Lecture 11

Photoexcited dynamics: Non-adiabatic excited state molecular dynamics, mixed quantum-classical algorithms, codes, modeling of spectroscopic observables, energy and charge transfer

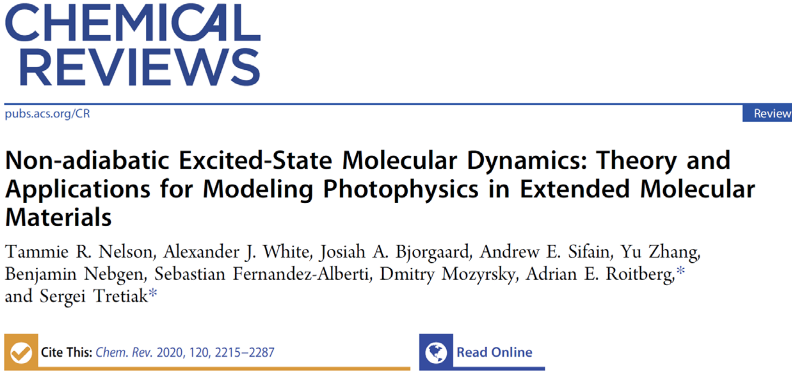
Sergei Tretiak

May 15, 2020

Advanced Materials modeling

Skoltech

Our plan for non-adiabatic molecular dynamics (NAMD) lecture



CHEMICAL REVIEWS

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Review

Non-adiabatic Excited-State Molecular Dynamics: Theory and Applications for Modeling Photophysics in Extended Molecular Materials

Tammie R. Nelson, Alexander J. White, Josiah A. Bjorgaard, Andrew E. Sifain, Yu Zhang, Benjamin Nebgen, Sebastian Fernandez-Alberti, Dmitry Mozyrsky, Adrian E. Roitberg,* and Sergei Tretiak*

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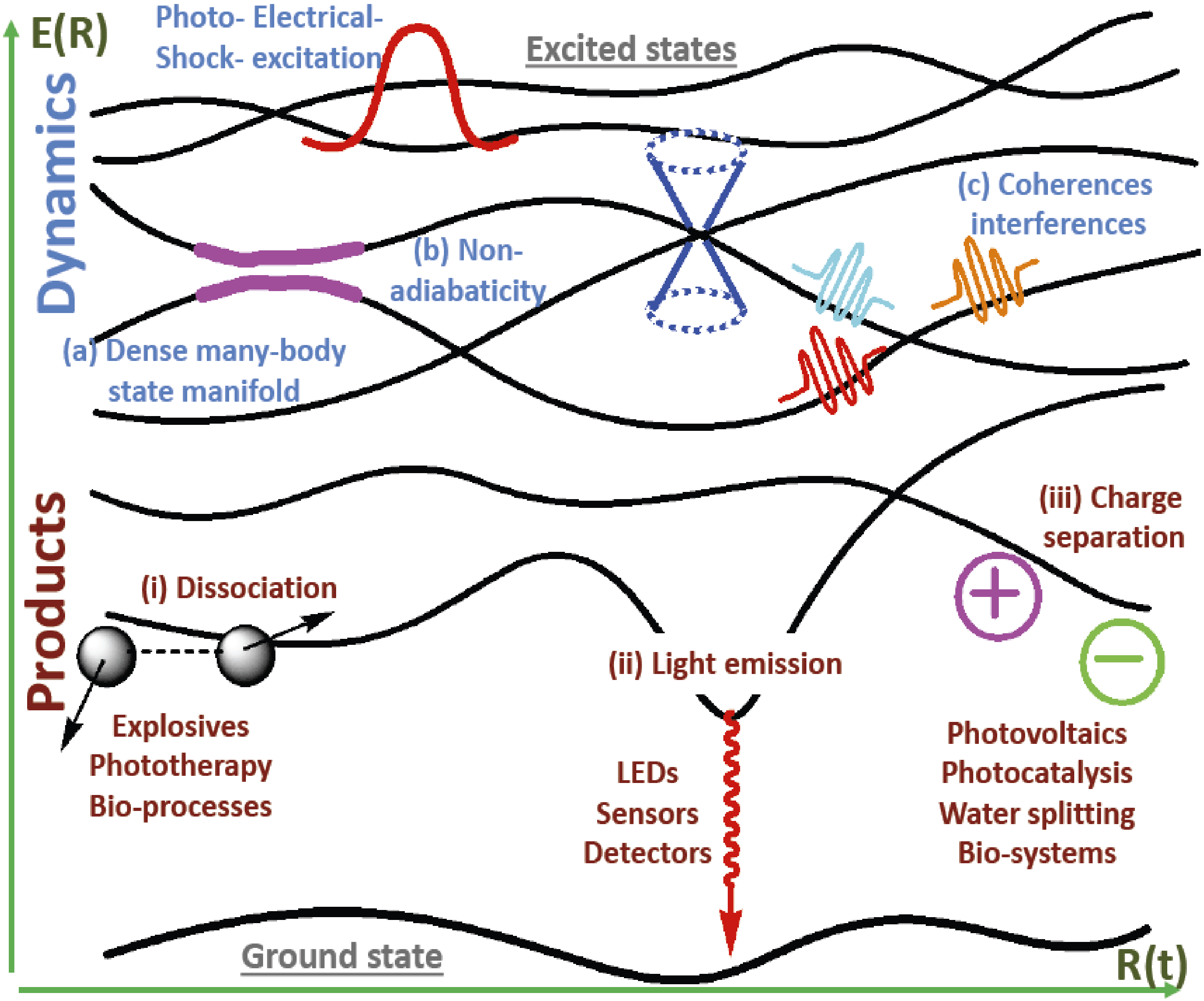
Read Online

- ➢ *Introduction: what are we taking about?*
- ➢ *Born-Oppenheimer Approximation*
- ➢ *Early models, Landau-Zener approximation*
- ➢ *Non-adiabatic regions, Conical Intersections (CI)*
- ➢ *Need for atomistic methods, mixed quantum-classical approach*
- ➢ *Ehrenfest dynamics and examples*
- ➢ *Surface Hopping methodology: solids and molecular systems*
- ➢ *Gaussian wavepacket dynamics*
- ➢ *Ab Initio Multiple Spawning (AIMS)*
- ➢ *Multi-configurational Ehrenfest with Ab Initio Multiple Cloning (MCE-AIMC)*
- ➢ *Multi Configuration Time Dependent Hartree (MC-TDH)*
- ➢ *Practical aspects: spectra, rates, wavefunction analysis*
- ➢ *Overview of available codes*

Literature:

- *Yarkony, D. (1996). "Diabolical Conical Intersections". Reviews of Modern Physics. 68, 985 (1996)*
- *Crespo-Otero, R.; Barbatti, M. "Recent Advances and Perspectives on Nonadiabatic Mixed Quantum-Classical Dynamics". Chem. Rev. 2018, 118, 7026*
- *Kapral, R. "Progress in the Theory of Mixed Quantum-Classical Dynamics". Annu. Rev. Phys. Chem. 2006, 57, 129*
- *Tully, J. C. "Perspective: Nonadiabatic Dynamics Theory". J. Chem. Phys. 2012, 137, 22A301.*
- *Akimov, A. V.; Prezhdo, O. V. "The Pyxaid Program for Non-Adiabatic Molecular Dynamics in Condensed Matter Systems". J. Chem. Theory Comput. 2013, 9, 4959.*
- *Curchod, B. F. E.; Martinez, T. J. "Ab Initio Nonadiabatic Quantum Molecular Dynamics". Chem. Rev. 2018, 118, 3305*
- *Jackle, A.; Worth, G.A.; Meyer, H.D.; Beck, M. "The multiconfiguration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagating wavepackets" Physics reports. , 2000, Vol.324, p.1-105*

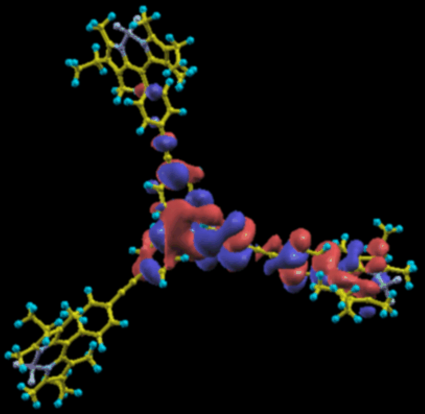
Photoexcited dynamics

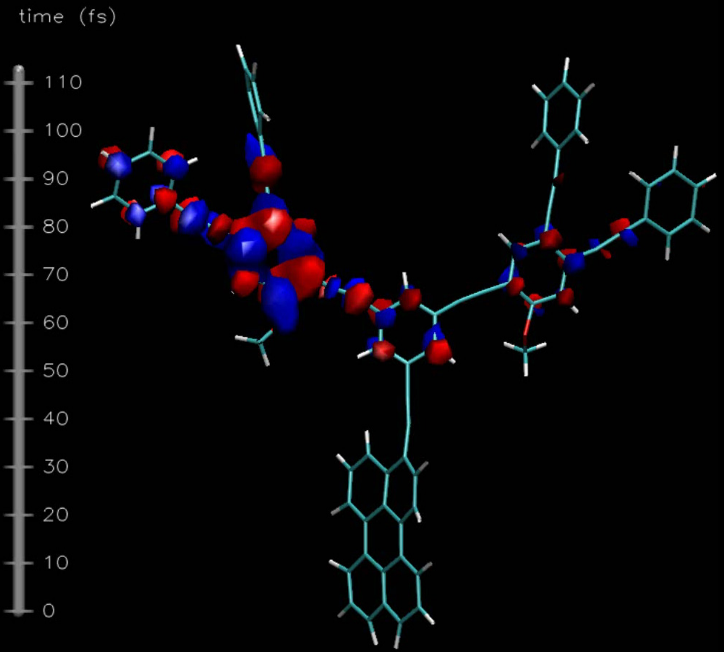


Excited state relaxation timescales:

- ☐ Fluorescent decay
  ~ 1 ns
- ☐ Intraband relaxation
  ~ 10 ps
- ☐ Level crossing
  ~ 100 fs

0 fs

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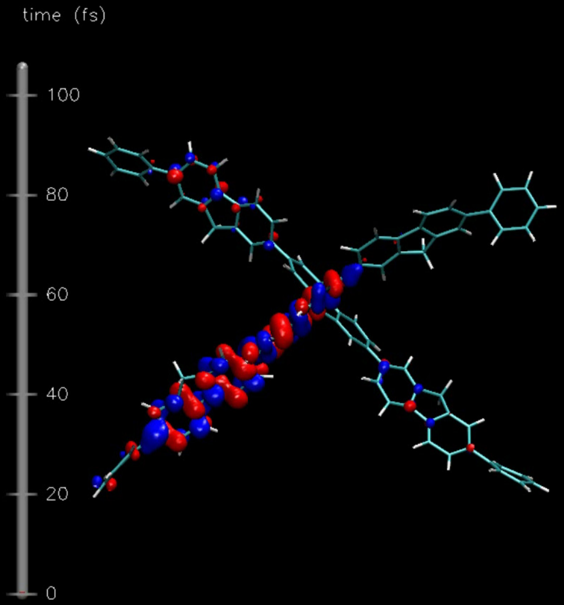
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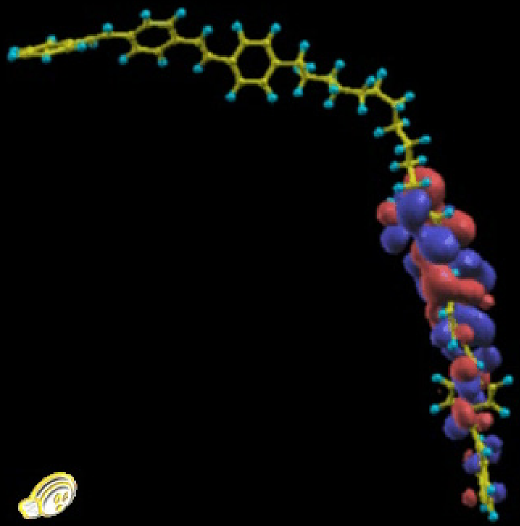

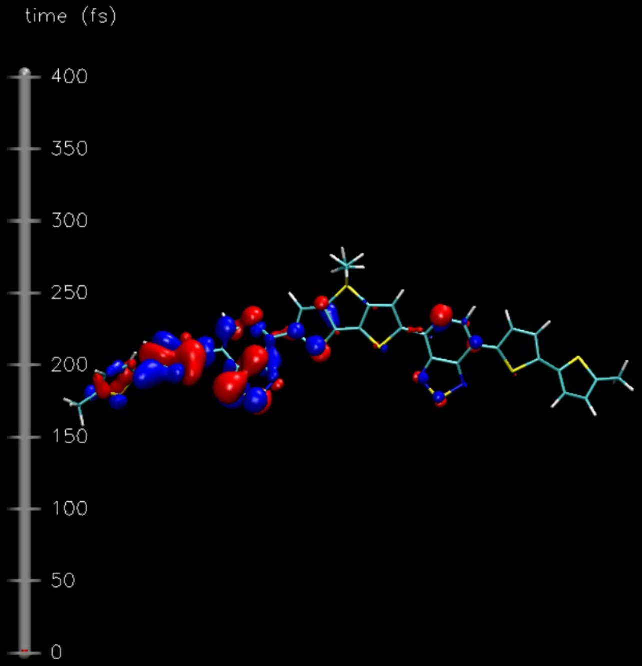
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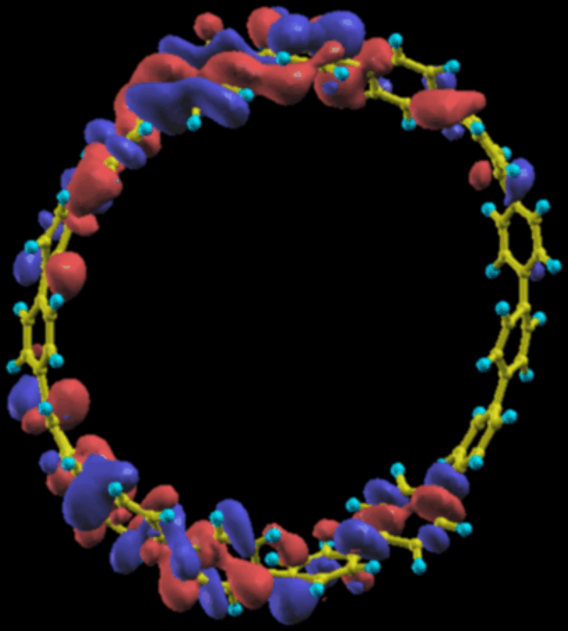


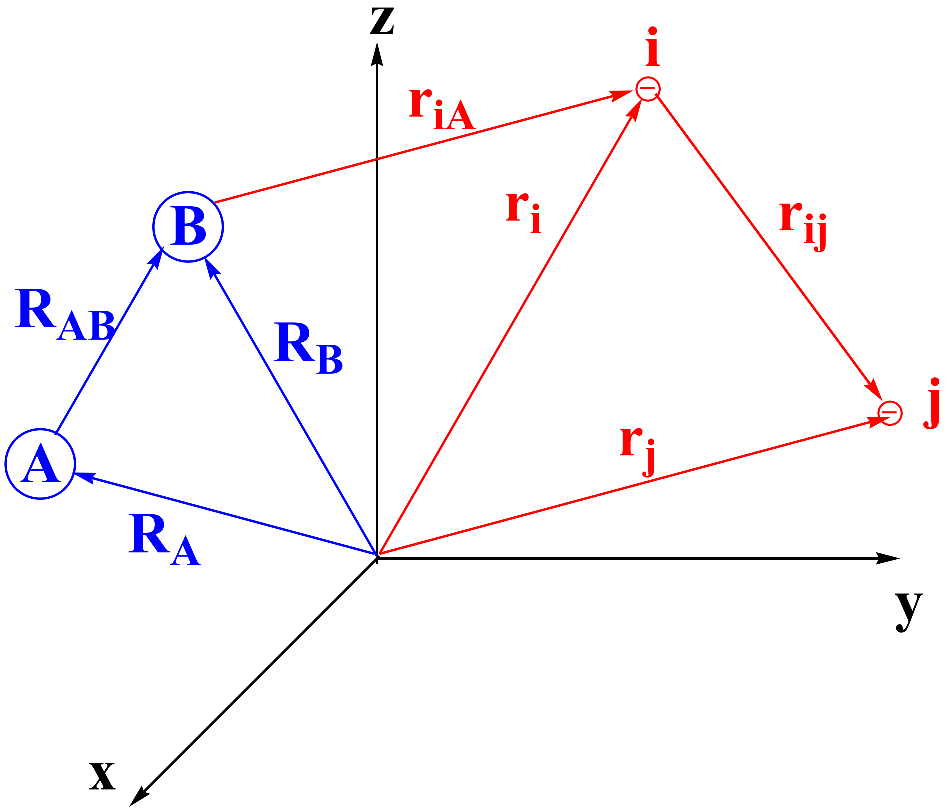
The molecular Hamiltonian

$$\hat{H} = -\sum_{A} \frac{1}{2M_A}\nabla_A^2 - \sum_{i} \frac{1}{2}\nabla_i^2 + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{Ai} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}}$$

OR

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

"EXACT" nonrelativistic Hamiltonian in absence of field, i.e. quantum system of particles interacting with Coulomb potential



Atomic units (au) sets to be unity:

Electron mass m_e

Elementary charge e

Reduced Planck's constant $\hbar = h/(2\pi)$

Coulomb's constant $1/(4\pi\epsilon_0)$

What is neglected? Relativistic mass corrections (mostly inner electrons in heavy atoms), the most important is spin-orbit couplings (**L*S**)

The Born-Oppenheimer Approximation

Given separable Hamiltonian $\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2)$ ***for*** $\hat{H}\psi(q_1, q_2) = E\psi(q_1, q_2)$

Then $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$ ***(factorization) and*** $E = (E_1 + E_2)$ ***(additive)***

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

Approximately separable! $\phi_T(\mathbf{r}, \mathbf{R}) = \phi_e(\mathbf{r}; \mathbf{R})\phi_N(\mathbf{R})$

$$\hat{H}\phi_e(\mathbf{r}; \mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r}; \mathbf{R})\phi_N(\mathbf{R})$$

Electronic problem: $\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$

$$\hat{H}_e\phi_e(\mathbf{r}; \mathbf{R}) = \left\{ -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}} \right\} \phi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R})\phi_e(\mathbf{r}; \mathbf{R})$$

Nuclei problem: $\{\hat{T}_N + E_e + \hat{V}_{NN}\}\phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R})$

$$\hat{H}_N\phi_N(\mathbf{R}) = \left\{ -\sum_A \frac{1}{2M_A}\nabla_A^2 + E_e(\mathbf{R}) + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} \right\} \phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R})$$

i.e., the nuclei move in a potential created by the electrons.

Bottom line: The Born-Oppenheimer Approximation allows definition of potential energy surfaces *E(**R**),* introducing ‘states’ and permitting, e.g., for ab initio MD adopting classical nuclei

What are we neglecting in BO approximation?

We have extra terms in the nuclei Hamiltonian due to other electronic levels and center of mass motion

Small parameter

$$m/M_A \sim 1/10000$$

$$\Psi_{\mathrm{tot}}(\mathbf{R},\mathbf{r}) = \sum_{i=1}^{\infty} \Psi_{\mathrm{n}i}(\mathbf{R})\Psi_i(\mathbf{R},\mathbf{r})$$

i and j run over the electronic levels

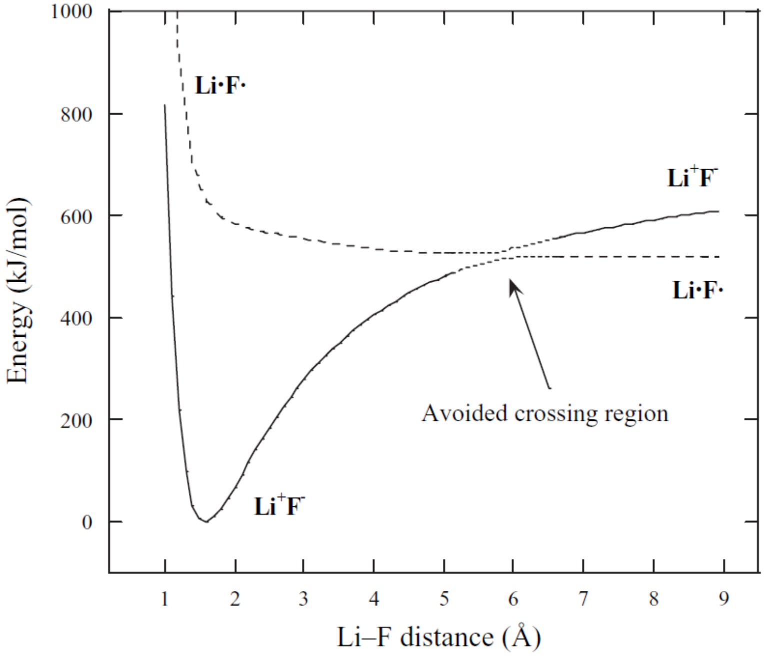
$$\nabla_{\mathrm{n}}^2\Psi_{\mathrm{n}j} + E_j\Psi_{\mathrm{n}j} + \sum_{i=1}^{\infty}\left\{\begin{matrix} 2\langle\Psi_j|\overset{\boxed{1}}{\nabla_{\mathrm{n}}}|\Psi_i\rangle(\nabla_{\mathrm{n}}\Psi_{\mathrm{n}i}) + \langle\Psi_j|\overset{\boxed{2}}{\nabla_{\mathrm{n}}^2}|\Psi_i\rangle\Psi_{\mathrm{n}i} + \\ \langle\Psi_j|\mathbf{H}_{\mathrm{mp}}|\Psi_i\rangle\Psi_{\mathrm{n}i} \quad \boxed{3} \end{matrix}\right\} = E_{\mathrm{tot}}\Psi_{\mathrm{n}j}$$

1) First order non-adiabatic terms: VERY IMPORTANT!!! (make Born-Oppenheimer approximation invalid in the vicinity of any electronic level crossing)

2) The diagonal correction (small compared to E_i, accounted in adiabatic approximation, neglected in BO approximation)

3) Mass-polarization (cannot separate the center of mass motion from the internal motion of particles)

$$\mathbf{H}_{\mathrm{mp}} = -\frac{1}{2M_{\mathrm{tot}}}\left(\sum_{i}^{N_{\mathrm{elec}}}\nabla_i\right)^2$$



Time-dependent Schrödinger equation (TDSE)

General form TDSE

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

$$\hat{H}(\boldsymbol{R},\boldsymbol{r}) = \hat{T}(\boldsymbol{R}) + \hat{H}_{el}(\boldsymbol{R},\boldsymbol{r})$$

$$\hat{H}_{el}(\boldsymbol{r},\boldsymbol{R})\psi_a(\boldsymbol{r},\boldsymbol{R}) = E_a(\boldsymbol{R})\psi_a(\boldsymbol{r},\boldsymbol{R})$$

$$\langle\psi_a(\boldsymbol{r},\boldsymbol{R})|\psi_b(\boldsymbol{r},\boldsymbol{R})\rangle_{\boldsymbol{r}} = \delta_{ab}$$

Adiabatic and diabatic representation

Electrons Nuclei Electrons Nuclei

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \sum_a \psi_a(\boldsymbol{r},\boldsymbol{R})\chi_a(\boldsymbol{R},t) = \sum_a \phi_a(\boldsymbol{r})\chi'_a(\boldsymbol{R},t)$$

Adiabatic Diabatic

Adiabatic **electronic wavefunctions** (eigenfunctions) are found in quantum chemistry with $E_a(\boldsymbol{R})$ defining potential energy surfaces (PESs)

Time-dependent Schrödinger equation (TDSE) for nuclei wavefunctions: central to this lecture

$$i\hbar\frac{\partial\chi_a(\boldsymbol{R},t)}{\partial t} = \underbrace{\left[-\frac{1}{2}\hbar^2\nabla_{\boldsymbol{R}}\cdot\hat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}} + E_a(\boldsymbol{R}) - \sum_b\frac{1}{2}\hbar^2\,\boldsymbol{d}_{ab}(\boldsymbol{R})\cdot\hat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{d}_{ab}(\boldsymbol{R})\right]}_{\text{Adiabatic part}}\chi_a(\boldsymbol{R},t) + \underbrace{\sum_b\frac{1}{2}\hbar^2\left[\boldsymbol{d}_{ab}(\boldsymbol{R})\cdot\hat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}} + \nabla_{\boldsymbol{R}}\cdot\hat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{d}_{ab}(\boldsymbol{R})\right]\chi_b(\boldsymbol{R},t)}_{\text{Non-Adiabatic terms}}$$

$\hat{\boldsymbol{m}}_{\boldsymbol{R}}$ Diagonal nuclear mass matrix

$$\boldsymbol{d}_{ab}(\boldsymbol{R}) = \langle\psi_a(\boldsymbol{r},\boldsymbol{R})|\nabla_{\boldsymbol{R}}|\psi_b(\boldsymbol{r},\boldsymbol{R})\rangle_{\boldsymbol{r}} = \frac{\langle\psi_a(\boldsymbol{r},\boldsymbol{R})|\nabla_{\boldsymbol{R}}\,\hat{H}_{el}(\boldsymbol{r},\boldsymbol{R})|\psi_b(\boldsymbol{r},\boldsymbol{R})\rangle_{\boldsymbol{r}}}{E_b(\boldsymbol{R}) - E_a(\boldsymbol{R})},\ \boldsymbol{d}_{aa}(\boldsymbol{R}) = 0$$

Non-adiabatic derivative coupling vectors (NACs)

Adiabatic basis: singularity at level crossings! Can be lifted by rotating basis into diabatic representation (not uniquely defined!)

