Photoexcited dynamics in molecular materials with Non-adiabatic EXcited state Molecular Dynamics (NEXMD) code

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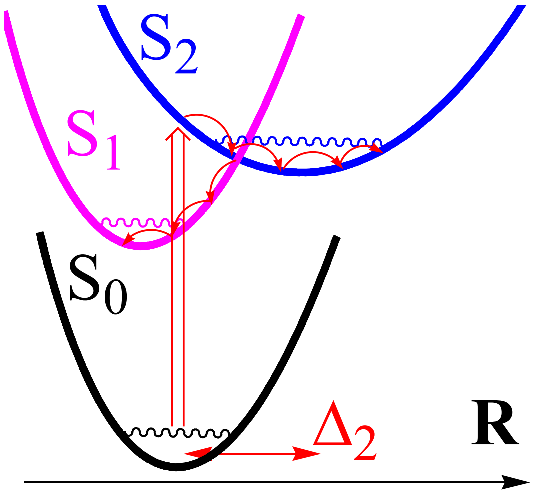
CyberTraining Workshop, Buffalo University

Overcoming the NAMD numerical expense

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

10^9 calculations of excited states



NEXMD

Software package

https://github.com/lanl/NEXMD

- ***Surface hopping (FSSH), Ehrenfest or ab initio multiple cloning with multiconfigurational Ehrenfest (AIMC-MCE);***
- **Efficient semiempirical 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 (PCE or QM/MM), extended Lagrangian =dynamics, open shells, polaritons, etc.***

NEXMD allows calculations ~1000 atoms molecules and ~10ps timescales

NEXMD

Open-source release version

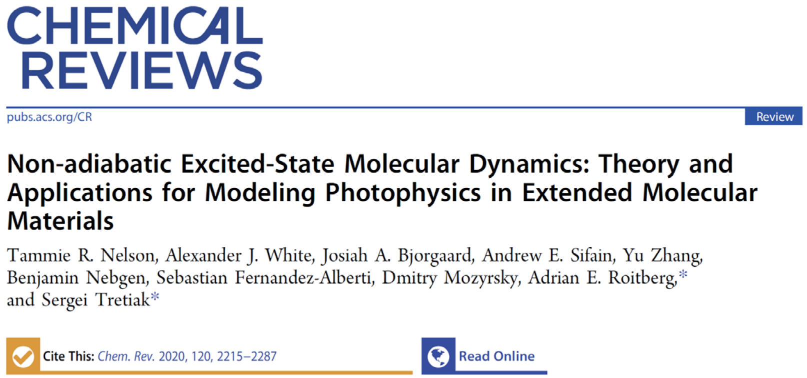
https://github.com/lanl/NEXMD

- ***Excited states/dynamics***
- ***TSH, Ehrenfest***
- ***Trivial crossings, decogherence***
- ***Solvent effects***
- ***Extended Lagrangian dynamics***

Developmental Version

(mainly supported by Walter Malone)

- ***MCE-AIMC suite***
- ***Open shells***
- ***Polaritonics***
- ***Automatic state reduction***



CHEMICAL REVIEWS

pubs.acs.org/CR 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*

Cite This: *Chem. Rev.* 2020, 120, 2215−2287 **Read Online**

Additional Literature:

"NEXMD Software Package for Non-adiabatic Excited State Molecular Dynamics Simulations" J. Chem. Theory Comput. **16**, 5771 – 5783 (2020).

"GPU-Accelerated Semi-Empirical Born Oppenheimer Molecular Dynamics using PyTorch" J. Chem. Theory Comput. **16**, 4951 – 4962 (2020).

"First Principles Non-Adiabatic Excited-State Molecular Dynamics in NWChem Software" J. Chem. Theory Comput. **16**, 6418 – 6427 (2020).

PySeQM

Open-source release version

https://github.com/lanl/PYSEQM

(mainly supported by Guiqing Zhou)

- ***Front end machine learning fitting of Hamiltonians. PyTorch, backpropagation utility***
- ***Very fast ground state quantum dynamics, GPU based, SP2 acceleration, extended Lagrangian***

NWChem

Developmental version

(mainly supported by Wilson Song)

- ***Some NEXMD capabilities implemented in NWChem software***
- ***No-adiabatic dynamics with TDDFT***
- ***TSH, MCE-AIMC, trivials, decoherence, etc.***

Our plan for the lecture

PART I: Methodology and Applications

- *Introduction: what are we taking about?*
- *Born-Oppenheimer Approximation*
- *Need for atomistic methods, mixed quantum-classical approach*
- *Electronic structure theory in NEXMD*
- *Ehrenfest dynamics*
- *Surface Hopping methodology*
- *Trivial crossings and decoherence effects*

