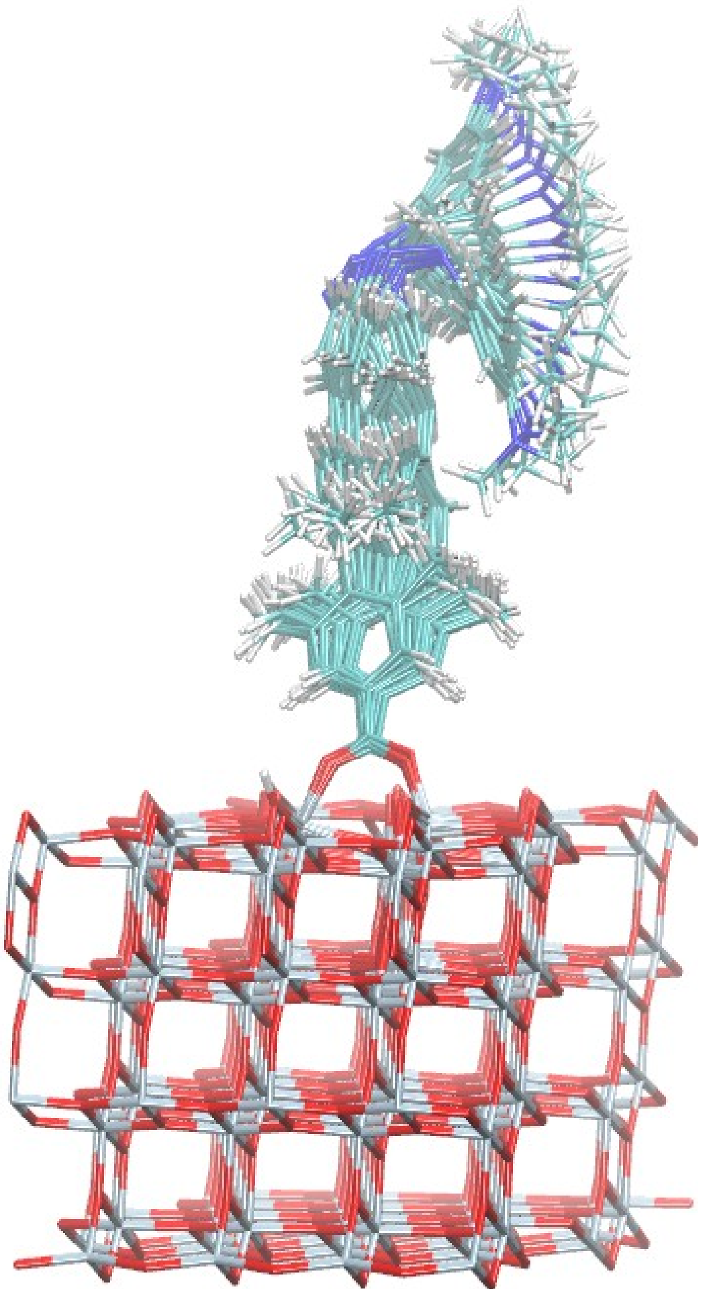
**CT-3**



**CT-3**

# Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics





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CAPES

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