$\nabla_{\boldsymbol{R}}|\phi(\boldsymbol{r})\rangle \equiv 0$ diabatic electronic wavefunctions do not depend on $\boldsymbol{R}$

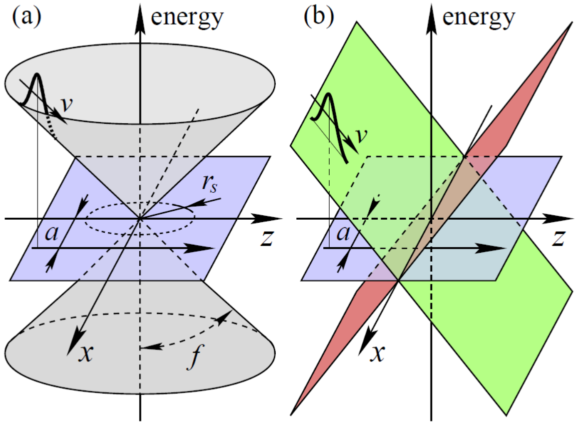
$\langle\phi_a(\boldsymbol{r})|\nabla_{\boldsymbol{R}}^2|\phi_b(\boldsymbol{r})\rangle \equiv 0$ Kinetic energy terms for diabatic wavefunctions

Electronic Hamiltonian in the diabatic basis (no longer diagonal!)

$$H_{ab}(\boldsymbol{R}) \equiv \langle\phi_a(\boldsymbol{r})|\hat{H}_{el}(\boldsymbol{r},\boldsymbol{R})|\phi_b(\boldsymbol{r})\rangle \neq 0$$

$H_{aa}(\boldsymbol{R})$ are diabatic potential energy surfaces (PESs)

Example: conical intersection in adiabatic and diabatic bases



Adiabatic Diabatic

Early models: Landau-Zener tunneling

Importance of modeling non-adiabatic processes (electron-vibration energy exchange) started in the 1930s and were focused on transition probabilities for atomic collisions and small molecules

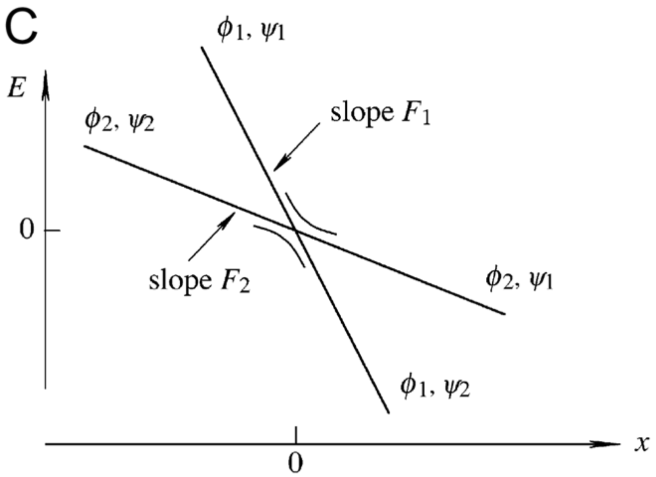
Topology of crossing of PESs: eigenvalues of an Hermitian matrix (Hamiltonian) representing a quantum observable (energies) and depending on N continuous real parameters (nuclei degrees of freedom) can become equal in value ("cross") in a manifold of N-2 dimensions (due to so called non-crossing rule)

In a **diatomic molecule** (one bond length), the levels cannot cross at all (**avoided crossing**)
In a **triatomic molecule**, the levels can cross only at a single point (**conical intersection**).

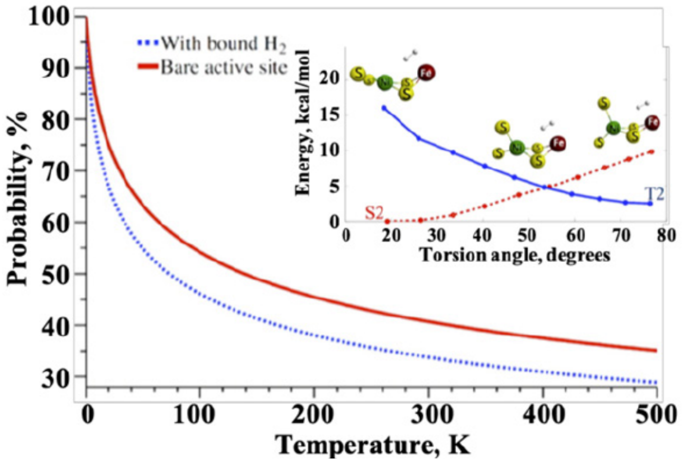
An analytic function for the transmission probability of a single passage through an avoided crossing, i.e., between two crossing diabatic electronic states is given by the Landau−Zener formulae

$$P_{LZ} = \exp\left[-\frac{2\pi}{\hbar}H_{12}^2\Big/\left|\left(\frac{\partial H_{11}}{\partial x}-\frac{\partial H_{22}}{\partial x}\right)\dot{x}\right|\right].$$

Level crossing for the Landau−Zener model, with linear diabatic potential energies and constant coupling.

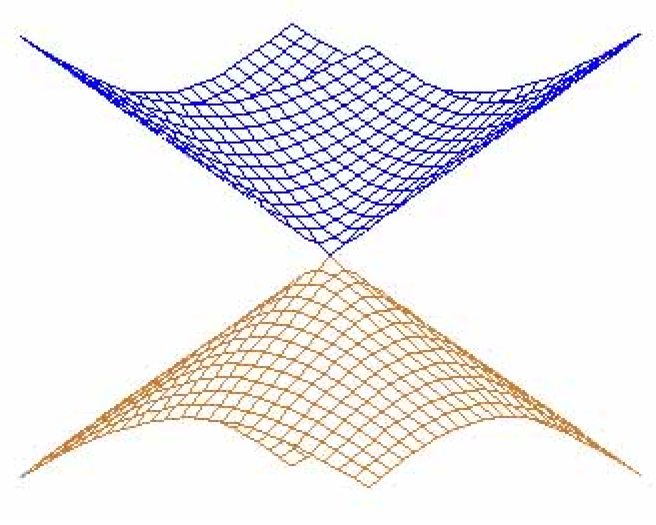


Example: Landau−Zener probabilities of spin-forbidden singlet−triplet non-adiabatic transition in [NiFe] hydrogenase model system with (blue) and without (red) H2 binding.



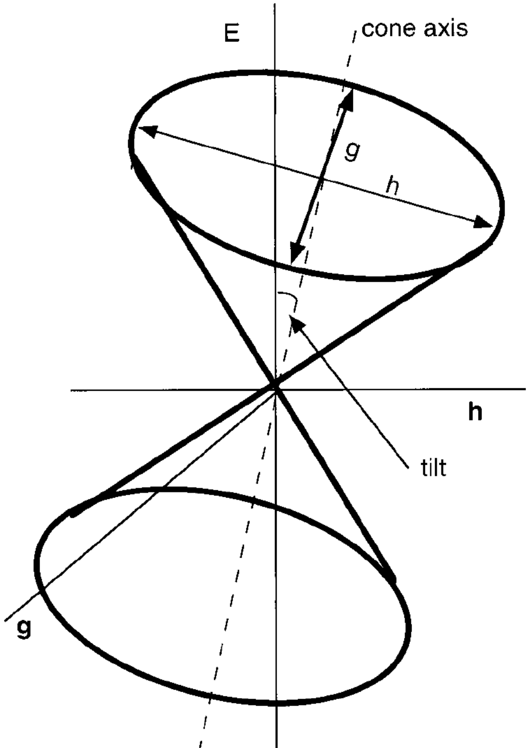
Conical Intersections

Conical intersections (CI) characterize points where potential energy surfaces cross. The dimension of the conical intersection **seam** is N-2 (N is the number of internal vibrational degrees of freedom)



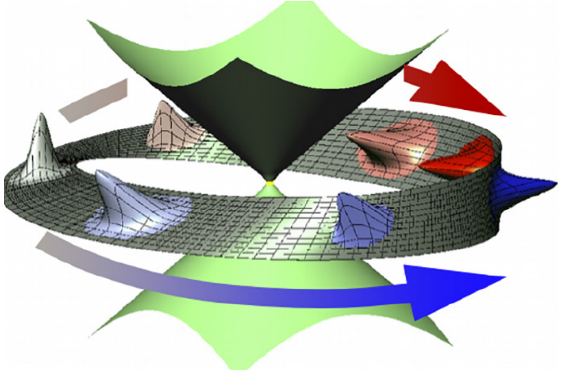
Conical intersections are described in terms of the characteristic parameters g, h, s (i.e. linear expansion near the crossing point). g-h define branching plane whereas s defines tilt. g, h, s can be derived from quantum-chemical calculations of the adiabatic states

$$E_{\pm} = E_0 + s_x \mathrm{x} + s_y \mathrm{y} \pm \sqrt{g^2 \mathrm{x}^2 + h^2 \mathrm{y}^2}$$



Geometric Phase Effects near Conical Intersections

Unique topology of conical intersections leads to the appearance of geometric (or Berry) phase: adiabatic electronic state wavefunction changes sign when transported continuously along a closed loop enclosing the point of conical intersection.



Acc. Chem. Res. 2017, 50, 7, 1785

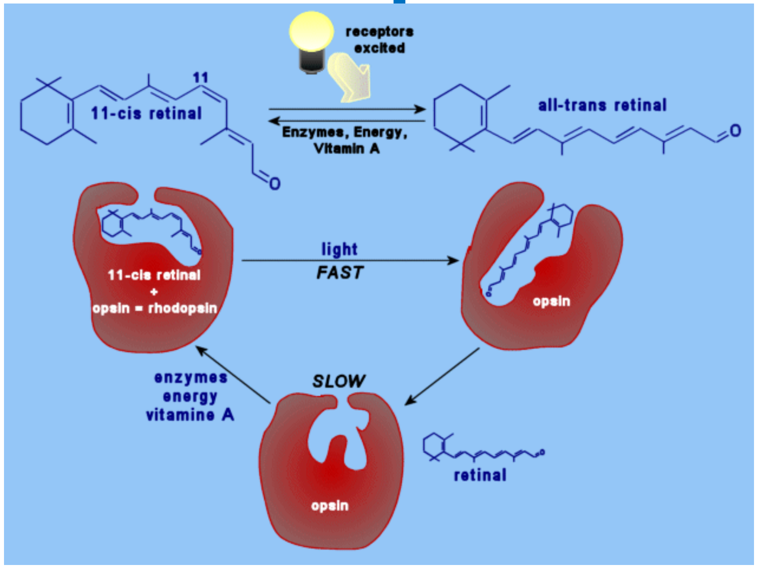
$$\theta(2\pi) - \theta(0) = i \int_C \langle \tilde{\Phi}_k(\mathbf{R}) | \nabla \tilde{\Phi}_k(\mathbf{R}) \rangle \, \mathrm{d}l = \pi$$

Geometric phase is a unique signature of CI observed in experiment which profoundly affects quantum dynamics in few-atoms systems

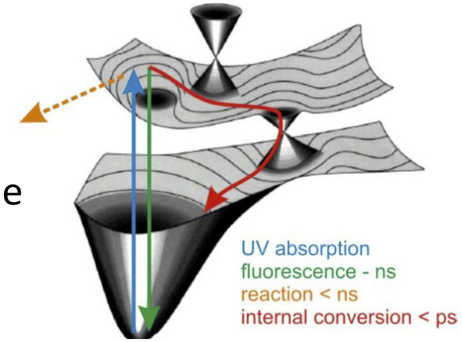
Conical Intersections: examples

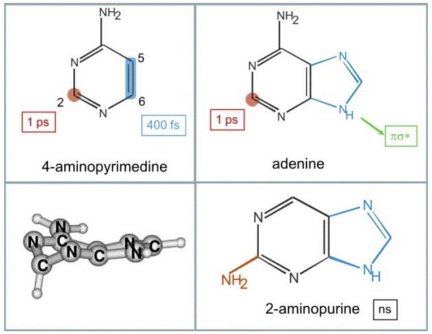
Conical intersections (or **molecular funnels** or **diabolic points**) are critical in reaction mechanisms in photochemistry.

Example 1: Ultrafast conformational changes of the retinal (~100 fs) after absorbing a quantum of light constitutes the primary process of human/animal vision



Example 2: CIs are primarily responsible for DNA damage from UV light. In contrast, they may deactivate the molecule preventing damage in some bio-systems   Top Curr Chem. 2015; 355 33



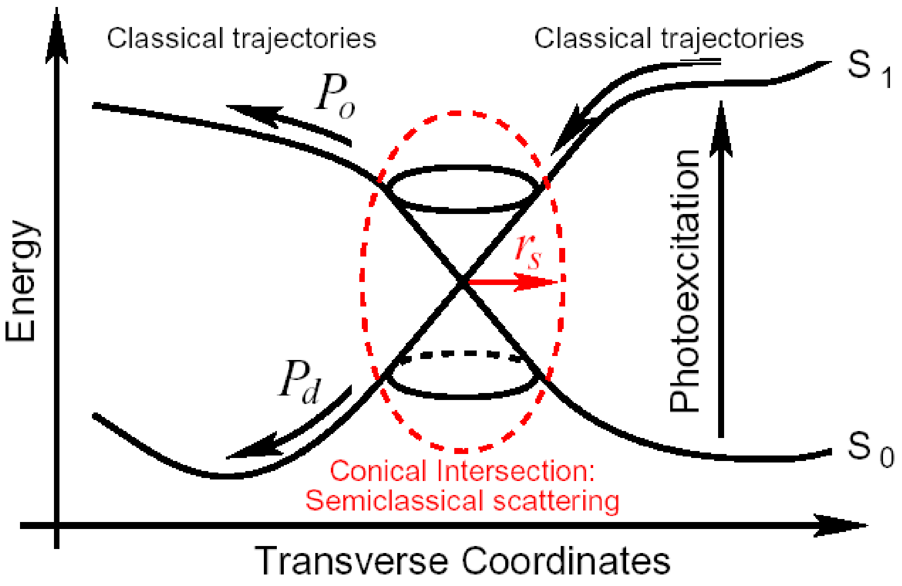


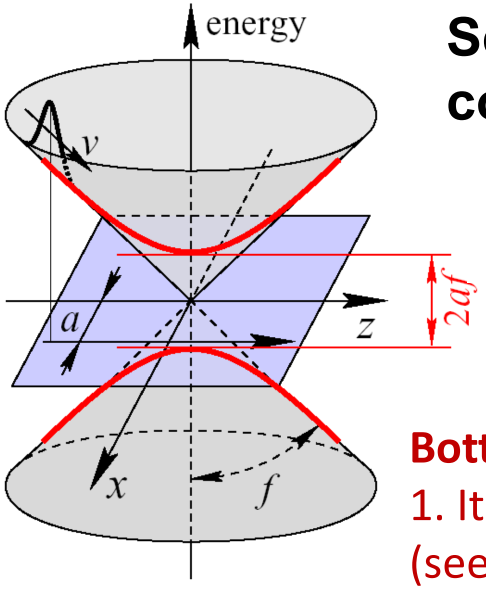
Example 3: Non-adiabatic reaction of oxygen and water in the extreme conditions (e.g. rocket engines) proceeds through CI. Lead to the ultraviolet plume from the Soyuz space shuttle control engines.

$$\mathrm{O}(^3\mathrm{P}) + \mathrm{H_2O} \rightarrow \mathrm{OH}(\mathrm{X}^2\Pi) + \mathrm{OH}(\mathrm{A}^2\Sigma^+)$$

Bottom line: while CI are ubiquitous, their role is most pronounced in rather small systems with a few separated levels, where CI is a major passage for relaxation

Landau-Zener approach for Conical Intersections





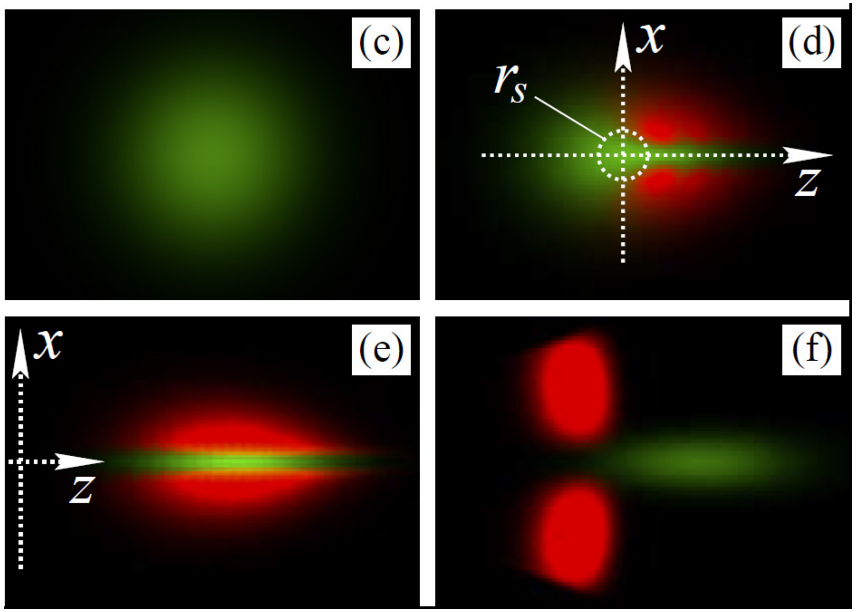
Scattering between conical surfaces

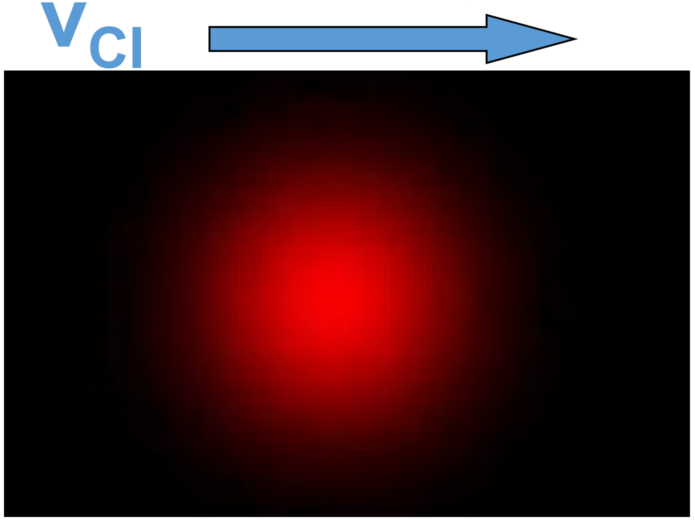
$$P_d = \exp\left(-\frac{\pi f a^2}{\hbar v}\right)$$

PRL 95, 223001 (2005)

Bottom line:

1. It is quantum mechanics (see wiggles of vibrational wavepacket
2. Nice physics and ideas but not too practical

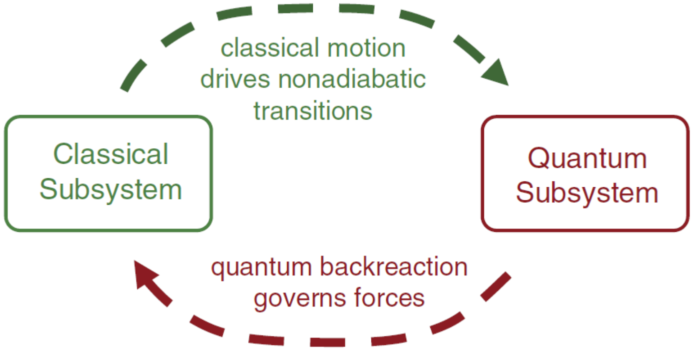




Mixed Quantum-Classical Dynamics (MQC)

To use full scale quantum chemistry for nonadiabatic dynamics (even as a black-box), a compromise is needed! Numerical cost of adiabatic dynamics is about 1,000x of that of single point; Numerical cost of non- adiabatic dynamics is about 1,000,000x of that of single point!
Mixed quantum-classical dynamics treat the slow coordinate (nuclear) motion by classical mechanics, but the forces that govern the classical motion incorporate the influence of nonadiabatic transitions.

However, MQC methods suffer from the fundamental inconsistencies between quantum and classical mechanics.
A major issue is proper incorporation of feedback between the quantum and classical degrees of freedom.
This remains a formidable challenge!