☐ ***Basic use: non-radiative relaxation modeling***

PART II: Some advanced NEXMD capabilities

- *Multi-configurational Ehrenfest with Ab Initio Multiple Cloning (MCE-AIMC)*
- *Environmental effects*
- *Extended Largangian excited state MD*
- *Open shell, bond breaking*
- *Polaritonics, molecules in the cavity*
- *Practical aspects: spectra, rates, wavefunction analysis*

☐ ***Developers: new methodologies, deep understanding***

Feel free to ask question on the fly…

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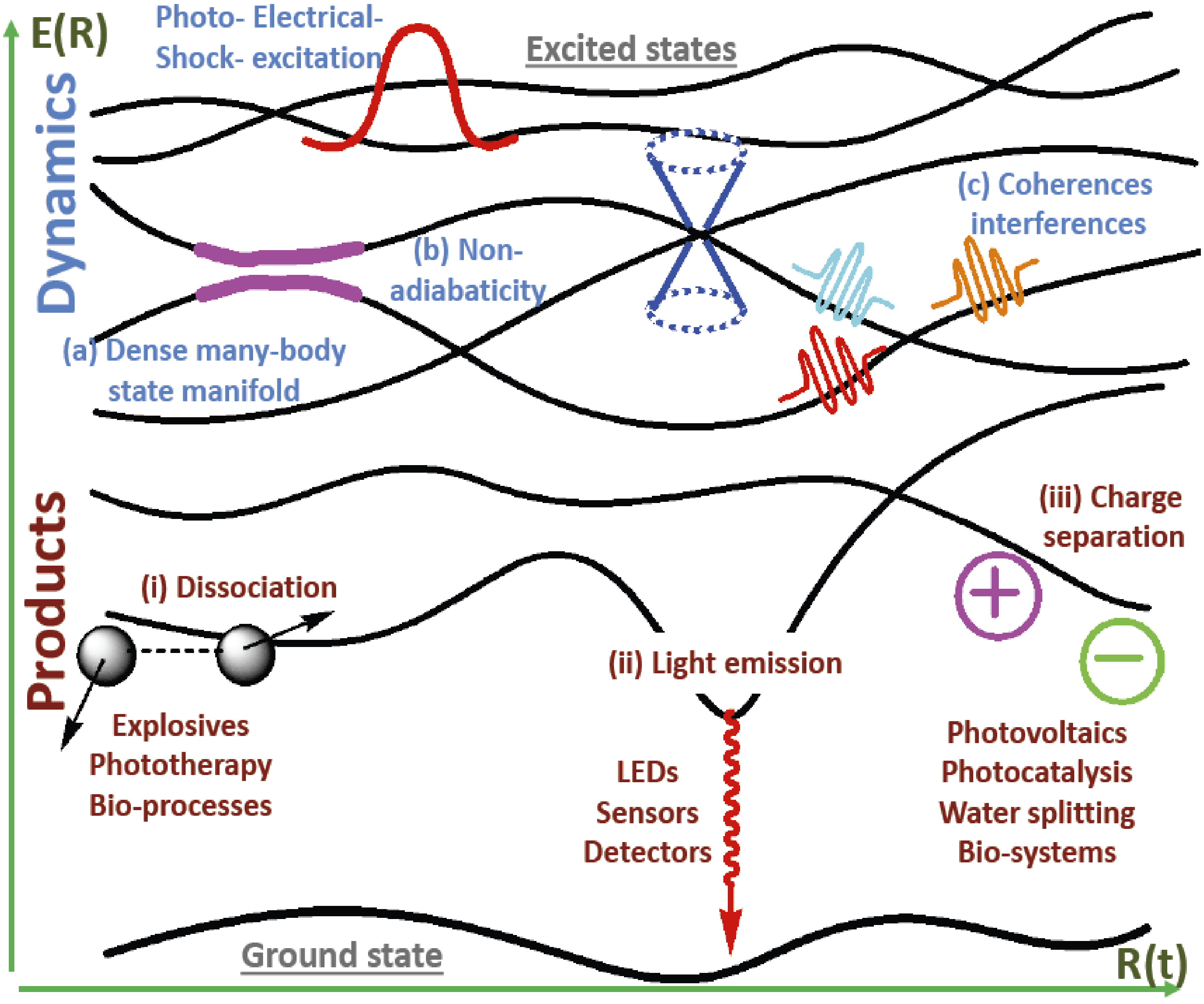
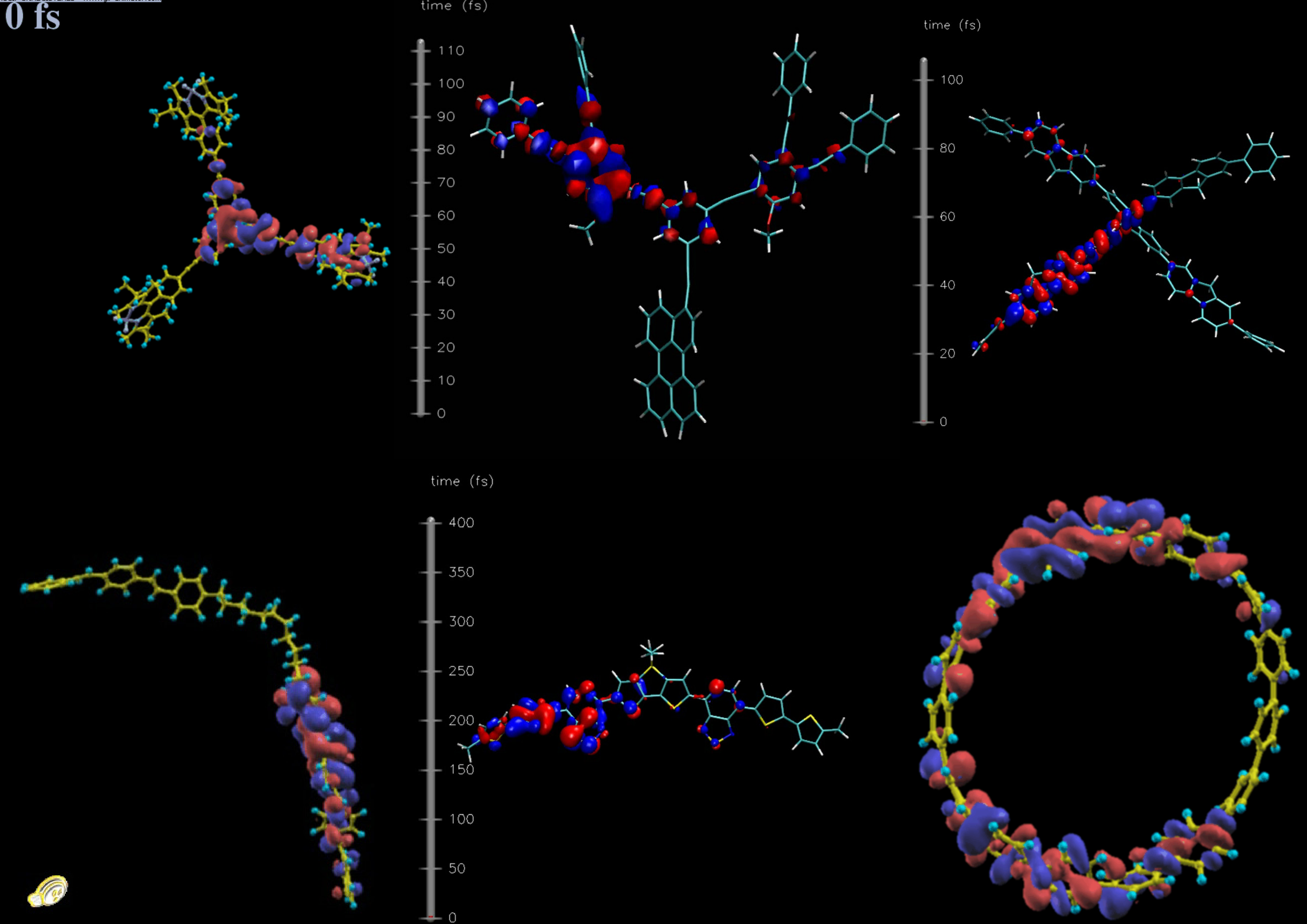
Photoexcited dynamics