J. Chem. Phys. 137, 22A301 (2012)

Some MQC methods (e.g. Ehrenfest and surface hopping) problems

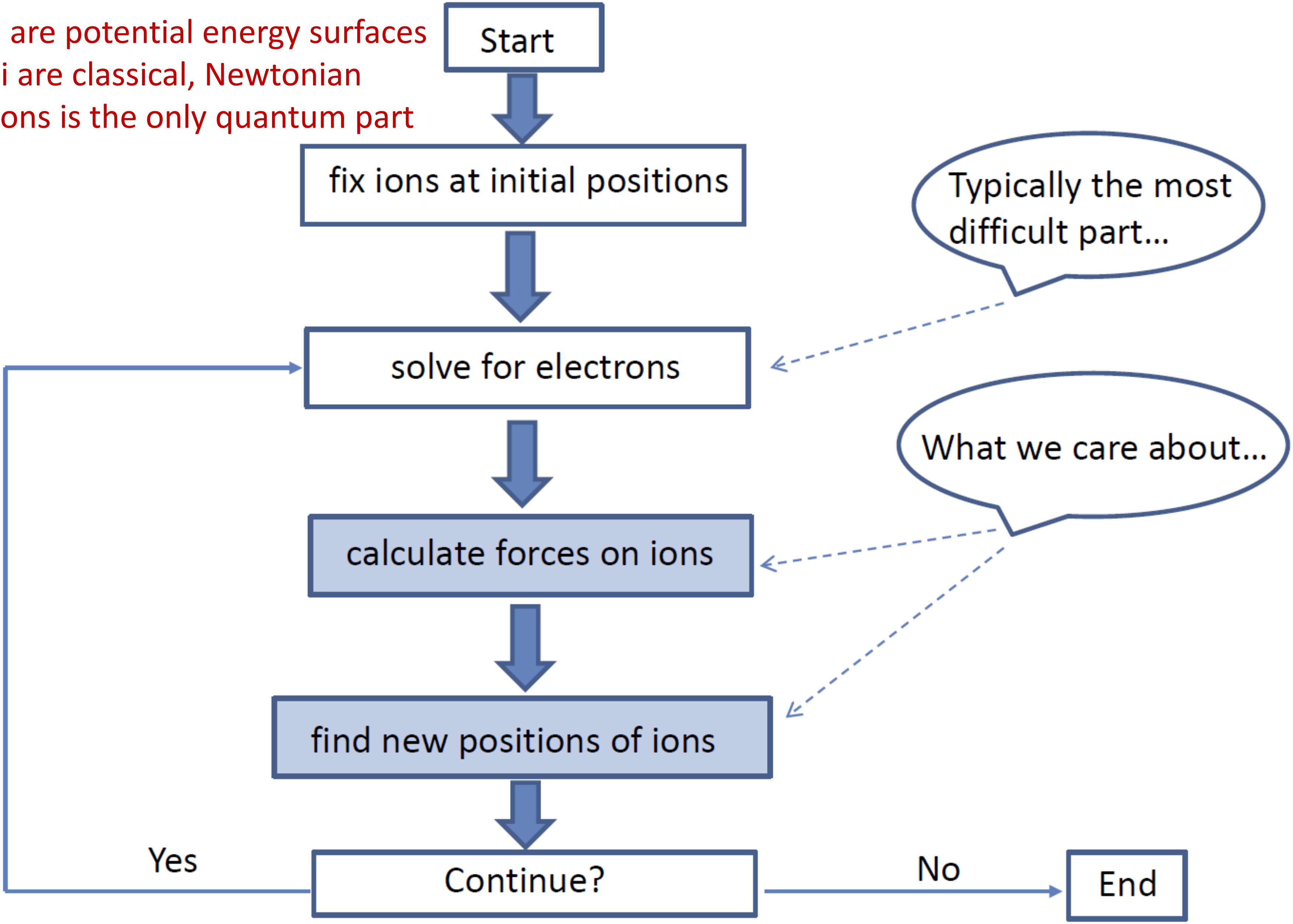
1. Self-consistency between the classical and quantum coordinates
2. Proper treatment of quantum coherence and decoherence phenomena
3. Incorporation of detailed balance (respect temperature, distribution and relaxation down!)
4. Lack of vibrational quantum effects such as tunneling, zero-point motion, and quantized energy levels

Main message of THIS lecture: non-adiabatic dynamics simulation is a severe compromise between accuracy and computational cost: it ALWAYS has 2 distinct and uncontrollable sources of errors

1. Electronic calculator (i.e. HF, TD-DFT, CI, EOM-CC, MR-SCF, CAS) error
2. Non-adiabatic driver (e.g. MQC Ehrenfest or Surface hopping) error

‘On the fly’ MQC Molecular Dynamics

There are potential energy surfaces
Nuclei are classical, Newtonian
Electrons is the only quantum part



Start

fix ions at initial positions

solve for electrons

calculate forces on ions

find new positions of ions

Continue?

Yes

No

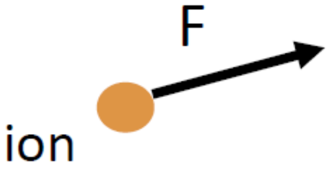
End

Typically the most difficult part…

What we care about…

Forces in adiabatic and non-adiabatic case

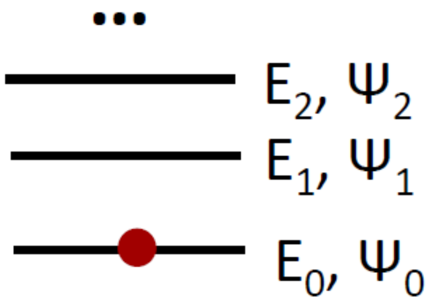
Adiabatic situation



$$F = -\frac{\partial E_0}{\partial x}$$

Hellman-Feynman relation

Electronic States

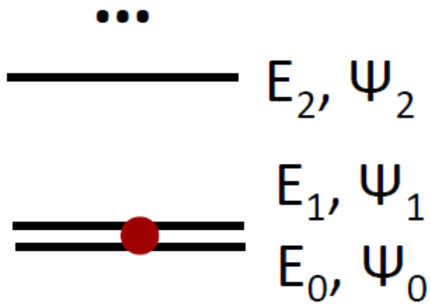


Non-adiabatic situation

$$F = -p_0 \frac{\partial E_0}{\partial x} - p_1 \frac{\partial E_1}{\partial x} - \ldots$$

occupation probabilities

Electronic States



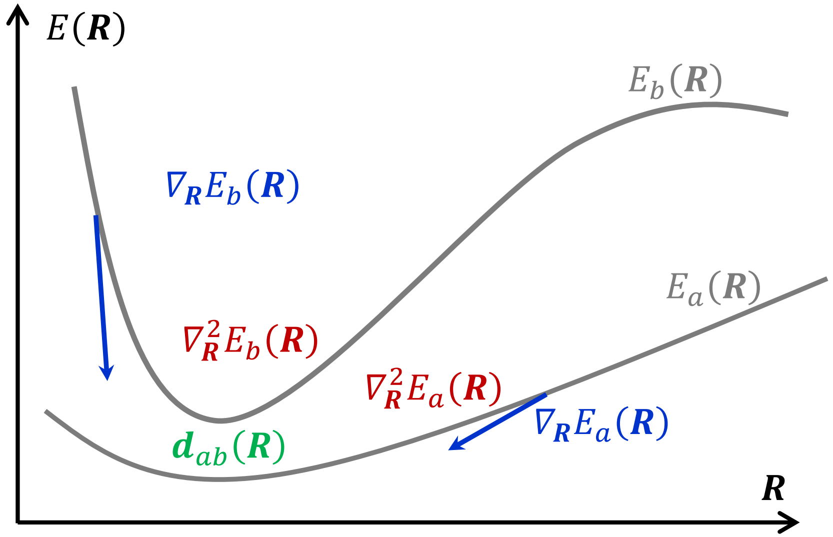
What do we need from the electronic structure calculator for a given geometry $\boldsymbol{R}$?

1. Solve electronic Schrödinger equation for energies $E_a(\boldsymbol{R})$ defining PESs

$$\widehat{H}_{el}(\boldsymbol{r},\boldsymbol{R})\psi_a(\boldsymbol{r},\boldsymbol{R}) = E_a(\boldsymbol{R})\psi_a(\boldsymbol{r},\boldsymbol{R})$$

2. Get gradients of energies (forces) $\nabla_{\boldsymbol{R}} E_a(\boldsymbol{R})$ defining motion of nuclei on PESs

3. Get derivative non-adiabatic couplings scalars NACT and vectors NACR $\boldsymbol{d}_{ab}(\boldsymbol{R})$ defining non-adiabatic transitions between PESs



NACT: $\dot{\boldsymbol{R}}_t \cdot \boldsymbol{d}_{ab}(\boldsymbol{R}) = \left\langle \psi_a(\boldsymbol{r},\boldsymbol{R}) \middle| \frac{d}{dt} \middle| \psi_b(\boldsymbol{r},\boldsymbol{R}) \right\rangle_{\boldsymbol{r}}$

NACR: $\boldsymbol{d}_{ab}(\boldsymbol{R}) = \langle \psi_a(\boldsymbol{r},\boldsymbol{R}) | \nabla_{\boldsymbol{R}} | \psi_b(\boldsymbol{r},\boldsymbol{R}) \rangle_{\boldsymbol{r}}$

3. Optional: get Hessians $\nabla^2_{\boldsymbol{R}} E_a(\boldsymbol{R})$ defining curvatures of PESs

Note 1. Vector quantities such as $\nabla_{\boldsymbol{R}} E_a(\boldsymbol{R})$, $\boldsymbol{d}_{ab}(\boldsymbol{R})$, $\nabla^2_{\boldsymbol{R}} E_a(\boldsymbol{R})$ better to calculate using analytical (not numerical approach), remember pre-factors ~3N or ~(3N)^2, N being number of nuclei. Hint: analytical = use density matrix of state or transition density matrix between states

Note 2. Hessians $\nabla^2_{\boldsymbol{R}} E_a(\boldsymbol{R})$ calculations is very involved and there are only a few electronic structure methods where it is available (e.g. TDDFT), however there are useful for decoherence schemes in advanced methods.

Mean field Ehrenfest dynamics

Ansatz for **electronic-nuclei wavefunctions** $\Psi(\boldsymbol{r},\boldsymbol{R},t) = \chi_0(\boldsymbol{R},t)\sum_a c_a(t)\psi_a(\boldsymbol{r},\boldsymbol{R}),$

$\chi_0(\boldsymbol{R},t)$ is a normalized localized phase-less wavepacket (implicit construct in the calculations)

TDSE (slide 8) becomes Ehrenfest equation to propagate in the adiabatic basis

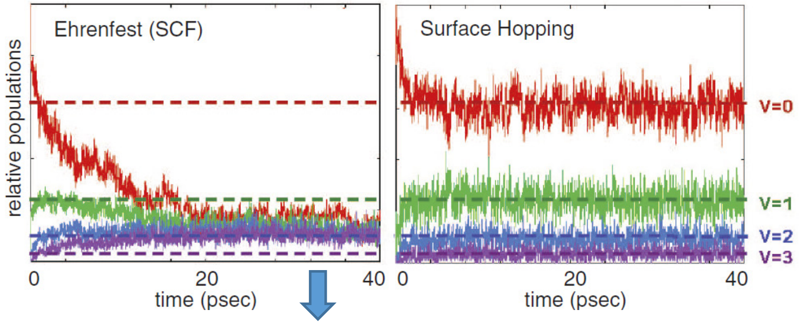
$$i\hbar\frac{\partial c_a(t)}{\partial t} = E_a(\boldsymbol{R}_t)c_a(t) - i\hbar\sum_b \underbrace{\boldsymbol{d}_{ab}(\boldsymbol{R}_t)\cdot\dot{\boldsymbol{R}}_t}_{\text{NACT: }\left\langle\psi_a(\boldsymbol{r},\boldsymbol{R})\middle|\frac{d}{dt}\middle|\psi_b(\boldsymbol{r},\boldsymbol{R})\right\rangle_{\boldsymbol{r}}} c_b(t)$$

Ehrenfest Force

Nuclei dynamics: $$\hat{\boldsymbol{m}}_{\boldsymbol{R}}\ddot{\boldsymbol{R}}_t = \boldsymbol{F}_t = -\sum_a |c_a(t)|^2\,\nabla_{\boldsymbol{R}}E_a(\boldsymbol{R}_t) - \sum_{ab} c_a^*(t)c_b(t)\boldsymbol{d}_{ab}(\boldsymbol{R}_t)[E_b(\boldsymbol{R}_t) - E_a(\boldsymbol{R}_t)]$$

Adiabatic average Non-adiabatic part

- Trajectory-based approach using state energies, gradients, NACT and NACR
- Problem: neglects both differences in zero-point energy (ZPE) for different states and tunneling
- Problem: mean field, nuclei “feel” the mean field potential across the distribution of electronic states
- Problem: No detailed balance (spontaneous heating of the system on longer timescales)



Equal population= does not respect Boltzmann distribution

J. Chem. Phys. 137, 22A301 (2012)

Some practical applications of Ehrenfest

Practical implementations of Ehrenfest dynamics are typically done on DFT basis: Real-Time Time-Dependent DFT (RT-TDDFT) or Real-time Time-Dependent Kohn-Sham Theory (RT-TDKS). Codes: NWChem, Gaussian, Libra, GPAW, NEXMD, CPMD, OCTOPUS

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)]$$

Beware sometimes in RT-TDDFT/RT-TDKS nuclei are frozen and focus is on the electronic dynamics solely (still a mean field)

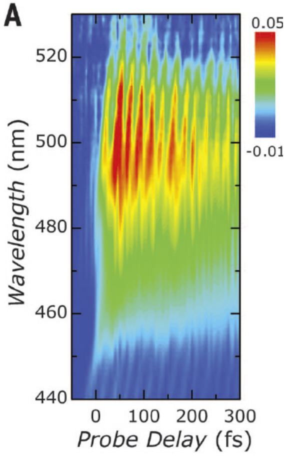
Example of Ehrenfest RT-TDKS dynamics:

S. M. Falke et al. *Science*, 344, 1001 (2014)

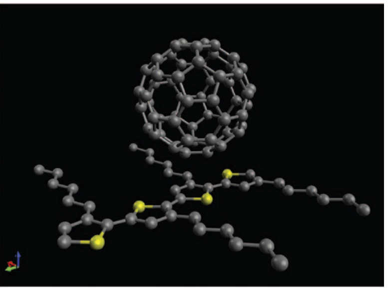
$$i\frac{\partial \psi_p(\mathbf{r},t)}{\partial t} = \left[-\frac{1}{2}\nabla^2 + v^{\text{eff}}(\mathbf{r},t)\right]\psi_p(\mathbf{r},t)$$

Coherent ultrafast charge transfer in an organic photovoltaic blend. Experiments and theory found oscillatory fashion of charge transfer from P3HT conjugated polymer to C60 fullerene with beating period of ~25 fs

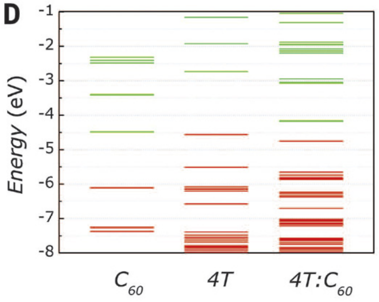
Experiment

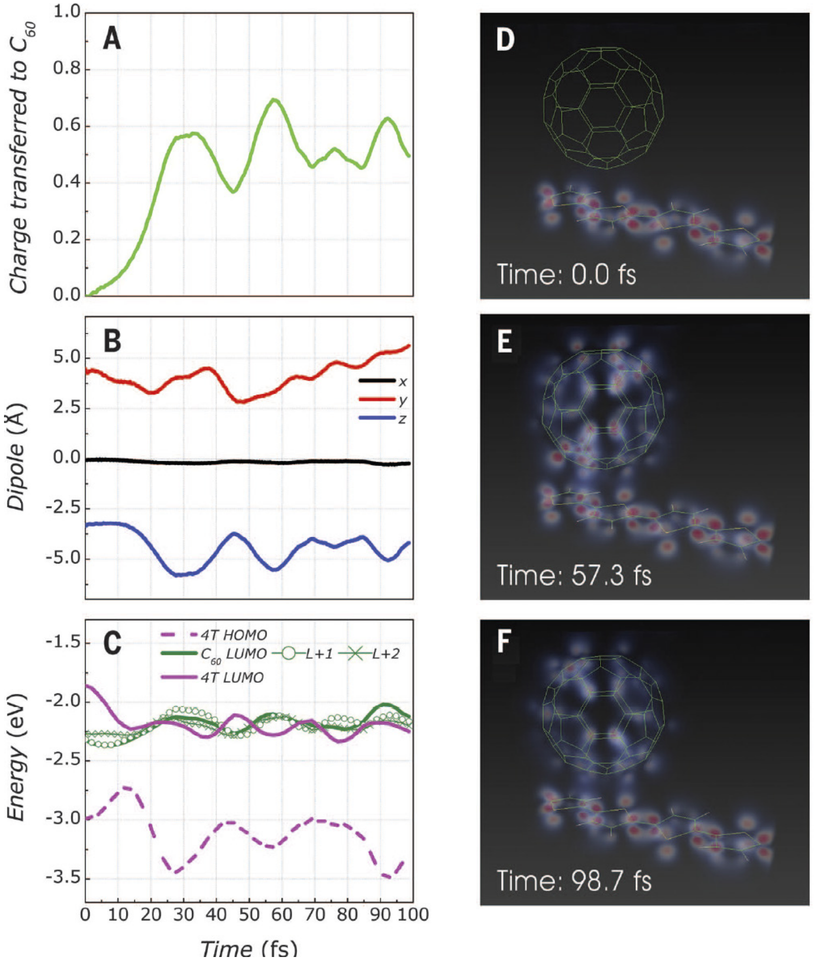


Model system



KS Levels





Surface hopping as an alternative to Ehrenfest

Trajectory surface hopping approaches are the MAIN current tools to model excited state non-adiabatic dynamics. Here we consider *ad hoc* Tully’s Fewest Switching Surface Hopping (FSSH)

Main idea: Monte-Carlo like stochastic dynamics

- Run an ensemble of **independent** trajectories every one of them proceeds in an adiabatic fashion (*a* is a current state):

$$\hat{\boldsymbol{m}}_{\boldsymbol{R}}\ddot{\boldsymbol{R}}_t = \boldsymbol{F}_t = -\nabla_{\boldsymbol{R}} E_a(\boldsymbol{R}_t)$$

- Propagate occupation probabilities for elections according to mean field TDSE equation (Ehrenfest). This is an auxiliary variable!

$$i\hbar\frac{\partial c_a(t)}{\partial t} = E_a(\boldsymbol{R}_t)c_a(t) - i\hbar\sum\nolimits_b \boldsymbol{d}_{ab}(\boldsymbol{R}_t)\cdot\dot{\boldsymbol{R}}_t\, c_b(t)$$

- Evaluate the probability for a “hop”:

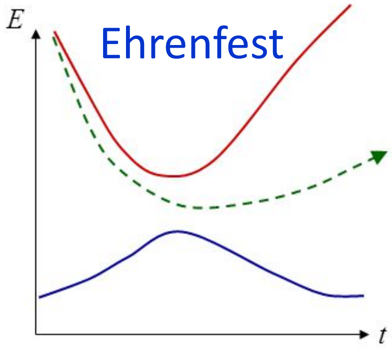
$$P_{a\to b}(t) = Max\left[0, -\frac{\delta t\,\frac{2}{\hbar}\,\mathrm{Re}\left[c_a^*(t)c_b(t)\left[\boldsymbol{d}_{ab}(\boldsymbol{R}_t)\cdot\dot{\boldsymbol{R}}_t\right]\right]}{c_a c_a^*}\right]$$

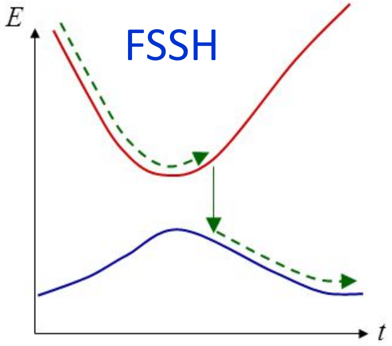
The “hop” is evaluated at every numerical step (δt):

1) The probability to hop to all included states is determined. If the probability to hop to a state is negative, it is set to zero.

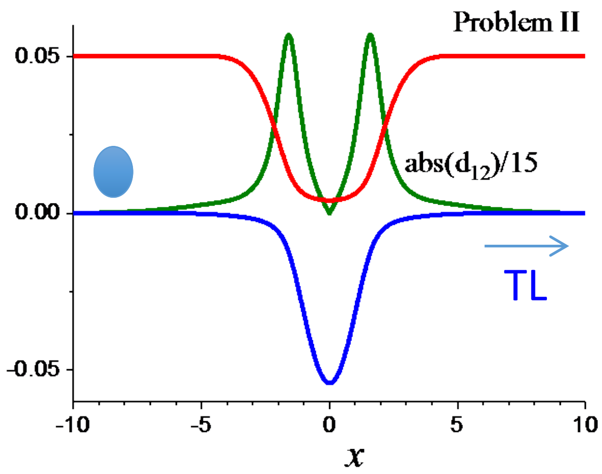
2) A random number is compared to these probabilities to determine if a hop occurs and to which state (‘flip a coin’).

3) If a hop occurs the nuclear velocity $\dot{\boldsymbol{R}}_t$ is adjusted along the direction of the NACR $\boldsymbol{d}_{ab}(\boldsymbol{R}_t)$ such that the total energy is conserved. For hops which increase the potential energy, if there is not enough kinetic energy in this direction then the hop is “frustrated” and does not occur.

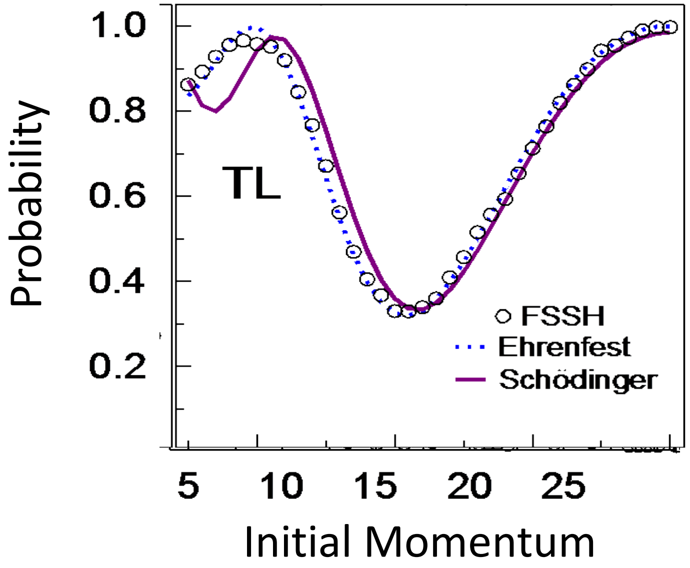


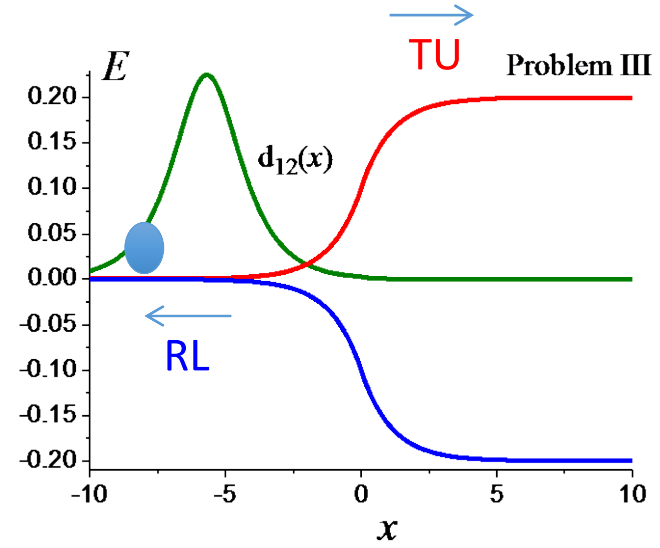


How does all this work? 3 Tully's problems

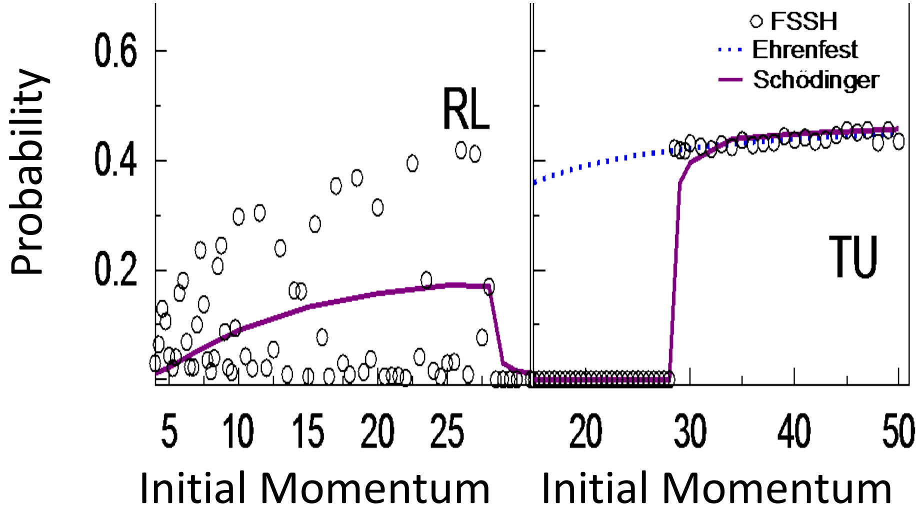


Tully's model II: Dual avoided crossing: Stueckelberg oscillations





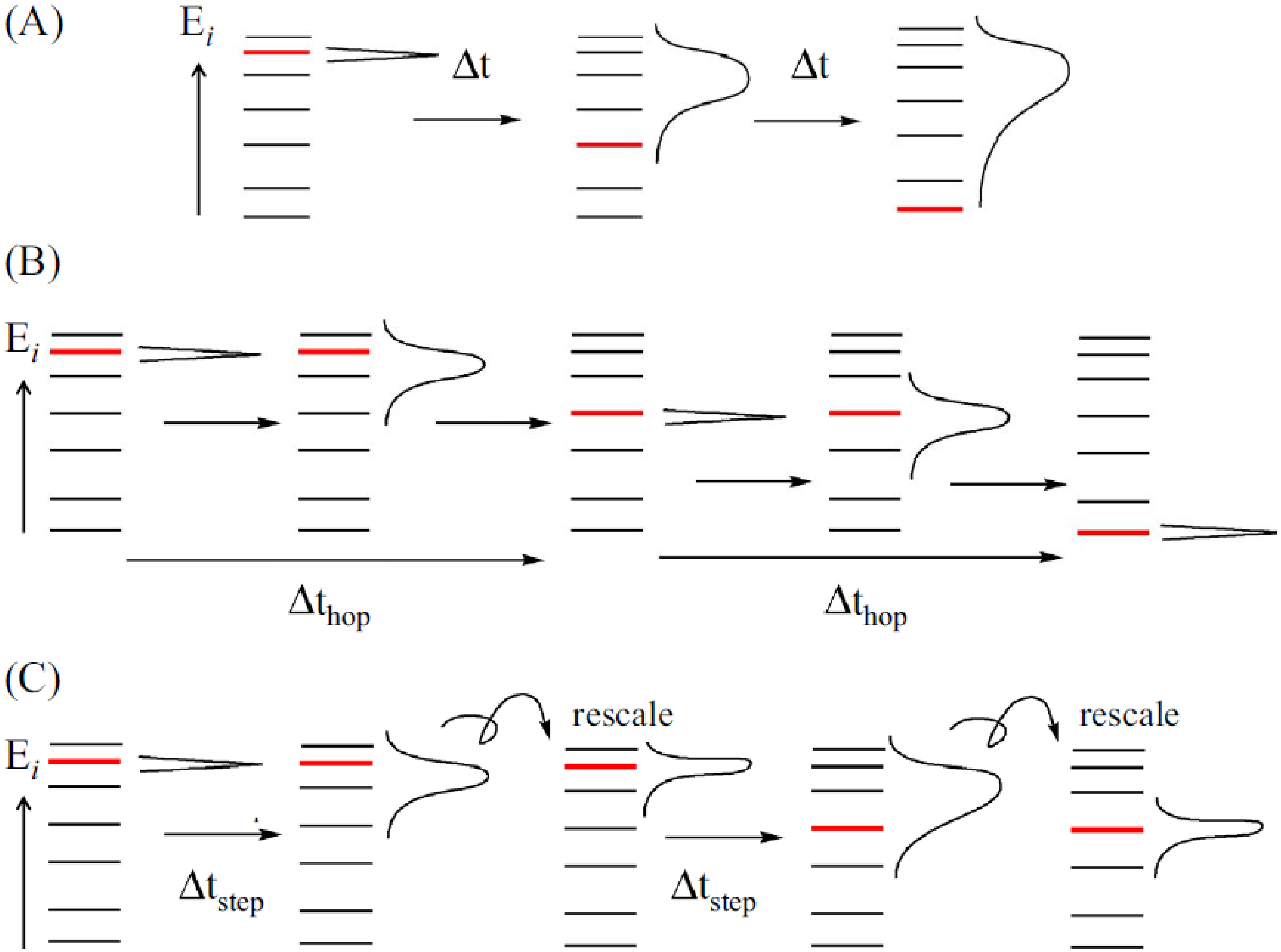
Tully's model III: Extended coupling with reflection



Bottom line: While overall working, there is a failure of FSSH and Ehrenfest to describe coherences and interferences

The main TSH problem: decoherence corrections

Lack of electronic decoherence -> internal inconsistency of FSSH. There are well over 100 schemes how to fix it, ranging from empirical to completely new SH algorithms (Rossky, Prezhdo, Bittner, Subotnik, Truhlar, Granucci, etc)!



Pristine FSSH (quantum wavepacket is left ‘behind’)

Empirical fix: Instantaneous decoherence schemes

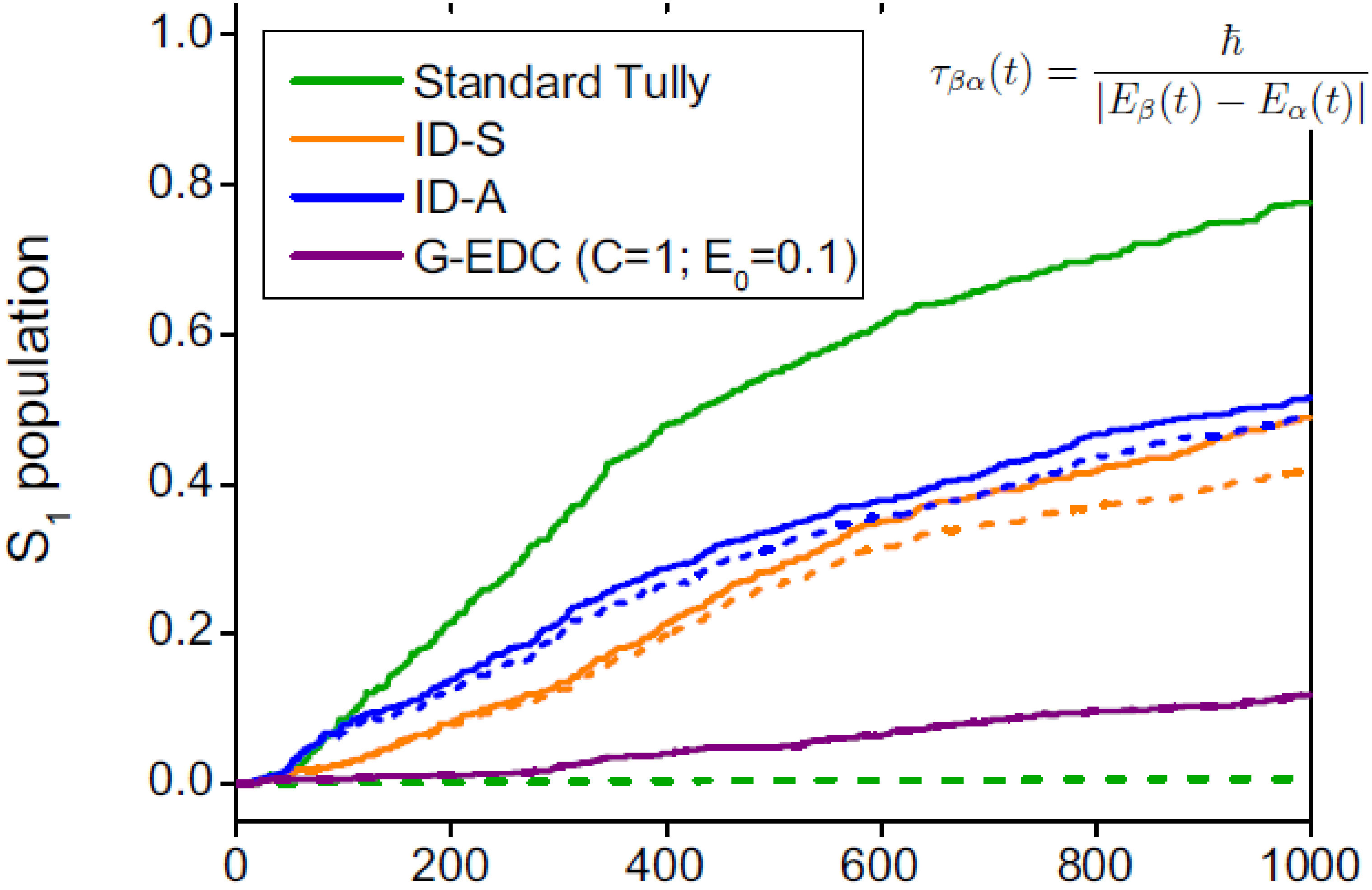
Empirical fix: Energy-based decoherence schemes (Granucci, Truhlar)

Real life example of decoherence effects

Here we are exciting the second excited state S_2 in stilbene and watching build up of population on S_1 state (i.e. S_2 -> S_1 non-radiative relaxation)

$$c'_\beta(t) = c_\beta(t)e^{-\Delta t/\tau_{\beta\alpha}(t)}$$

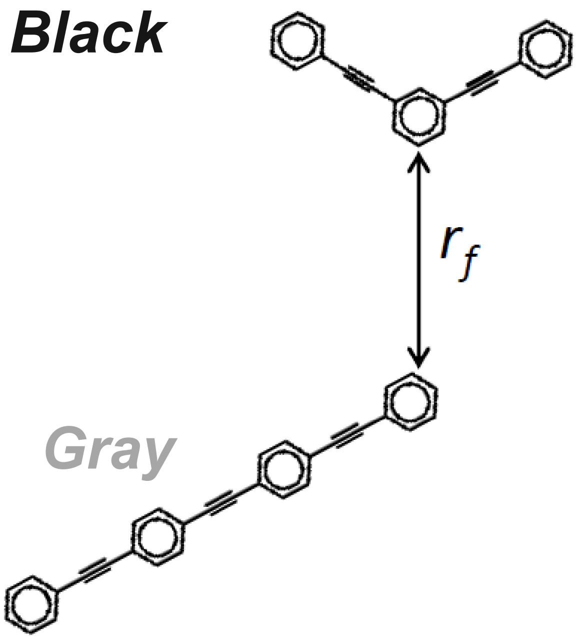
$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_\beta(t) - E_\alpha(t)|}\left(C + \frac{E_0}{E_{kin}(t)}\right)$$

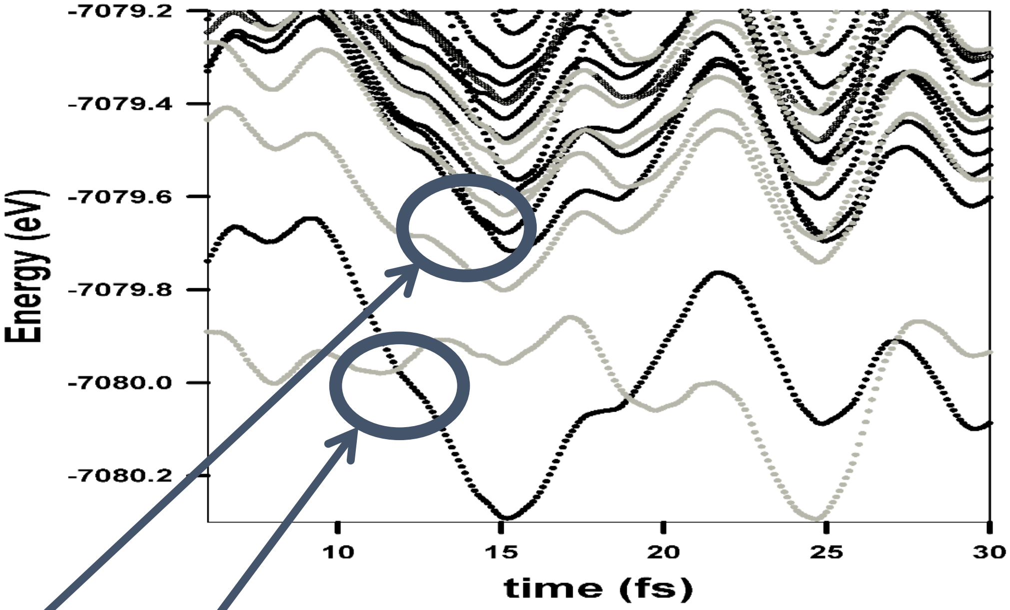


J. Chem. Phys., 138 224111 (2013)

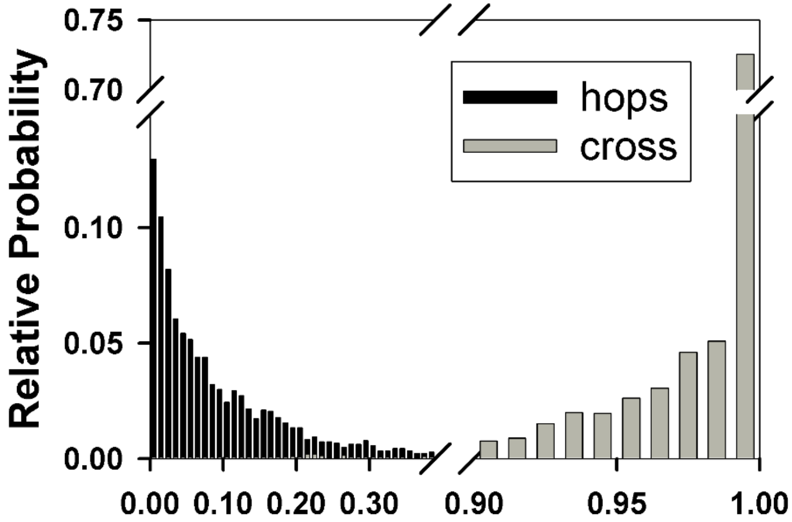
Non-obvious problem: trivial crossings

This problem was identified only recently when we learn how to treat large systems. This calls for following the diabatic passage preserving the identity of states (Levine, Prezhdo, etc.)





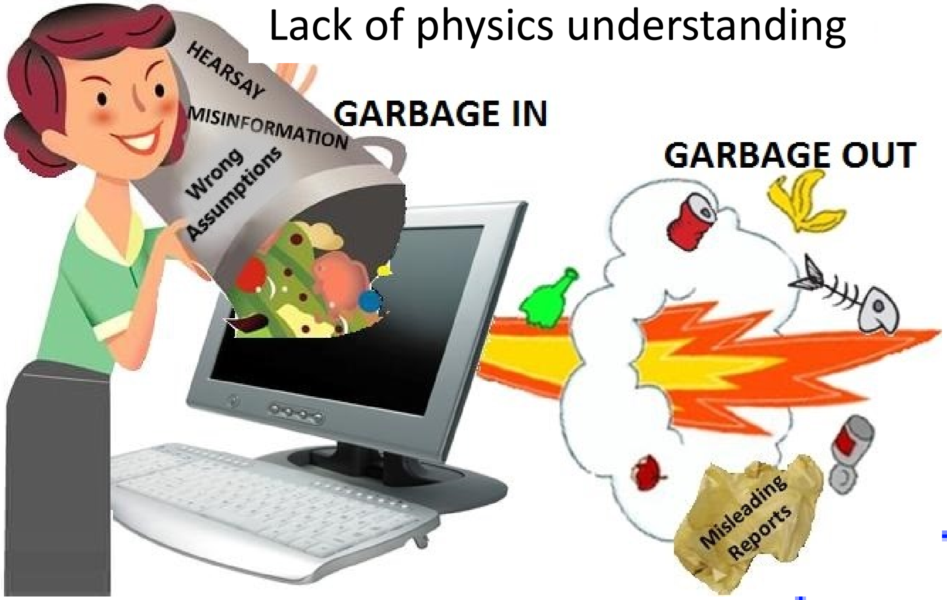
- Tully’s FSSH method for crossing of ‘coupled’ states (conical intersections, weakly and strongly avoided crossings);
- Need an algorithm (aka min-cost) for crossing of ‘uncoupled’ states. Idea: identify every crossing whether it is coupled or not



J. Chem. Phys. 137, 014512 (2012)

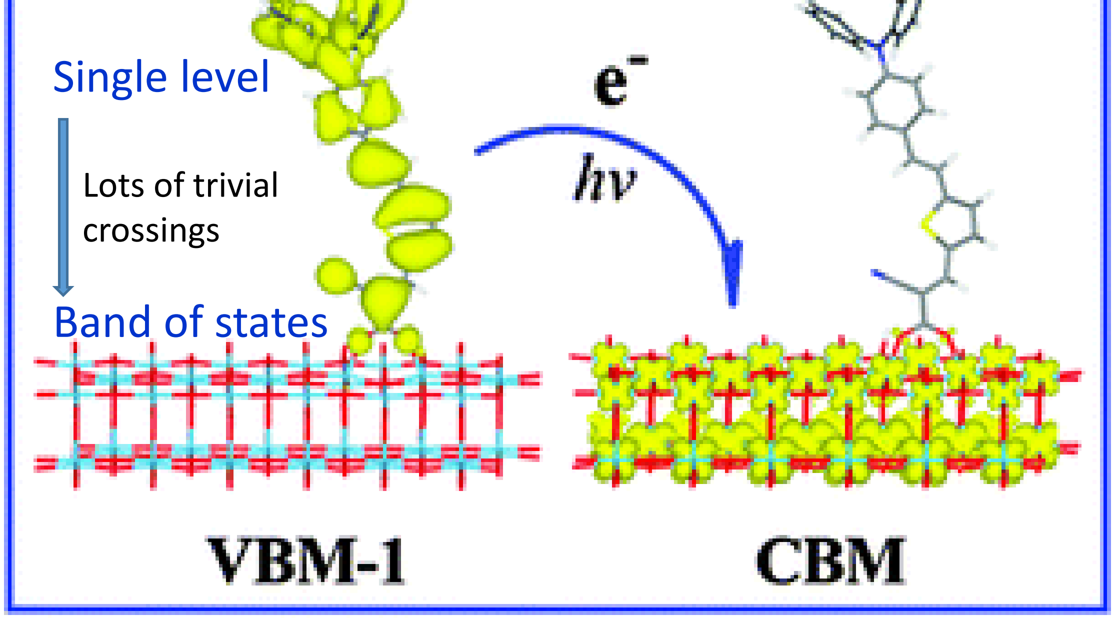
Example: ‘garbage in, garbage out’

Lack of physics understanding



The largest horror of computational chemist is to produce garbage! This is frequently facilitated by the black-box use of codes, algorithms and models. ‘Because I can’, prevails over efforts to understand physics and limitations of theoretical models (e.g. DFT models, or NAMD algorithms). But… there is no free lunch…

Example: Spectroscopy probing electron transfer from a molecule to TiO_2 semiconductor found transfer rate as fast as 100 fs. Theoretical modeling suggests that the rates can be even faster up to 3-5 fs, suggesting promises of the system as energy harvester…



Single level

Lots of trivial crossings

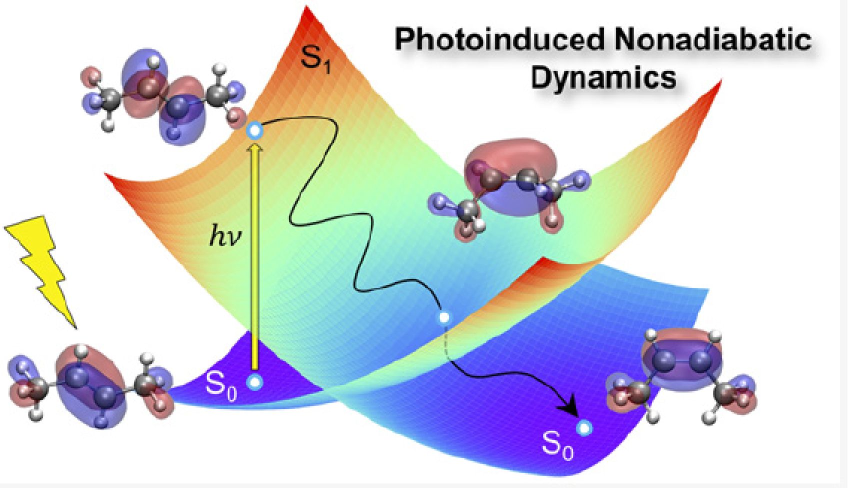
Band of states

Disclaimer: The picture (and paper) has nothing to do with the erroneous theory statement

Summary: MQC surface hopping approaches (aka Tully FSSH)

The Good:

- Trajectory-based approach using state energies, gradients, NACT and NACR
- Respects detailed balance and Boltzmann distribution
- Accounts for branching into different products
- Extremely robust, never fails computationally



The Bad

- Lack of decoherence and interferences (independent trajectory, no phase information)
- Simulations must include empirical corrections such as decoherence or trivials
- Works only in adiabatic representation (fails in diabatic basis)
- Neglects both differences in zero-point energy (ZPE) for different states and tunneling

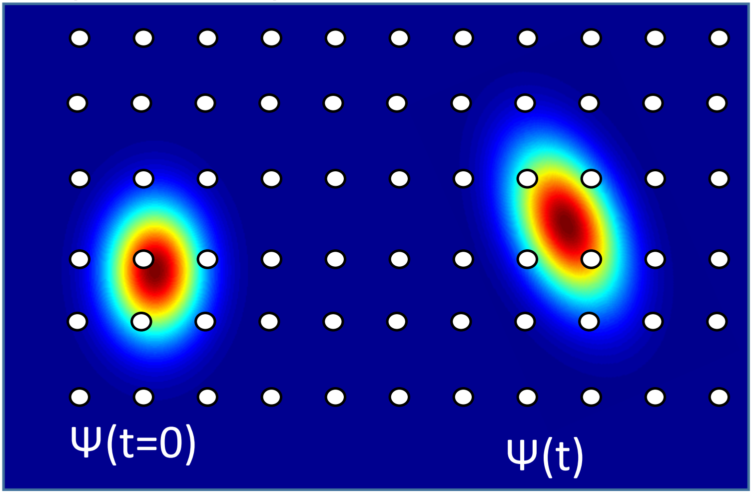
The Ugly

- Completely ad hoc. Impossible to derive.
- The number of variations competes with DFT

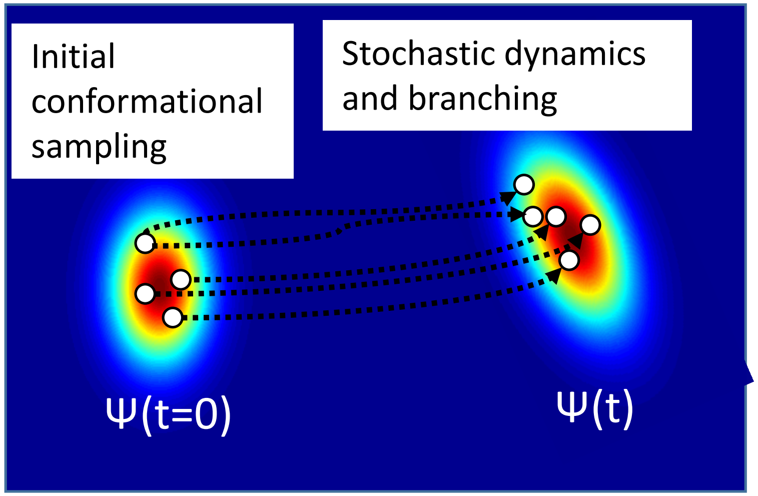
Practical implementations of surface hopping dynamics are typically done across MANY approaches ranging from tabulated PESs to semiempirical Hamiltonians to DFT and TDDFT, to MR-CI to EOM-CC to CASSCF. Codes: ANT, COBRAMM, JADE, NEWTON-X, SHARC, Turbomole, NWChem, Q-Chem, PIXAID, Libra, NEXMD, CPMD, OCTOPUS, CHEMSHELL.

MQC (Ehrenfest or FSSH) implementations

Regular static grid

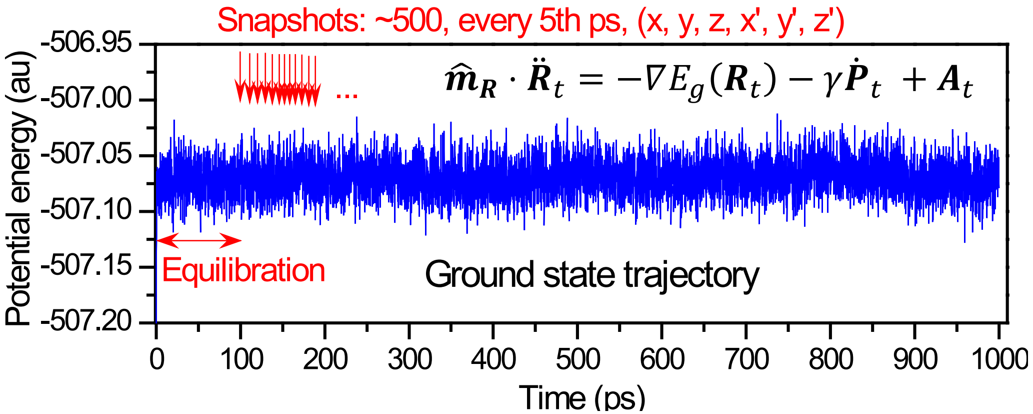


Trajectory guided grid

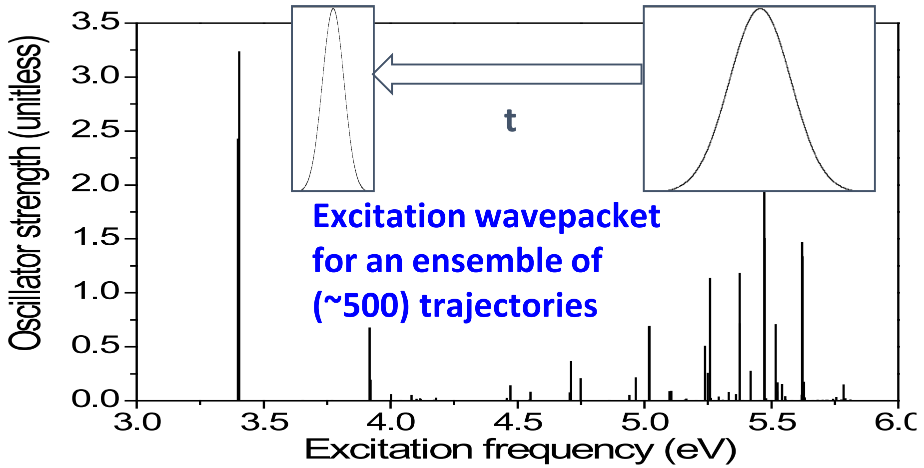


Ehrenfest and surface hopping are trajectory-based approaches. Importantly that trajectory guided basis allows to run **on the fly dynamics**

1. Conformational sampling of initial conditions via ground state dynamics (alternative is Wigner sampling)



2. Each conformation follows with calculation of absorption spectrum and initial excited state (or superposition)



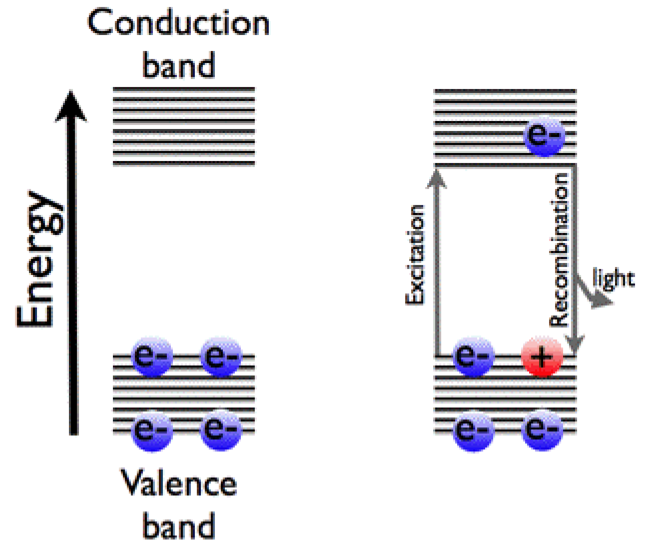
3. Prepared initial conditions give rise to propagation of swarm of trajectories representing photoexcited wavepacket

SH implementation for solids (Prezhdo)

Idea of TD-KS non-adiabatic dynamics:

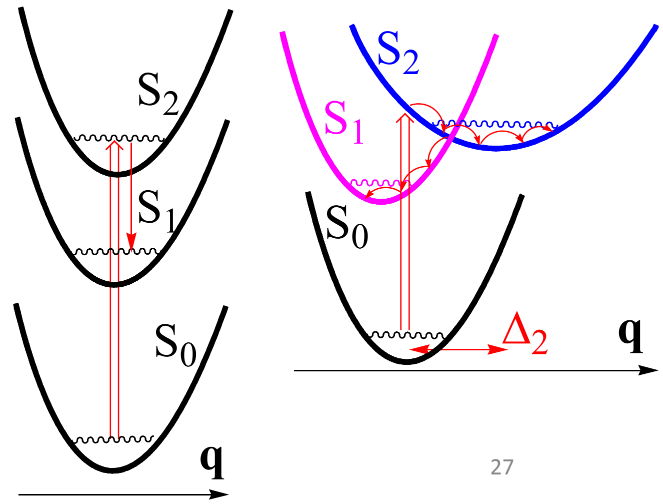
- Commonly DFT electronic calculator
- Use mono-electron states (Kohn-Sham orbitals) as electronic states (i.e., no correlations/excitonic effects)
- Employ classical path approximation: potential energy surfaces of states are the same (compared to thermal quantum). This is valid for systems with weak electron-phonon couplings such as semiconductors.
- Use FSSH (or similar) to perform NAMD for electrons and holes separately. No need for NACR, NACT only!

Mono-electron states and classical path approximation provide HUGE numerical efficiency: one needs to run a single AIMD trajectory. The subsequent NAMD is calculated along this trajectory via random seeds of initial conditions to obtain a swarm of trajectories needed for FSSH.



Classical path approximation

Typical molecular case



Main ingredients:

- KS equations of motion

$$i\hbar\frac{\partial \varphi_a(x,t)}{\partial t} = H[\varphi(x,t),\mathbf{R}(t)]\,\varphi_a(x,t)$$

- Expansion into adiabatic KS states from AIMD

$$\varphi_p(x,t) = \sum_{k}^{N_e} c_{pk}(t)\left|\widetilde{\varphi}_k\,(x;R)\right\rangle$$

- NACT scalars

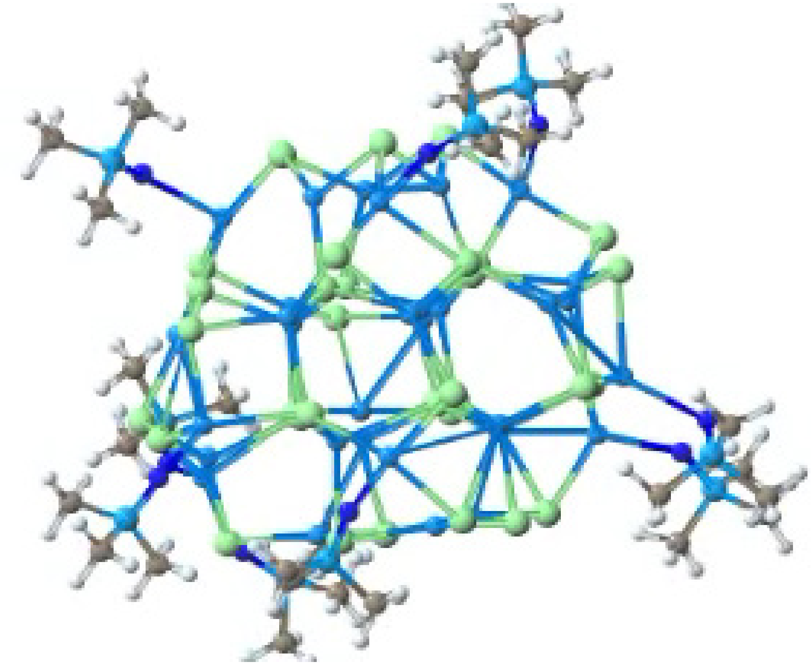
$$\boxed{\mathrm{d}_{\mathrm{jk}}\dot{\mathbf{R}} = -i\hbar\left\langle\phi_j\right|\frac{\partial}{\partial t}\left|\phi_k\right\rangle}$$

Codes: PIXAID and Libra provide wrappers for NAMD interfacing with VASP, NWChem, Quantum Expresso, etc.

Practical example of TD-KS NAMD:

Relaxation of electrons and holes in ligated quantum dots (QDs)

Main finding: Surface ligand coverage of quantum dots with ligands can significantly increase electron-phonon coupling and thus non-radiative relaxation rates for electrons and holes. This directly competes with useful multi-exciton generation rates



Such phenomena as multiple exciton generation in QDs, single fission in organics, hot electron extraction, can result in a more efficient photovoltaics

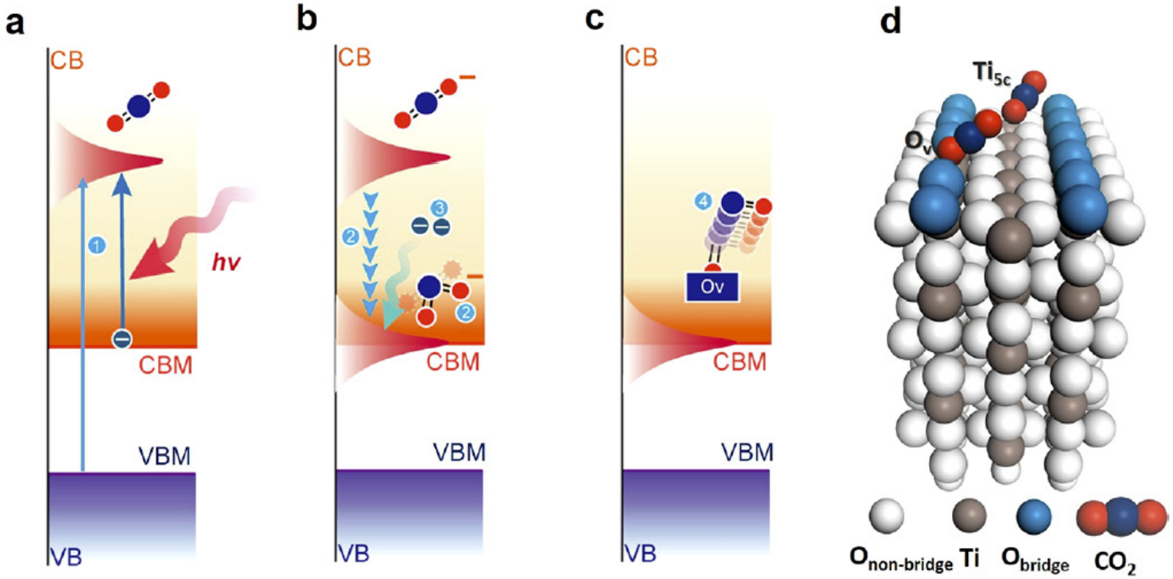
↔ **Gap**

↔ **Photoexcitation energy**

ACS Nano 6 6515 (2012); ACS Nano, 9, 9106 (2015)

Another practical example of TD-KS NAMD:

Exploring photo-reduction CO_2 on TiO_2 surface



Main finding: A critical step in the process is photoactivation of CO_2^- with electron transfer. This can be improved by excitation of bending and antisymmetric stretching vibrations of CO_2 - stabilizes the CO_2 LUMO below the conduction band minimum of TiO_2

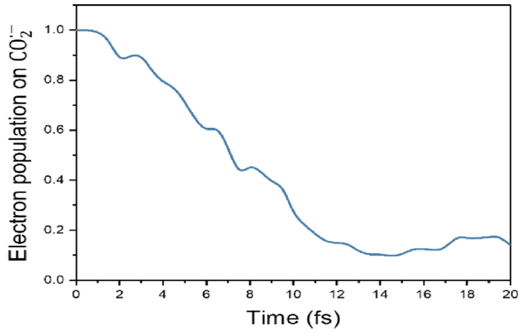
① Photo excitation generates a transient $CO_2^{\cdot -}$

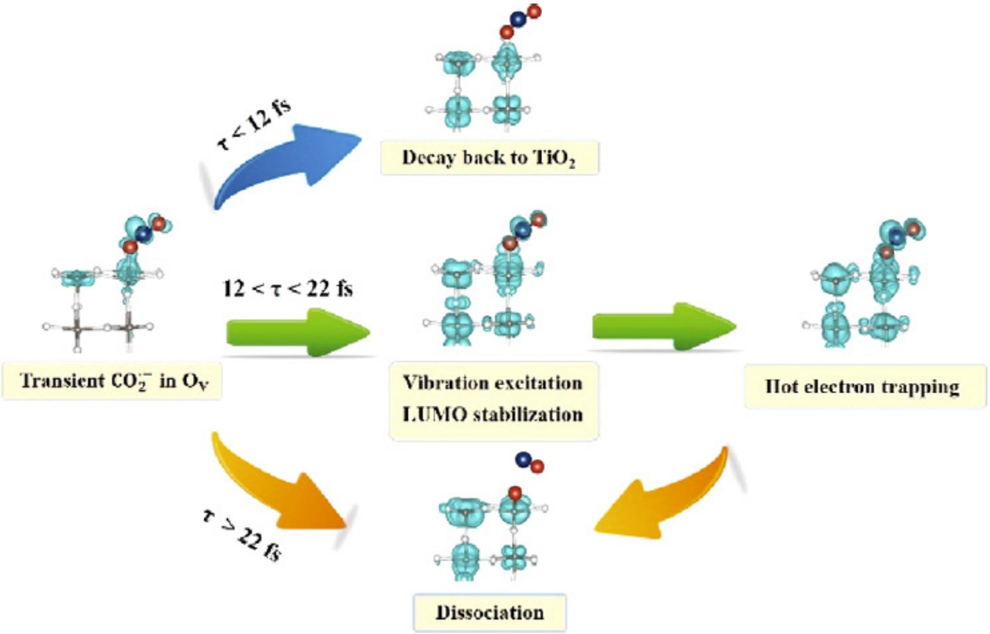
② Transient $CO_2^{\cdot -}$ ($\tau > 12$ fs) excites the bending and antisymmetric stretching
induce CO_2 LUMO stabilization (10 fs)

③ Hot electron trapped by CO_2 and form a new $CO_2^{\cdot -}$ (<80 fs)

④ $CO_2^{\cdot -}$ dissociates in Ov (30-40 fs)

Charge-transfer dynamics:





J. Am. Chem. Soc. 2020, 142, 3214−3221

NEXMD code for molecular systems

☐ 10 ps excited state dynamics;
☐ 0.05 fs time-step for electronic dynamics
☐ 500 trajectories

10^9 calculations of excited states

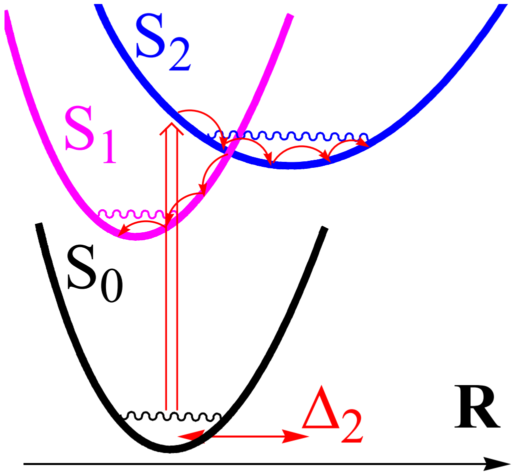
Software package NEXMD

Released to public

- Surface hopping (FSSH), Ehrenfest or ab initio multiple cloning with multiconfigurational Ehrenfest (AIMS-MCE);
- Efficient semiempirical model calculations of the excited states at TDHF or CIS level (Krylov space algorithms);
- Analytic gradients for excited state potential energy surfaces and non-adiabatic couplings;
- Various types of the excited state MD (Langevin, Anderson thermostats, energy conserving dynamics, etc.);
- Decoherence corrections, treatment of trivial crossings, state-specific solvation, PCM or QM/MM, extended Lagrangian excited state dynamics, open shells, polaritonics, etc.

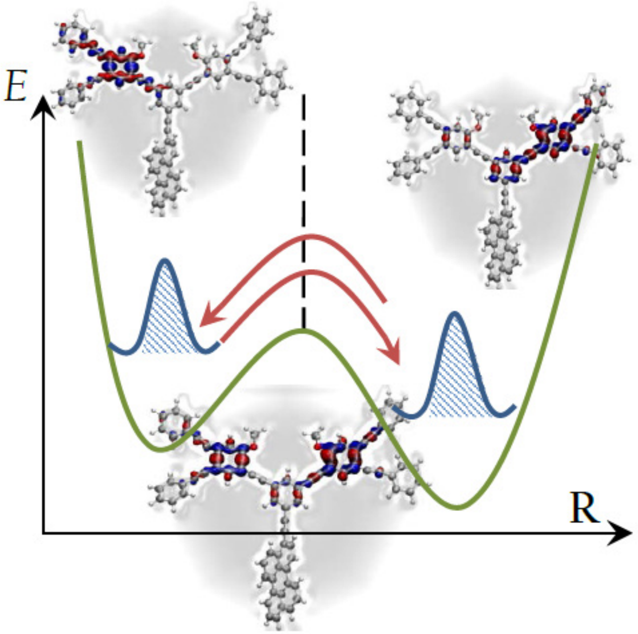
NEXMD calculations up to ~1000 atoms molecules and up to ~10ps timescales

Classical path approximation is not suitable to molecules

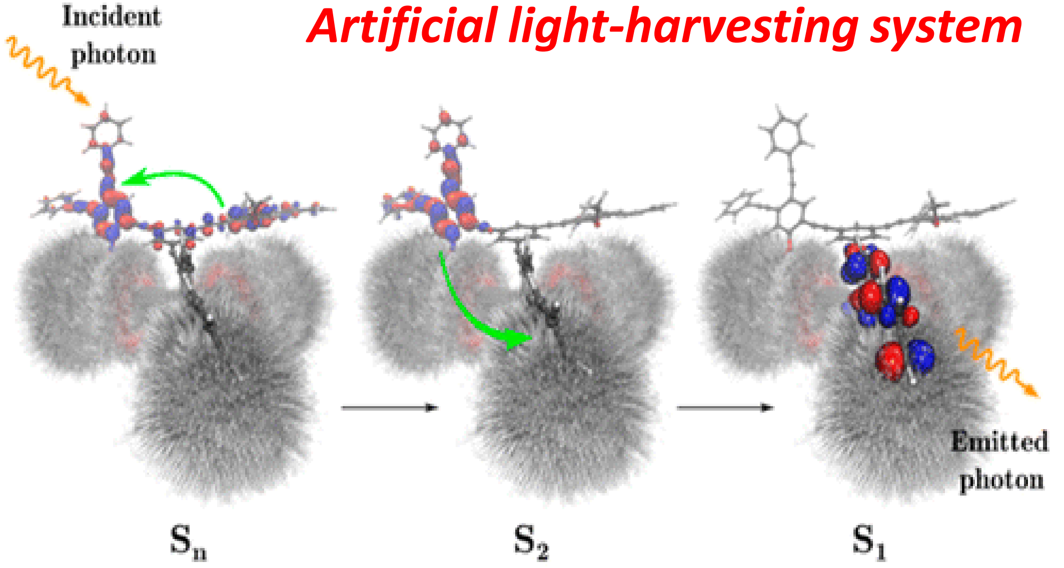


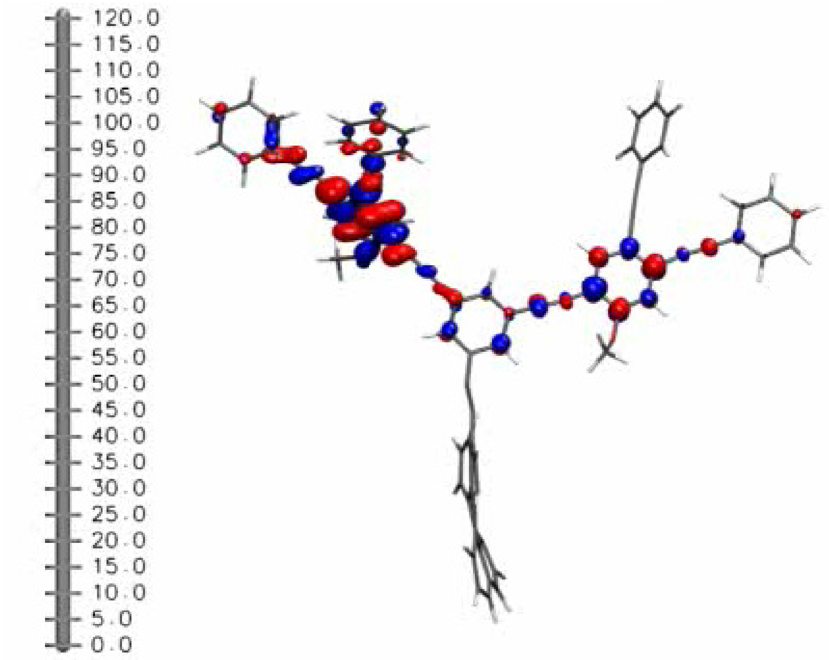
Acc. Chem. Res., 47, 1155 (2014);
Chem. Rev. 120, 2215 (2020)

FSSH example: Energy transfer in a dendrimer



Artificial light-harvesting system



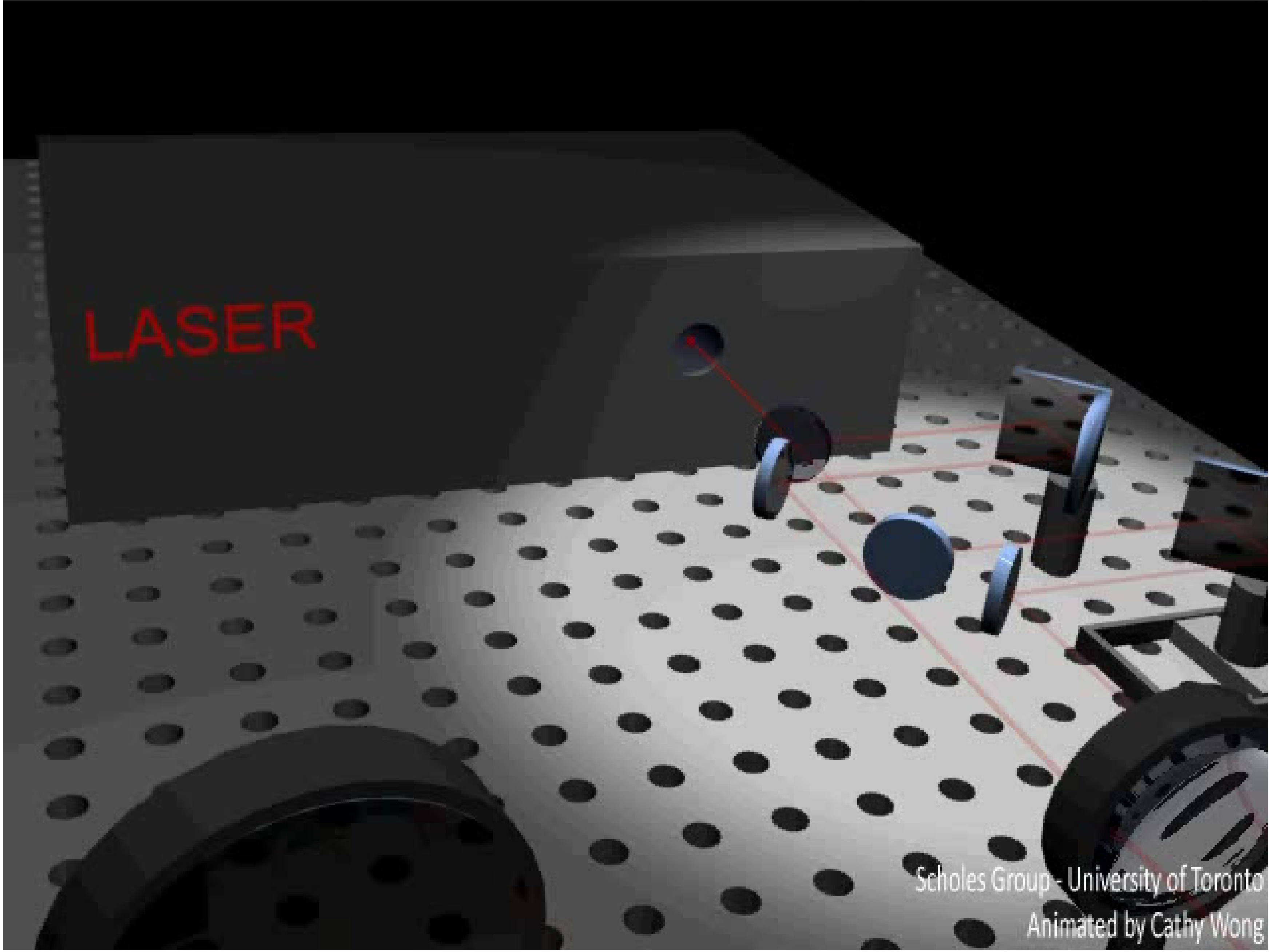


Some findings:

- Complex dynamic of energy transfer relying on multiple states;
- Huge conformational space of the molecule (structure ‘softness’)
- Coherent electron-vibrational dynamics, localization/delocalization and wave-like motion of the wavefunction

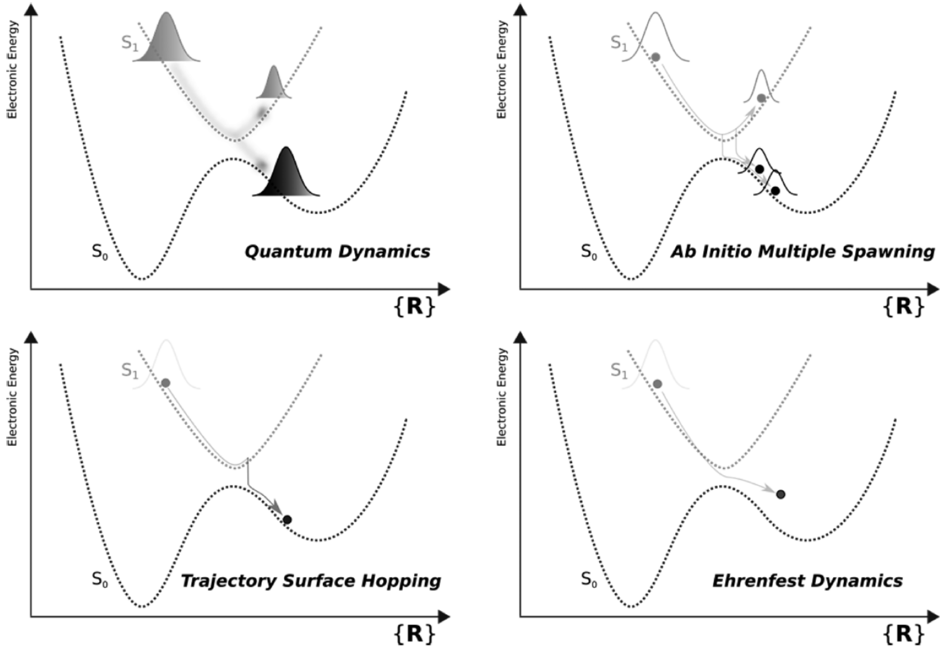
J. Am. Chem. Soc., 137, 11637 (2015)
Nature Comm. 9, 2316 (2018)

Coherent 2D electronic spectroscopy



The need to go beyond MQC NAMD

- Improved coherent multi-pulse time-resolved spectroscopy resolved ultrafast electronic and vibrational coherences – new ways to control photodynamics outcome;
- Even better resolutions are offered by XFEL facilities (both X-ray and optical setups);
- Synthesis/fabrication are getting more precise & tunable (e.g. artificial intelligence);
- Computer powers increase toward Exascale computing, GPU and heterogeneous architectures.
- Electronic structure calculators are getting more accurate.



Chem. Rev. 2018, 118, 3305−3336

The Need:

- Departure from ad hoc and empirical methodologies;
- Need controllable approximations that can be systematically improved;
- Desirable to retain trajectory-based approaches using state energies, gradients, NACT and NACR, etc.;
- Need methods that are easily parallelizable and scalable.

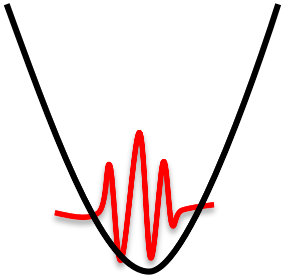
Note: Most of world computer power in materials modeling is spent on MD applications vs. electronic structure simulations.

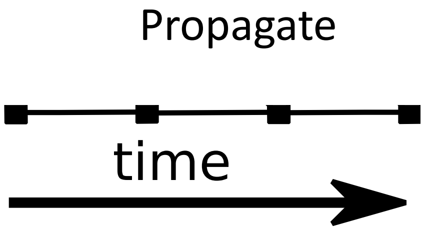
Trajectory independent approaches (aka Ehrenfest and surface hopping) are embarrassingly parallel and desirable (perhaps with post-processing)

Dependent trajectory approaches are hard to parallelize.

Tutorial example “when phase matters”: Semiclassical Gaussian wavepacket dynamics (GWD)

Idea: use Gaussians to represent nuclei wavefunctions. Back in 1975, Eric Heller suggested that the nuclear wavefunction has the form of a ‘thawed’ Gaussian (or superposition of Gaussians) function.





$$g(\boldsymbol{R}_t,\boldsymbol{P}_t,\boldsymbol{R},t)=\exp\left[\frac{i}{\hbar}[\gamma_t+\boldsymbol{P}_t\cdot(\boldsymbol{R}-\boldsymbol{R}_t)+\ (\boldsymbol{R}-\boldsymbol{R}_t)\cdot\widehat{\boldsymbol{\alpha}}\cdot(\boldsymbol{R}-\boldsymbol{R}_t)]\ \right]$$

This allows the introduction of classical trajectories into TDSE: equation of motion for Gaussian center position and momenta ($\boldsymbol{R}_t$, $\boldsymbol{P}_t$ - classical Newtonian ones!), complex width $\boldsymbol{\alpha}$ and phase γ_t (importantly, curvature of *E*(***R***) should not change significantly on the length of Gaussian, otherwise it will broaden). Note that for parabolas, Gaussians turn into frozen, $\widehat{\boldsymbol{\alpha}}$ = *const.*

$$\dot{\boldsymbol{R}}_t=\widehat{\boldsymbol{m}}_{\boldsymbol{R}}{}^{-1}\cdot\boldsymbol{P}_t$$

$$\dot{\boldsymbol{P}}_t=\boldsymbol{F}_t=-\nabla_{\boldsymbol{R}}E(\boldsymbol{R}_t)$$

$$\dot{\widehat{\boldsymbol{\alpha}}}=-2\widehat{\boldsymbol{\alpha}}\cdot\widehat{\boldsymbol{m}_{\boldsymbol{R}}}^{-1}\cdot\widehat{\boldsymbol{\alpha}}-\frac{1}{2}\nabla_{\boldsymbol{R}}(\nabla_{\boldsymbol{R}}E(\boldsymbol{R}_t))$$

$$\dot{\gamma}_t=i\hbar Tr\left[\frac{\widehat{\boldsymbol{\alpha}}}{M}\right]+\frac{1}{2}\boldsymbol{P}_t\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}{}^{-1}\cdot\boldsymbol{P}_t-E(\boldsymbol{R}_t)$$

This idea led to multiple follow ups (Herman-Kluk (HK) propagator, Miller-Meyer Stock-Thoss (MMST) Hamiltonian, etc.)

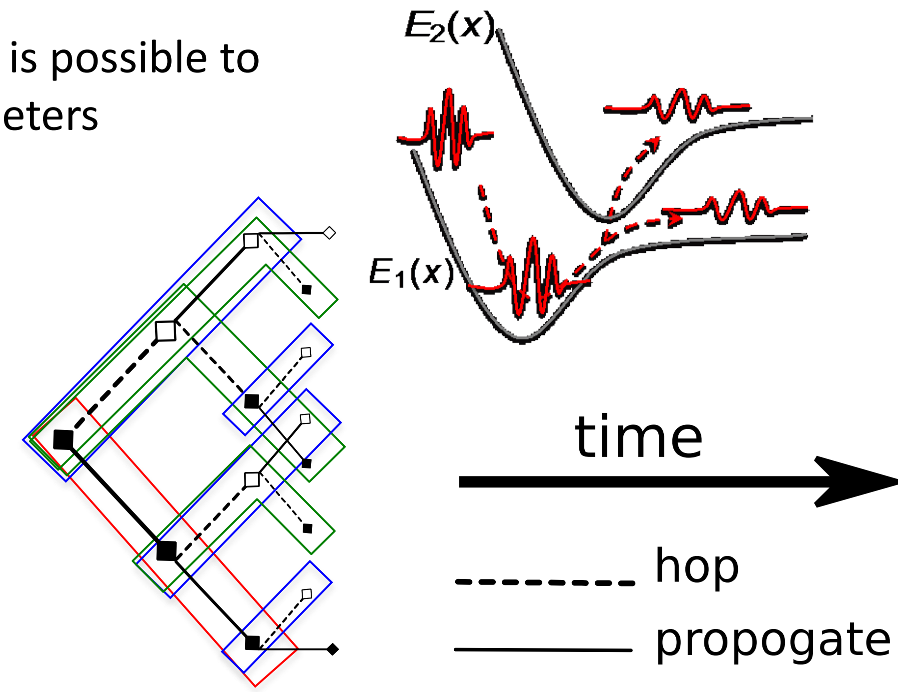
Extension of Heller’s GWD to Multiple Surfaces

Idea: Gaussians can split (hop) at crossings. It is possible to derive the new “off-spring” wavepacket parameters

$$x_1 = x_0 \qquad \gamma_1 = \gamma_0$$

$$p_1 - p_0 = \frac{d_{nm}[E_m - E_n]2M}{d_{nm}\cdot(p_0 + p_1)}$$

$$\alpha_1 - \alpha_0 = \frac{V''_{mn}M}{d_{nm}\cdot(p_0 + p_1)}$$



Two hops integrals

$$|\Psi(R,t)\rangle = \{\boxed{g_a(R,t)} + \boxed{\sum_{i,j}\int_0^t dt_2 \int_0^{t_2} dt_1\, d_{a,j}(t_2)d_{j,i}(t_1)g_{a,j,i}(R,t_1,t_2,t)} + \ldots\}|a\rangle$$

Fully adiabatic propagation

$$+\{\boxed{\sum_i \int_0^t dt_1\, d_{b,i}(t_1)g_{b,i}(R,t_1,t)} + \ldots\}|b\rangle$$

One hop integrals

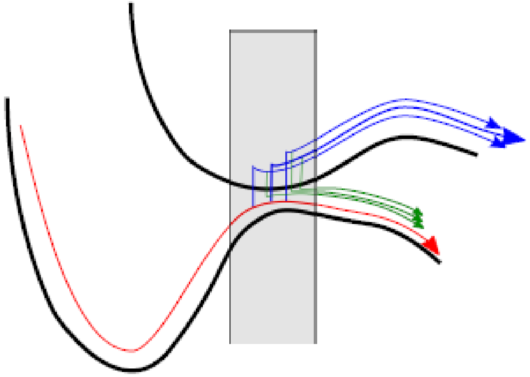
$$+\ldots$$

Now we have an integral expression for evolution of Gaussian vibrational wavefunction on multiple PES.

But… how to solve the integral equation

Markov-Chain Monte-Carlo approach where molecular dynamics classical trajectory with **its phase information** serves as a sampling point. Importance sampling function is NACT = $\boldsymbol{d}_{ab}(\boldsymbol{R}_0)\cdot\dot{\boldsymbol{R}}_t$

$$Prob_{a\rightarrow b}=\frac{\left|\boldsymbol{d}_{ab}(\boldsymbol{R}_0)\cdot\dot{\boldsymbol{R}}_t\right|\Delta t}{1+\sum_c\left|\boldsymbol{d}_{ac}(\boldsymbol{R}_0)\cdot\dot{\boldsymbol{R}}_t\right|\Delta t}\equiv\frac{|D_{ab}|}{1+\sum_c|D_{ac}|}.$$



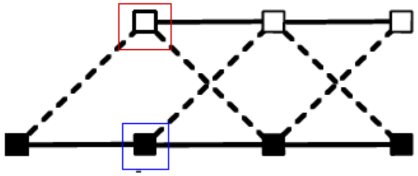
Nature Comm. 4. 2144, (2013)

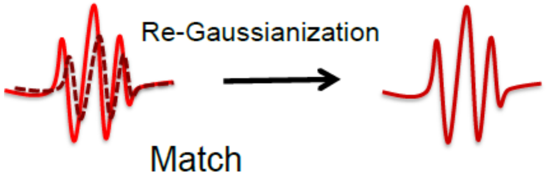
The algorithm is invariant with respect to the number of vibrational degrees of freedom, so that it is applicable to large molecular systems.

There is no free lunch! Convergence is achieved at ~50,000 trajectories

Note difference: FSSH converges at ~1,000 trajectories, here we have ~50,000! Why? ***Phases***

Idea: Let re-Gaussianize at each step/each crossing



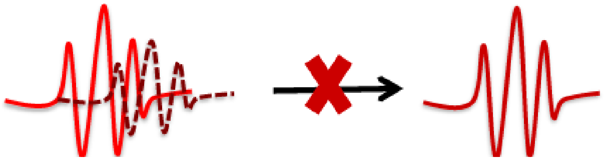


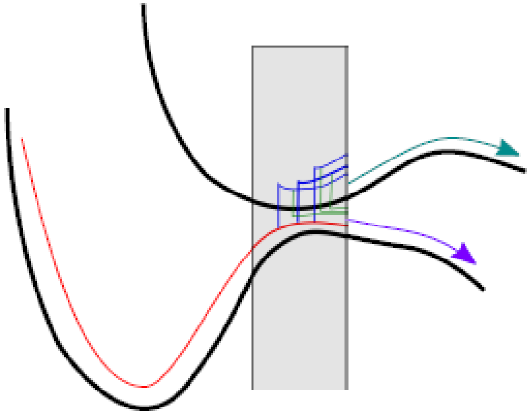
$$\langle\hat{x}\rangle,\langle\hat{p}\rangle,\langle\hat{x}^2\rangle,\langle\hat{p}^2\rangle\rightarrow x_{RG},p_{RG},\alpha_{RG}$$

$$|\langle RG|RG\rangle|^2=|\langle g_1+g_2|g_1+g_2\rangle|^2$$

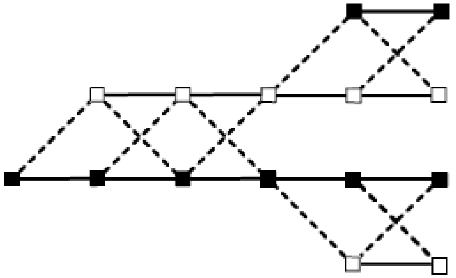
$$\langle RG|g_1+g_2\rangle\rightarrow\gamma_{RG}$$

However, this does not always work: when there is poor wavepacket overlap, we need to allow some branching. Great! We now have **a single parameter** controls the error



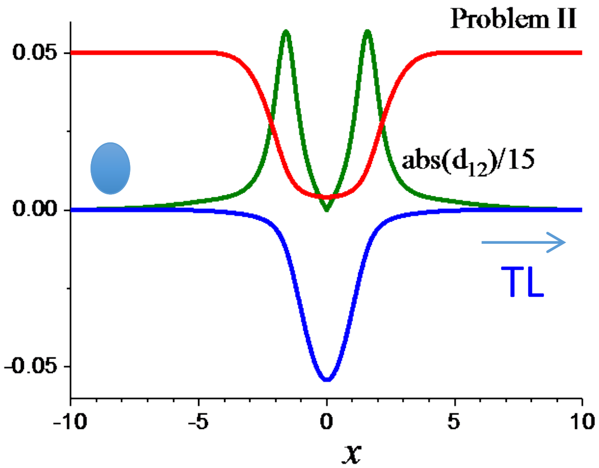


Does this work? Lesson learned!

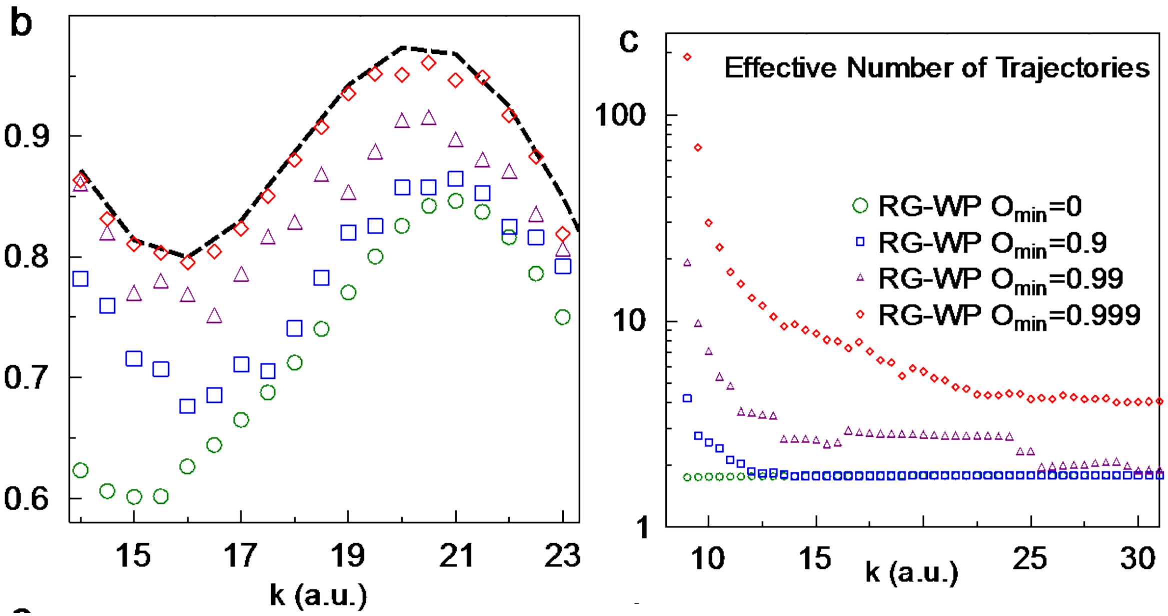


If $|\langle g_1|g_2\rangle| < O_{min}$ then branch

Higher min, increased cost and accuracy



Tully's model II: Dual avoided crossing: Stueckelberg oscillations



The Good:

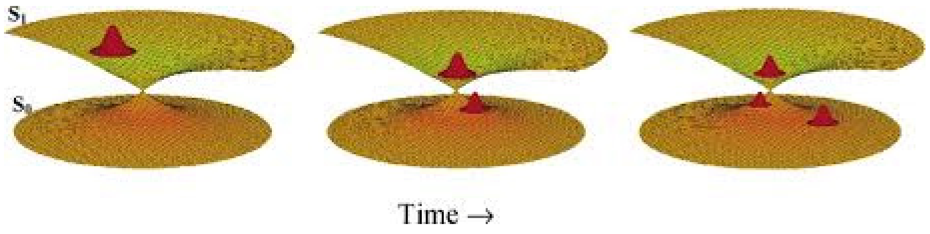
- It is always nice to have a controllable approximation!
- We can reproduce easily an exact solution of any model problem (1D Tully, 2D Subotnik, spin-boson…

The Ugly

- Very difficult to implement for realistic on-the-fly dynamics with 3N-6 vibrational space (poorly parallelizable, dependent trajectories);
- Main problem: 'thawed' Gaussians quickly get broadened requiring further splitting…

Ab Initio Multiple Spawning, AIMS (Martinez)

Full multiple spawning (FMS): nuclear wave functions are an adaptive linear combination of **frozen Gaussians** that follow classical trajectories. In a complete basis, this would be exact. Frozen Gaussians are trajectory basis functions (TBFs). In a sense it is similar to electronic basis set in ab initio



Chem. Rev. 2018, 118, 3305−3336

TBFs follow classical trajectories on electronic potential energy surfaces (center coordinate and momenta as well as complex phase)

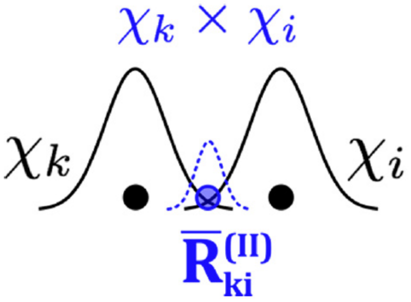
$$\frac{\partial \bar{R}_{i\rho}^{(J)}(t)}{\partial t} = \frac{\bar{P}_{i\rho}^{(J)}(t)}{M_\rho} \qquad \frac{\partial \bar{P}_{i\rho}^{(J)}(t)}{\partial t} = -\frac{\partial E_J(\mathbf{R})}{\partial R_{i\rho}}\bigg|_{R_{i\rho}=\bar{R}_{i\rho}^{(J)}(t)} \qquad \frac{\partial \bar{\gamma}_i^{(J)}(t)}{\partial t} = \sum_{\rho}^{3N} \frac{\left(\bar{P}_{i\rho}^{(J)}(t)\right)^2}{2M_\rho} - E_J\left(\bar{\mathbf{R}}_i^{(J)}(t)\right)$$

Numerical problem is evaluating couplings between surfaces leading to spawning of TBFs. Therefore **ab initio multiple spawning (AIMC)** employs approximations.

1. The Hamiltonian matrix on TBF basis is approximated as

$$H_{ki}^{JI} \approx \left\langle \chi_k^{(J)} \middle| \hat{T}_{\text{nuc}} \middle| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \delta_{JI} + E_I(\bar{\mathbf{R}}_{ki}^{(JI)}) \left\langle \chi_k^{(J)} \middle| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \delta_{JI}$$
$$- \sum_{\rho=1}^{3N} \frac{1}{M_\rho} \left\langle \chi_k^{(J)} \middle| \frac{\partial}{\partial R_\rho} \middle| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \langle \Phi_J | \frac{\partial}{\partial R_\rho} | \Phi_I \rangle_{\mathbf{r}} \bigg|_{R_\rho = (\bar{\mathbf{R}}_{ki}^{(JI)})_\rho}$$

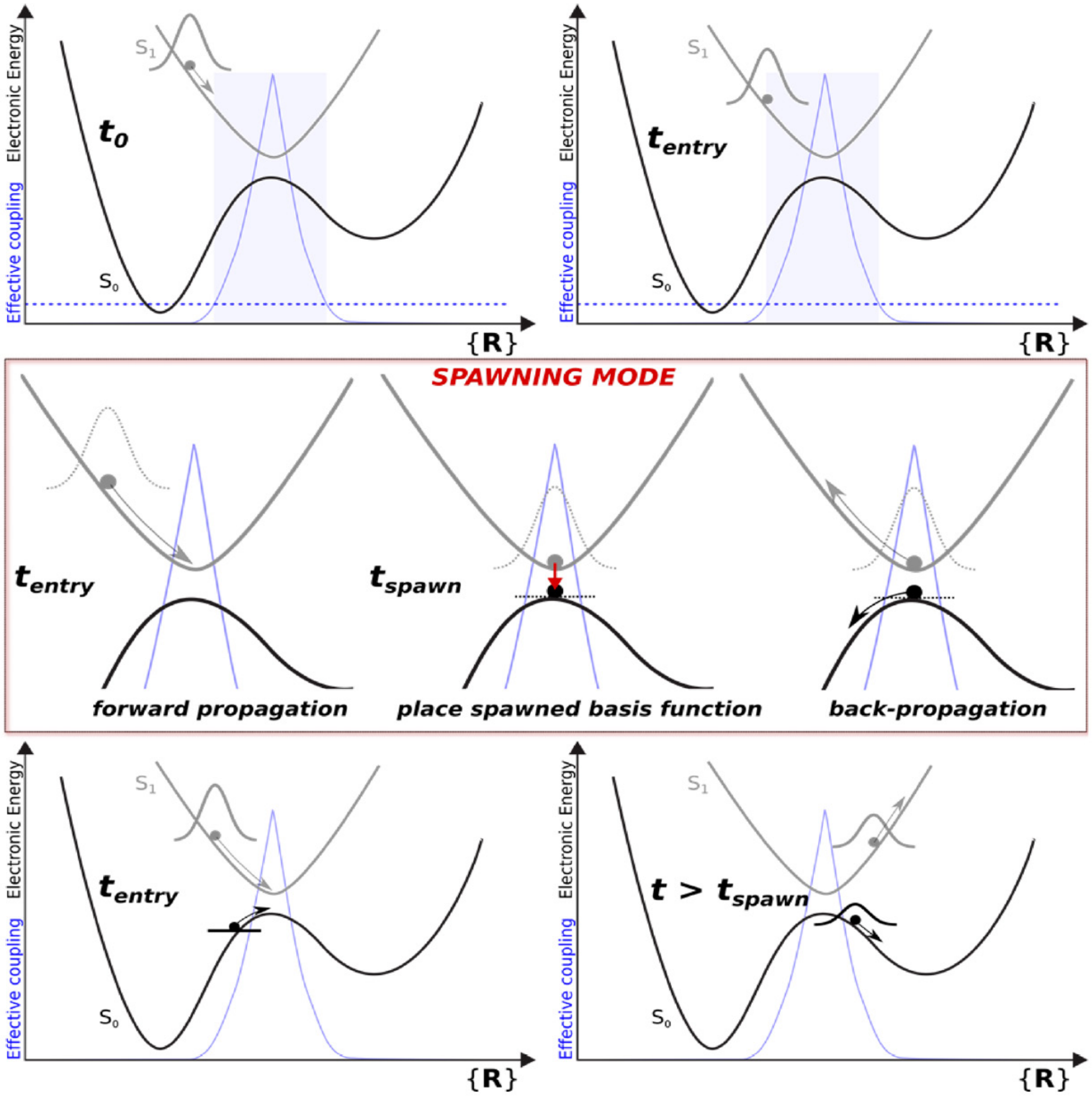
NACR



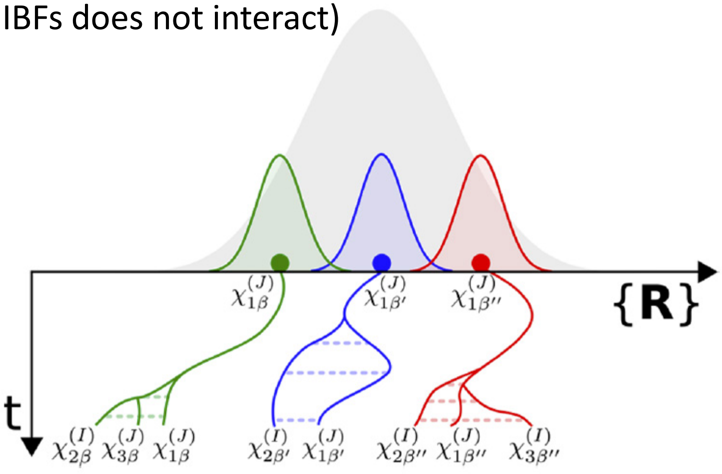
Product of Gaussians is a Gaussian

The AIMS procedure

Spawning is an adaptive expansion of the basis set in the regions of strong non-adiabatic coupling controlled by numerical criteria and back-propagation to match children wavepackets properly



Approximation 2: If excited state dynamics of high-dimensional molecular system, initial TBFs are uncoupled (ie. The first generation of IBFs does not interact)



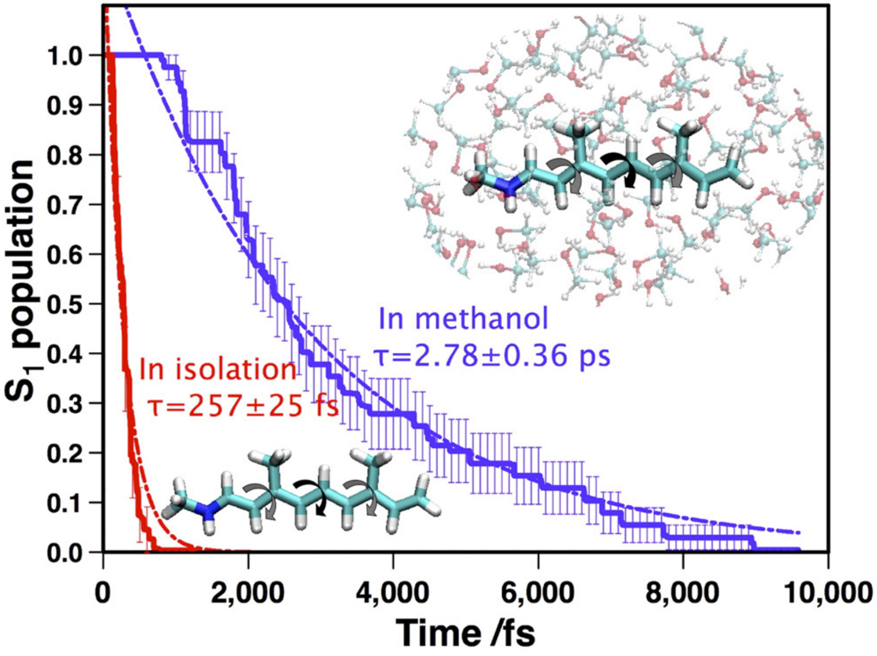
Approximation 3. You can propagate so many TBF on the computer! Weak hands cut off. In practice it is around ~100 frozen Gaussians.

Bottom line: AIMC is one of the first practical NAMD implementations featuring controlled approximation and calculation of phases of nuclei wavepackets. Can treat tunneling. ***Expensive:*** requires match with high-leve electronic structure theory. ***Codes:*** Molpro, Terachem, Gamess, Mopac

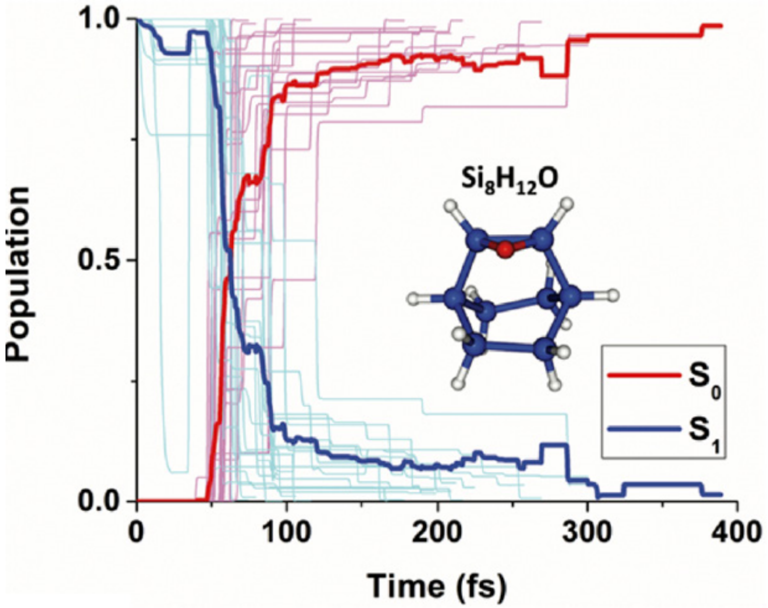
Chem. Rev. 2018, 118, 3305–3336

Practical examples of AIMS applications

Main finding: A primary step in the process is vision is retinal photoisometization. The photodynamics retinal protonated Schiff base (RPSB) is found to be highly sensitive to the environment of the molecule. AIMS with semiempirical FOMO-CASCI was used in combination with QM/MM of 85 MM methanol molecules. Dramatic difference in isomerization timescales (0.3 ps vs 3 ps) agrees with experiment and rationalized in terms of electrostatic effects changing rotational barriers.



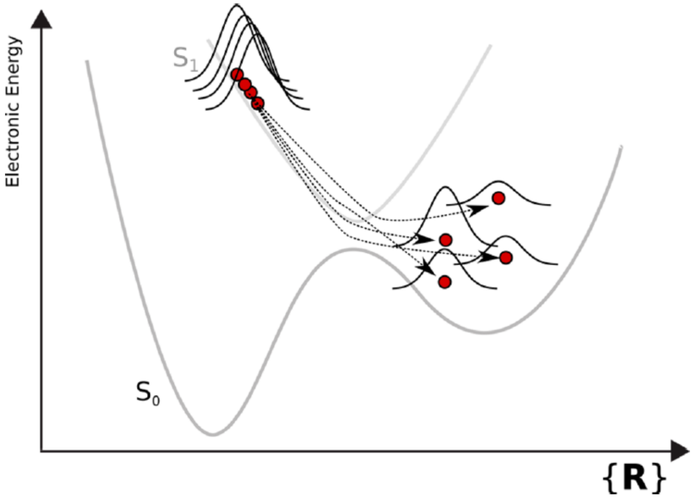
Main finding: AIMS/SA-CASSCF excited-state dynamics of $Si_8H_{12}O$: silicon epoxide defects in Si clusters lead to fast relaxation mediated by conical intersections between S_1 and S_0 states. This makes nanoclusters non-luminescent.



Chem. Rev. 2018, 118, 3305−3336

Multiconfigurational Ehrenfest, MCE (Shalashilin)

MCE is trajectory-guided approach: A swarm of Gaussian functions follows mean-field (Ehrenfest) trajectories. This allows to run **on the fly dynamics**



Wavefunction

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \sum_n d^{(n)}(t)\,\Psi^{(n)}(\boldsymbol{r},\boldsymbol{R},t)$$

Ehrenfest configuration

$$\Psi^{(n)}(\boldsymbol{r},\boldsymbol{R},t) \equiv \chi^{(n)}(\boldsymbol{R},t)\sum_a c_a^{(n)}(t)\psi_a^{(n)}(\boldsymbol{r},\boldsymbol{R})$$

Ehrenfest equation

$$i\hbar\frac{\partial c_a(t)}{\partial t} = E_a(\boldsymbol{R}_t)c_a(t) - \; i\hbar\sum_b \boldsymbol{d}_{ab}(\boldsymbol{R}_t)\cdot\dot{\boldsymbol{R}}_t\, c_b(t)$$

From time-dependent Schrödinger equation, expression for coefficients $d^{(n)}(t)$

$$i\hbar\frac{\partial}{\partial t}d^{(n)} = \sum_m \left\langle \Psi^{(n)}(\boldsymbol{r},\boldsymbol{R},t)\middle|\Psi^{(m)}(\boldsymbol{r},\boldsymbol{R},t)\right\rangle^{-1}\sum_l \left\langle \Psi^{(m)}(\boldsymbol{r},\boldsymbol{R},t)\middle|\hat{H}(\boldsymbol{R},\boldsymbol{r}) - i\hbar\frac{\partial}{\partial t}\middle|\Psi^{(l)}(\boldsymbol{r},\boldsymbol{R},t)\right\rangle d^{(l)}(t)$$

Finally vibrational wavefunctions follow the Ehrenfest trajectories (**can be spread over multiple PESs**)

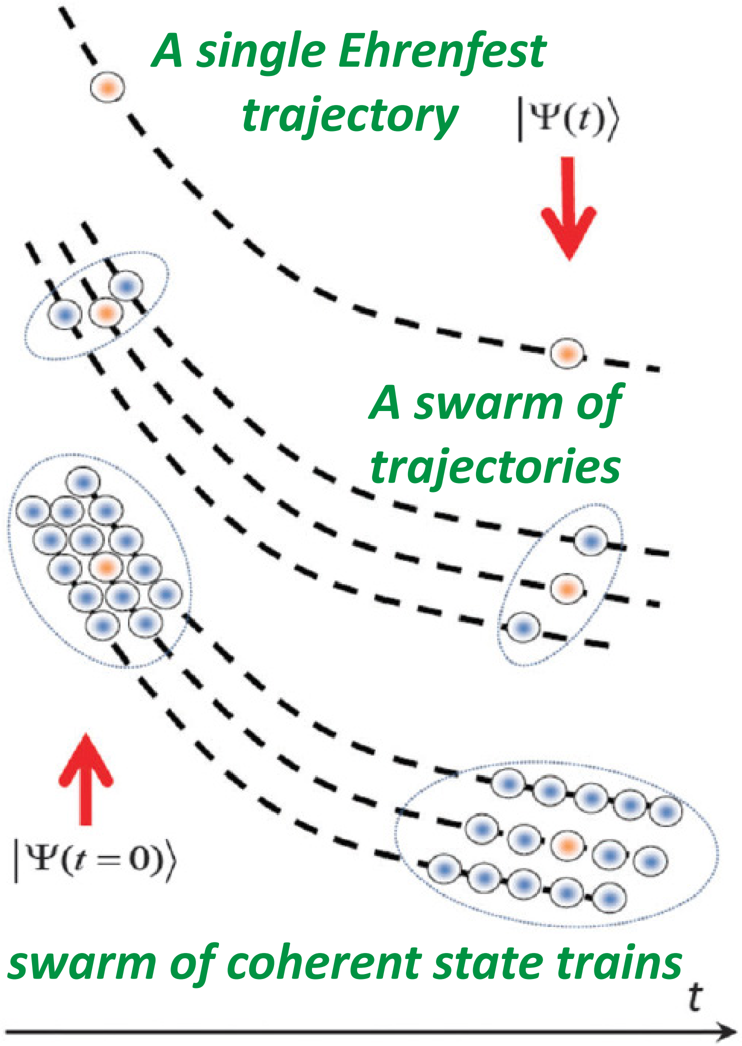
$$\chi^{(n)}(\boldsymbol{R}_t,\boldsymbol{P}_t,\boldsymbol{R},t) = \exp\left[\frac{i}{\hbar}[\gamma_t + \boldsymbol{P}_t\cdot(\boldsymbol{R}-\boldsymbol{R}_t) + \;(\boldsymbol{R}-\boldsymbol{R}_t)\cdot\hat{\boldsymbol{\alpha}}\cdot(\boldsymbol{R}-\boldsymbol{R}_t)]\;\right]$$

This is Gaussian wavepacket with a fixed, purely imaginary width, $\hat{\boldsymbol{\alpha}}(t) = i\hat{\boldsymbol{\alpha}}_I(0)$, and with a time-dependent phase factor: $\dot{\gamma}_t = \boldsymbol{P}_t\cdot M^{-1}\cdot\boldsymbol{P}_t/2$. The wavepacket (or a TBF is referred to as a Coherent State). Note that $d^{(n)}(t)$ represent couplings between trajectory basis functions (TBFs).

Bottom line: In MCE, one need to propagate an ensemble of Ehrenfest trajectories (this is primary variable). Parameters of nuclei wavepackets (e.g. phases) and wavefunctions are found by cheap post-processing of trajectories. Embarrassingly parallel and can reuse of Ehrenfest coding

Faraday Disc. 153, 105 (2011)

There are no free lunch: MCE complications



A single Ehrenfest trajectory

A swarm of trajectories

A swarm of coherent state trains

Numerical problem 1: Trivial crossing preclude propagation in a purely adiabatic basis $\psi_a(\boldsymbol{r},\boldsymbol{R})$. One need to introduce ***Time-dependent diabatic basis:*** Trajectories are still calculated in adiabatic basis, but overlaps are calculated in local diabatic basis $\phi_a(\boldsymbol{r})$

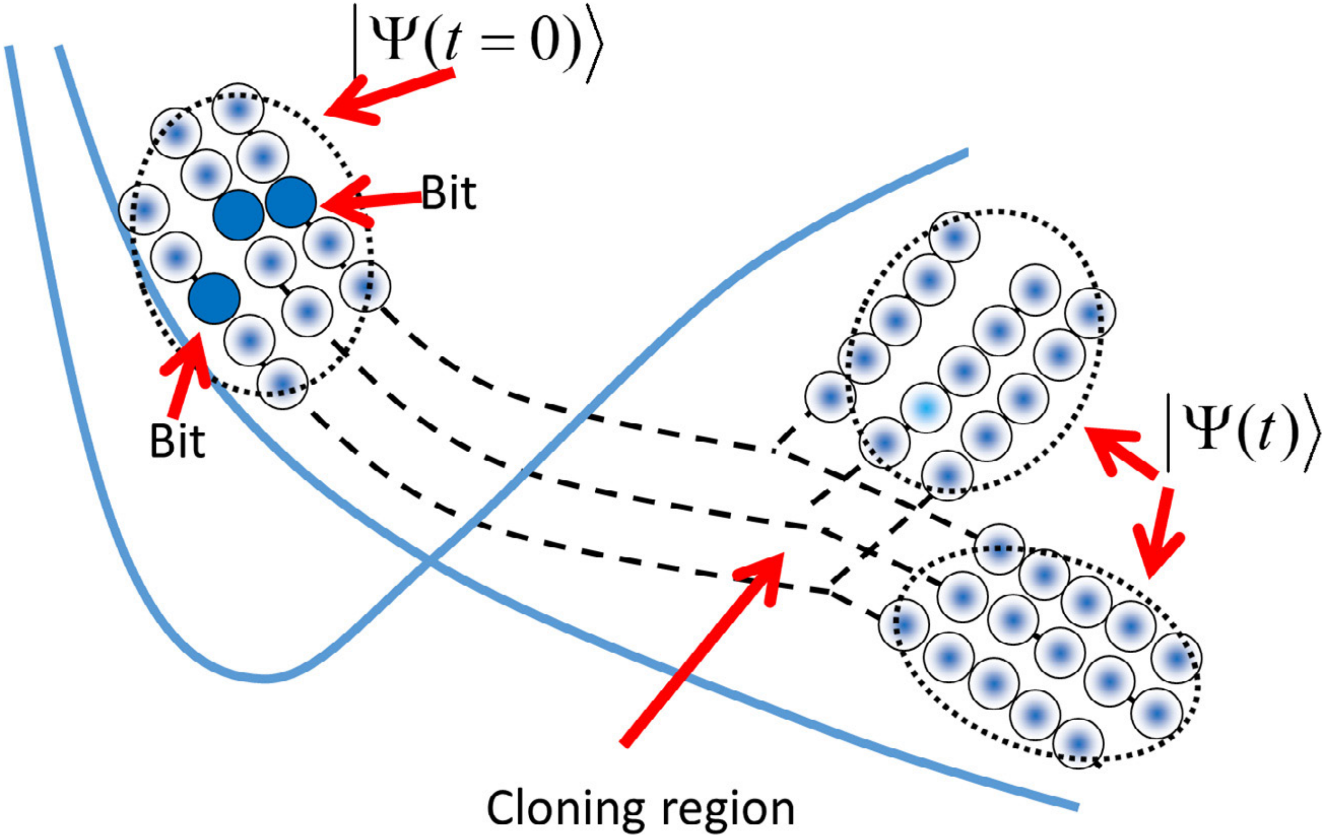
Phys. Chem. Chem. Phys. 18, 10028 (2016)

Numerical problem 2: The finite size of the basis set (i.e. TBFs) is the most serious limitation. Reaching the convergence is not simple.

Approximation: Ehrenfest is a mean field. Even though MCE has detailed balance, mean-field propagation requires a huge basis to converge and prevent sampling of the phase space.

This can be fixed with CLONING

AIMC-MCE: Ab initio multiple cloning



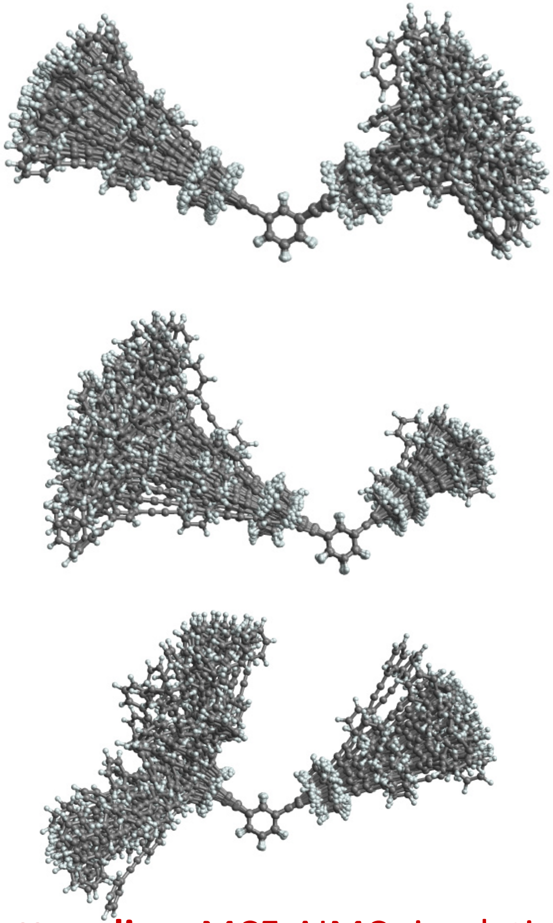
The difference between the shapes of the potential energy surfaces for different electronic states should lead to branching of the wave packet. This can be rigorously controlled with numerical criteria.

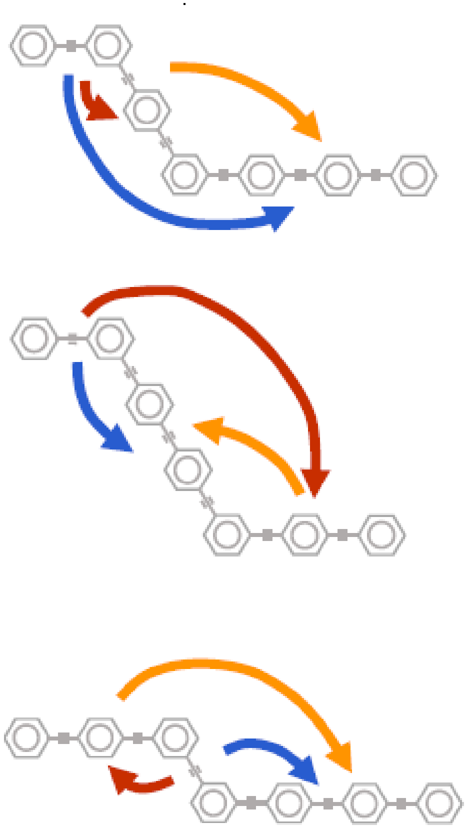
Bottom line: MCE-AIMC is one of the second practical semiclassical NAMD implementations featuring controlled approximation and calculations of phases of nuclei wavepackets. Can treat tunneling. ***Expensive:*** requires convergence of TBFs. ***Codes:*** NEXMD and some codes in Martinez and Levine groups

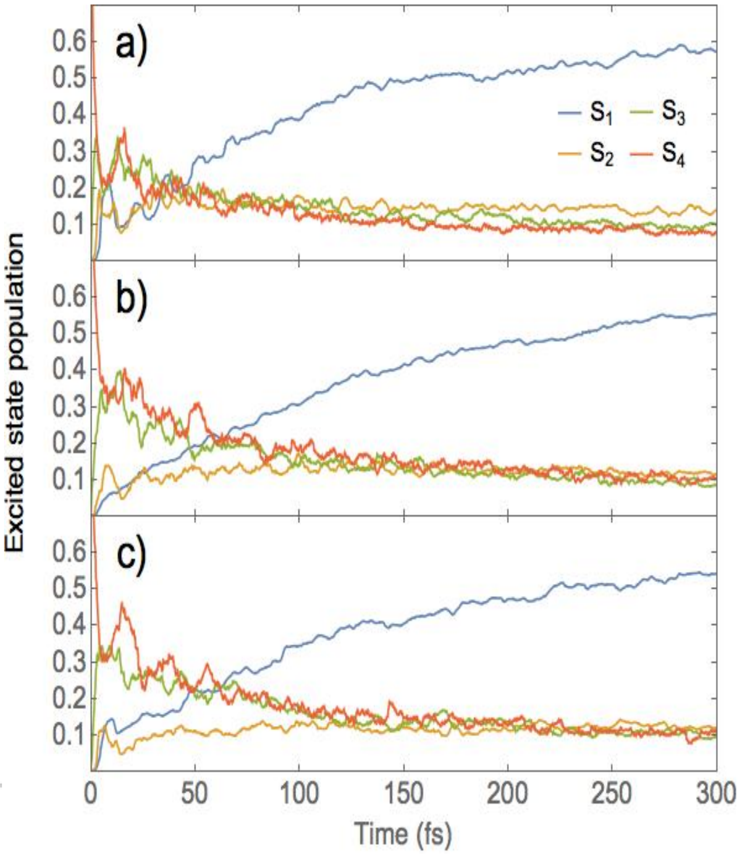
J. Chem. Phys., 141, 054110 (2014) Phys. Chem. Chem. Phys. 20, 17762, (2018)

Practical example of MCE-AIMC: energy transfer

Energy transfer pathways: Spatial arrangement from short (2 rings) to middle (3 rings) to long (4 rings) segments and electronically cross S_3 -> S_2 ->S_1 states. Goal is to understand effect of molecular topology and relarively soft structure (conformations).





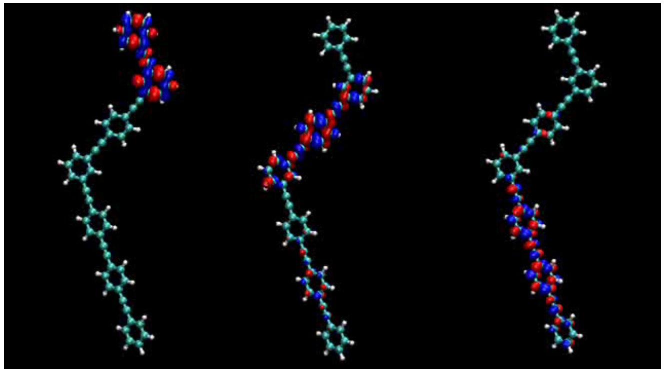


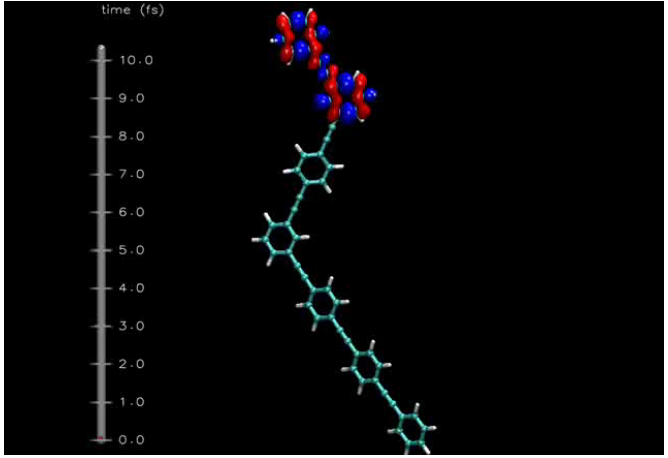
Bottom line: MCE-AIMC simulations suggest that energy moves in space most efficiently when all 3 processes are co-directional. There are notable electron-vibrational coherences appearing as beating across the entire trajectory ensemble (these are absent if surface hopping).

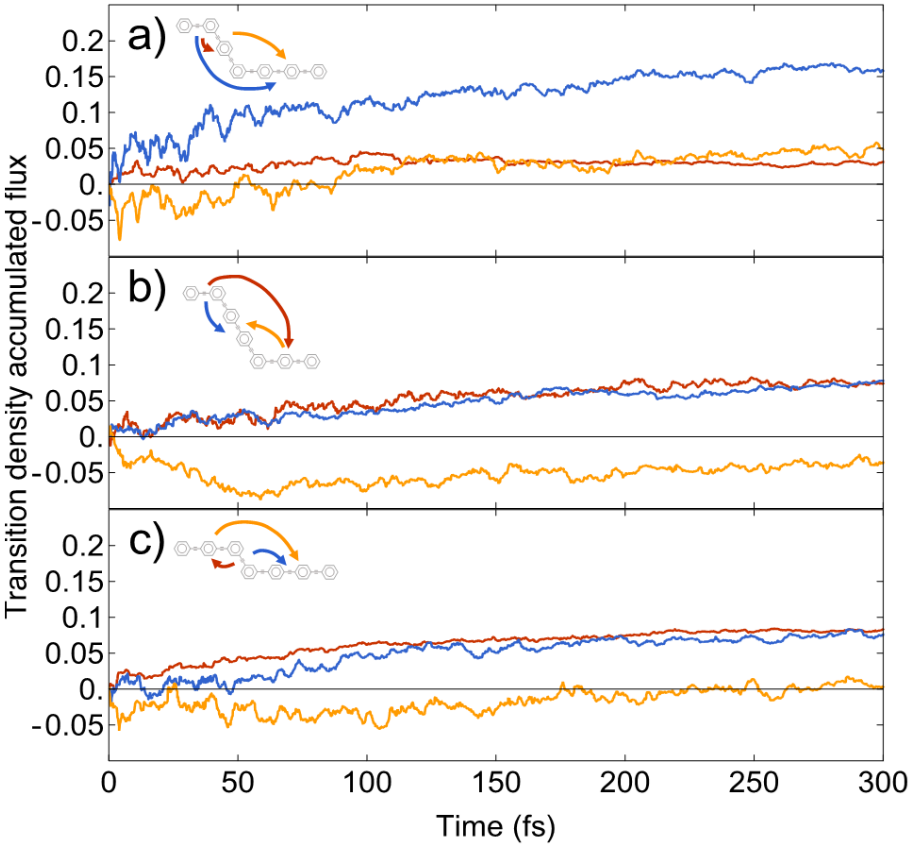
J. Chem. Phys., 150, 124301 (2019)

Analysis of spatial energy transfer pathways

Analysis: Electronic energy transfer is directional in space. Analysis of electronic wavefunctions and their fluxes in space is necessary. Transition density distributions and fluxes are convenient







Transition density (TD) matrix of *I*-th state

$$\left(\rho_I^{(n)}\right)_{i,j} = \langle \phi_I^{(n)} | \hat{c}_i^{\dagger} \hat{c}_j | \phi_g^{(n)} \rangle$$

TD localization on X-segment

$$\rho_{I,X}^{(n)} = \frac{\sum_{i \in X} \left(\rho_I^{(n)}\right)_{i,i}^2}{\sum_i \left(\rho_I^{(n)}\right)_{i,i}^2}$$

Occupation of X-segment

$$W_K = \frac{1}{\sum_{X=1}^{2} \left| \langle \hat{\rho}_X^{(K)} \rangle \right|^4}$$

J. Chem. Phys., 150, 124301 (2019)

Multi Configuration Time-Dependent Hartree (MCTDH)

MCTDH is an algorithm to solve the TDSE for multidimensional dynamical systems consisting of distinguishable particles (vibrations). MCTDH determines the quantal motion of the nuclei of a molecular system evolving on one or several coupled electronic potential energy surfaces.

General idea: Nuclei wavefunction is a multiconfiguration combination of Hartree product to be propagated. The difference with a standard wavepacket calculation is that the basis functions (the grid points) depend on time.

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

Nuclear coordinates

Expansion coefficients

Hartree product of single-particle functions

Draw analogy with electronic structure problem (except time):
TDH <-> Hartree-Fock, SCF
MCTDH <-> MCSCF

With an increasing expansion, MCTDH wavefunction monotonically converges toward the exact one

The MCTDH working equations derived from the Dirac-Frenkel variational principle $\langle \delta\Psi \,|\, H - i\partial_t \,|\, \Psi\rangle = 0$

$$\mathrm{i}\dot{A}_J = \sum_L \langle \Phi_J \,|\, H \,|\, \Phi_L \rangle A_L - \sum_{\kappa=1}^{f} \sum_{l=1}^{n_\kappa} g_{j_\kappa l}^{(\kappa)} A_{J_l^\kappa} ,$$

$$A_J = A_{j_1\ldots j_f} \qquad \Phi_J = \prod_{\kappa=1}^{f} \varphi_{j_\kappa}^{(\kappa)}$$

$$\mathrm{i}\dot{\boldsymbol{\varphi}}^{(\kappa)} = g^{(\kappa)}\mathbf{1}_{n_\kappa}\boldsymbol{\varphi}^{(\kappa)} + (1 - P^{(\kappa)})[(\boldsymbol{\rho}^{(\kappa)})^{-1}\langle \boldsymbol{H}\rangle^{(\kappa)} - g^{(\kappa)}\mathbf{1}_{n_\kappa}]\,\boldsymbol{\varphi}^{(\kappa)}$$

$$\boldsymbol{\varphi}^{(\kappa)} = (\varphi_1^{(\kappa)},\ldots,\varphi_{n_\kappa}^{(\kappa)})^{\mathrm{T}} \qquad \rho_{jl}^{(\kappa)} = \sum_J{}^{\kappa} A_{J_j^\kappa}^{*} A_{J_l^\kappa}$$

$$\langle \varphi_j^{(\kappa)}(0) \,|\, \varphi_l^{(\kappa)}(0)\rangle = \delta_{jl} \qquad \langle \varphi_j^{(\kappa)}(t) \,|\, \dot{\varphi}_l^{(\kappa)}(t)\rangle = -\mathrm{i}\langle \varphi_j^{(\kappa)}(t) \,|\, g^{(\kappa)} \,|\, \varphi_l^{(\kappa)}(t)\rangle$$

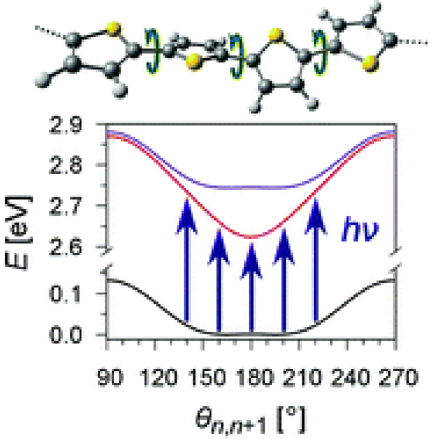
- the constraint single-particle operator

There are a lot of numerical tricks developed particularly for integration of MCTDH equations. Frequently, one needs a fitted potential energy surfaces. Some schemes explored on-the-fly calculations.

Bottom line: MCTHD simulations are very accurate. There are many limitations: most important should be a few vibrational degrees of freedom (~5-25). Applications are limited to small molecules and model systems (e.g. reduced molecular representation). **Best code:** The Heidelberg MCTDH Package

Physics reports. , 2000, Vol.324, p.1-105

Practical example of MCTDH: excited state dynamics in P3HT



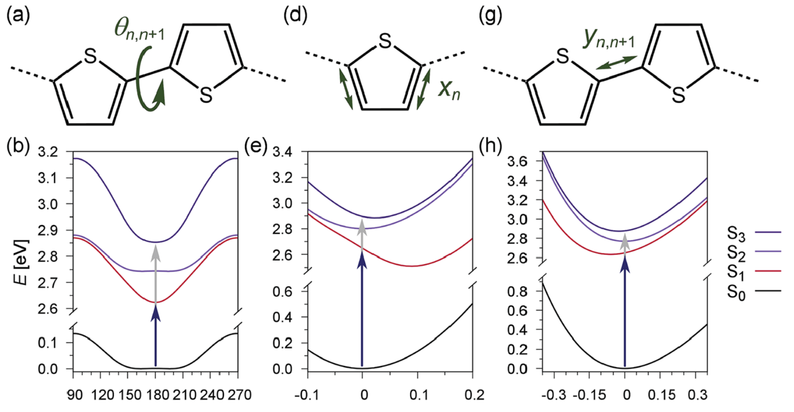
Use model ab initio parameterized Frenkel–Holstein Hamiltonian

$$\hat{H} = \sum_{n,n'=1}^{N} \hat{H}_{n,n'} |n\rangle\langle n'| + \hat{H}_{\text{bath}} \hat{\mathbf{1}} \qquad \hat{H}_{n,n'} = \delta_{n,n'}\hat{T} + \delta_{n,n'}\hat{V}_n^{\text{site}} + \hat{V}_{n,n'}^{\text{exc}}$$

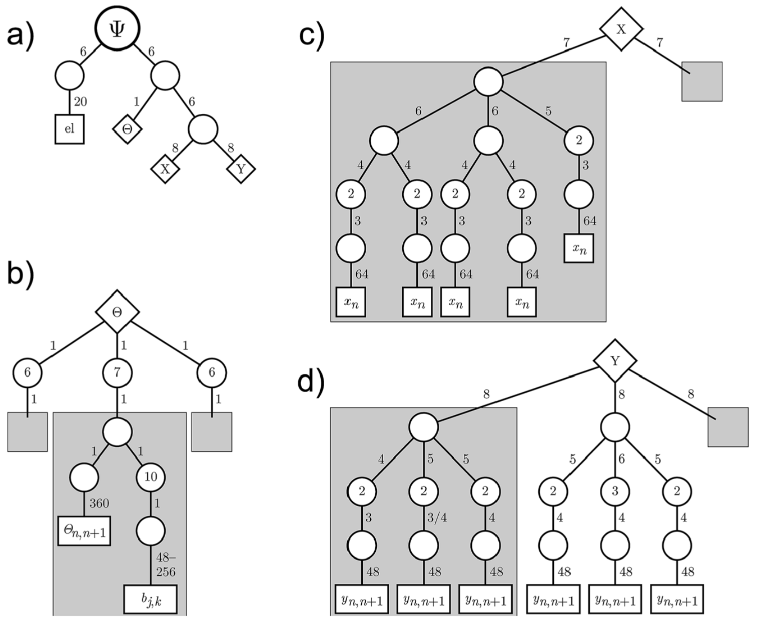
Excitonic states

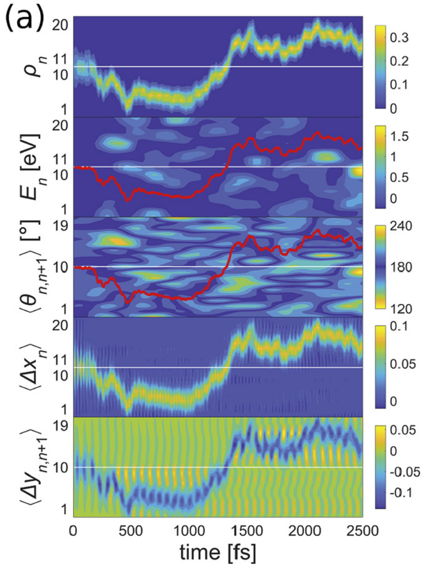
Excitonic couplings'

Essential normal modes and parameterization of Hamiltonian vs TDDFT



A multi-layer MCTDH solves quantum dynamics for groups of vibrations



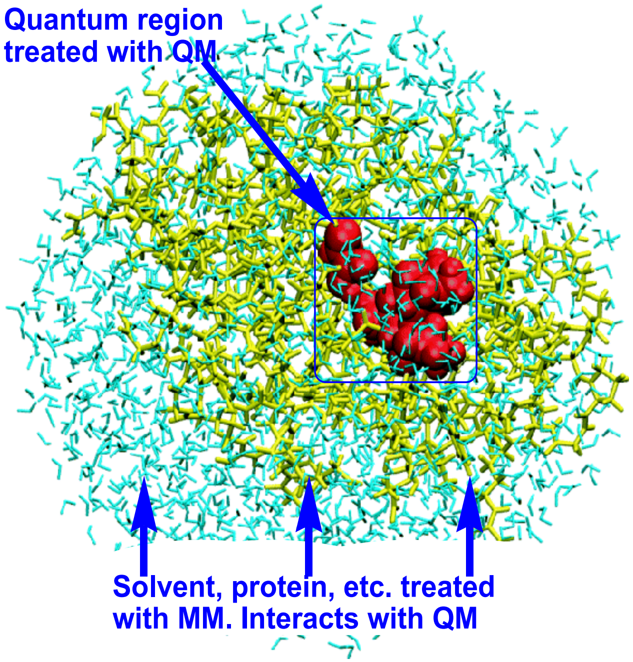


Bottom line: Exciton is a polaronic quasiparticle. High frequency modes (x and y) contribute to its self-trapping. Low frequency modes (torsion) determine energy landscape for energy motion along the polymer chain.

19 torsional modes, 20 ring-breathing modes, 19 bond-stretch modes, and 190 harmonic oscillator bath modes: a total of 248 vibrational degrees of freedom

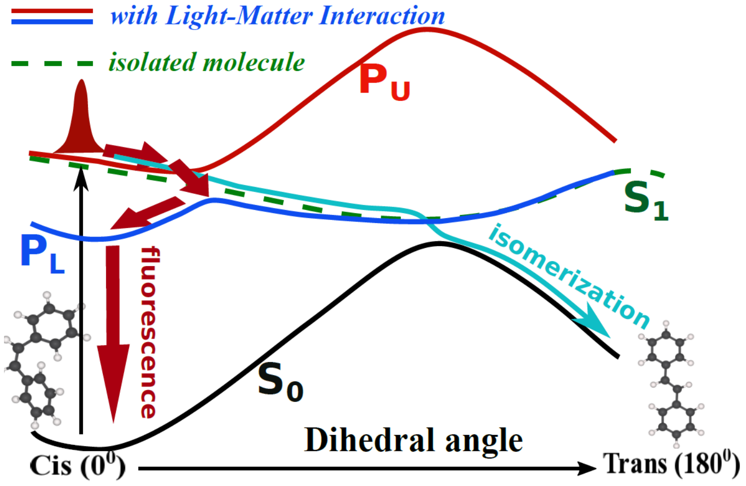
Faraday Discuss., 2020, 221, 406–427

What is left out?


Quantum region treated with QM

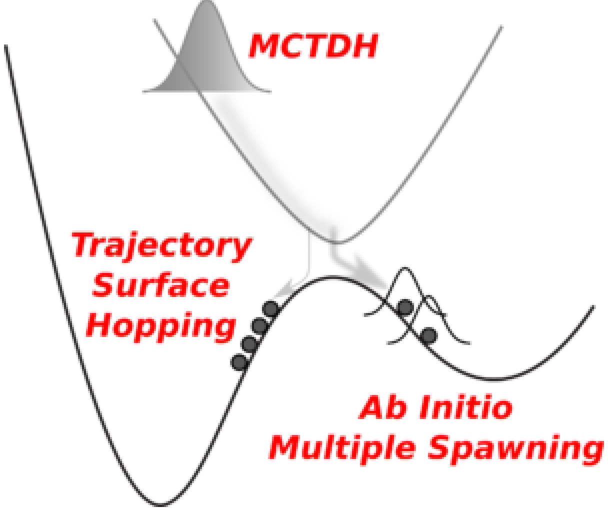
Solvent, protein, etc. treated with MM. Interacts with QM

- Lots of methodologies: Ring-polymer/path integral molecular dynamics, quantum-classical Liouville equation, Bohemian dynamics, Hardy Gross’ Green function approach;
- Solvation phenomena, Polarizable Continuum model or Quantum Mechanics/Molecular Mechanics approaches;
- Open-shell approaches, spin states, bond-breaking and photochemistry;
- Strong light-matter interactions, polaritonics and plasmonics, controlling reactions with a laser;
- Accelerated dynamics, meta-dynamics, extended Lagrangian excited state dynamics,

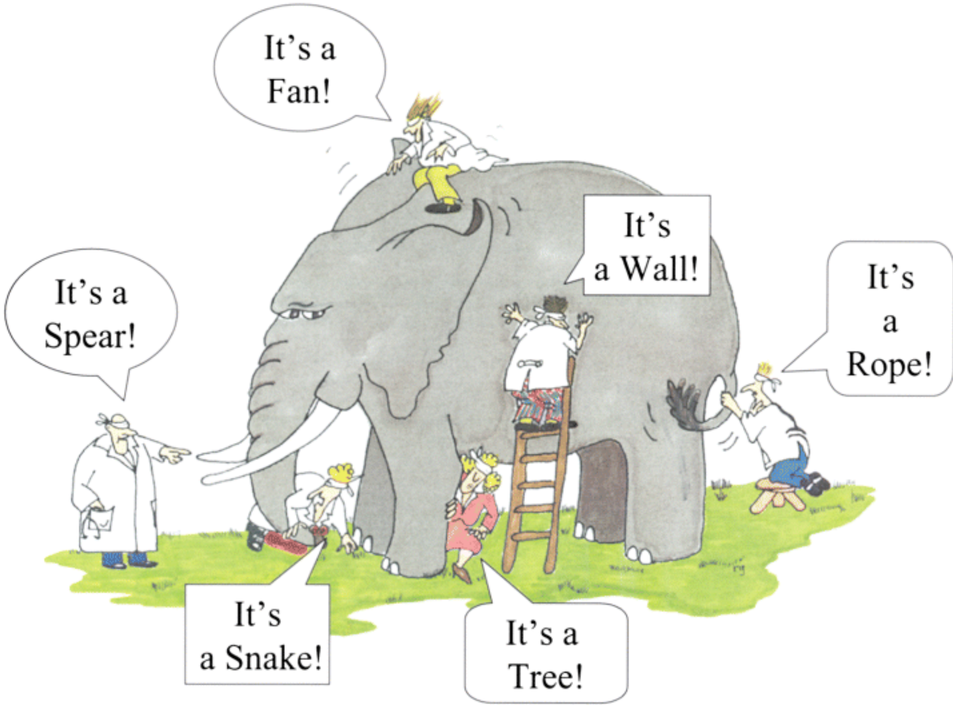


In conclusion:

- *Modeling of non-adiabatic dynamics (NAMD) is a lively fast developing field, becoming an important counterpart of experiment;*
- *There are plenty of methods available, from few level models to MQC techniques to high accuracy AIMS, MCE-AIMC and MC-TDH;*
- *There are many free/commercial codes available. Wrappers (aka Pyxaid, Newton-X and Sharc) are universal and slow; build in NAMD driver is faster (aka Molpro, Turbomole, NWChem and NEXMD);*
- *Always beware about 2 sources of error: electronic structure and NAMD driver errors;*
- *Science starts when we start asking the right questions: understand physics, pick up the right 'tool' to get answers, so that we can understand, control and improve…*
- *Communication between synthesis, experiments and theory is very important – we are touching different pieces of 'truth';*
- *Think about why are you doing this? Is there a road from science to technology?*



Thank you!



Questions for me

Questions for you

1. Derive Time-dependent Schrödinger equation (TDSE) on slide 8 for a vibrational wavepacket (refresh your 101 quantum mechanics!)

$$i\hbar\frac{\partial\chi_a(\boldsymbol{R},t)}{\partial t}=\left[-\frac{1}{2}\hbar^2\nabla_{\boldsymbol{R}}\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}}+E_a(\boldsymbol{R})-\sum\nolimits_b\frac{1}{2}\hbar^2\,\boldsymbol{d}_{ab}(\boldsymbol{R})\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{d}_{ab}(\boldsymbol{R})\right]\chi_a(\boldsymbol{R},t)+\sum\nolimits_b\frac{1}{2}\hbar^2\left[\boldsymbol{d}_{ab}(\boldsymbol{R})\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}}+\nabla_{\boldsymbol{R}}\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{d}_{ab}(\boldsymbol{R})\right]\chi_b(\boldsymbol{R},t)$$

From a general TDSE $i\hbar\frac{\partial\Psi(\boldsymbol{R},\boldsymbol{r},t)}{\partial t}=\widehat{H}(\boldsymbol{R},\boldsymbol{r})\Psi(\boldsymbol{R},\boldsymbol{r},t)$

Hint: use kinetic energy in $\widehat{H}(\boldsymbol{R},\boldsymbol{r})=\widehat{T}(\boldsymbol{R})+\widehat{H}_{el}(\boldsymbol{R},\boldsymbol{r})$

as $\widehat{T}(\boldsymbol{R})=-\frac{1}{2}\hbar^2\boldsymbol{\nabla}_R\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{\nabla}_R$ ***and utilize other expressions on the slide***

2. Phonon bottleneck appears when there are energetic gaps between bands in electronic spectra of molecules or solids. In few sentences, discuss its importance for non-radiative relaxation and technologically important phenomena such as hot electron extraction, multiexciton generation, etc.

3. In few sentences, describe examples of non-adiabatic dynamics in your research (e.g. non-radiative relaxation, internal conversion, intersystem crossing, etc.). Why is this important (or not important) for processes you are studying?