Excited state relaxation timescales:

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


0 fs
time (fs)
110
100
90
80
70
60
50
40
30
20
10
0
time (fs)
100
80
60
40
20
0
time (fs)
400
350
300
250
200
150
100
50
0

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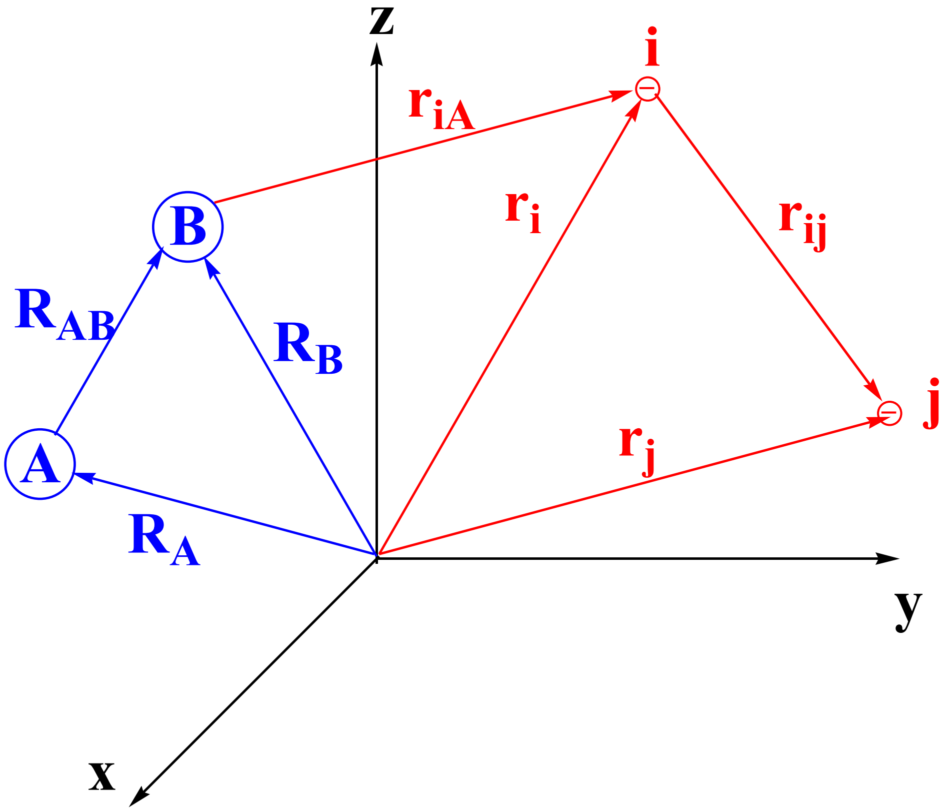
The molecular Hamiltonian

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

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

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

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \underbrace{\sum_a \overset{\text{Electrons}}{\psi_a(\boldsymbol{r},\boldsymbol{R})}\overset{\text{Nuclei}}{\chi_a(\boldsymbol{R},t)}}_{\text{Adiabatic}} = \underbrace{\sum_a \overset{\text{Electrons}}{\phi_a(\boldsymbol{r})}\overset{\text{Nuclei}}{\chi'_a(\boldsymbol{R},t)}}_{\text{Diabatic}}$$

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

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

$\hat{\boldsymbol{m}}_{\boldsymbol{R}}$ 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 $\boldsymbol{R}$

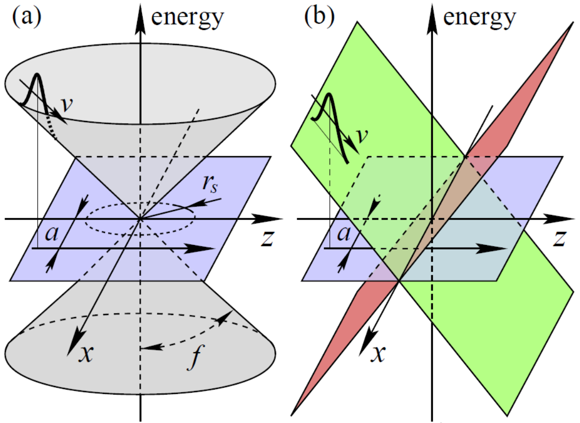
$\langle \phi_a(\boldsymbol{r})|\nabla_{\boldsymbol{R}}^2|\phi_b(\boldsymbol{r})\rangle \equiv 0$ Kinetic energy terms for diabatic wavefunctions

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

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☐ ***Basic use:*** ***non-radiative relaxation modeling***

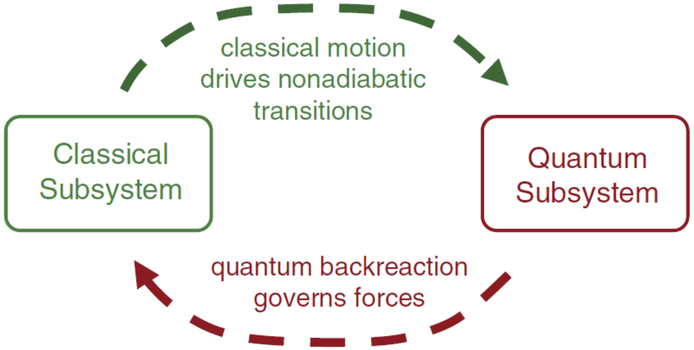
☐ ***Developers:*** ***new methodologies, deep understanding***

Feel free to ask question on the fly…

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

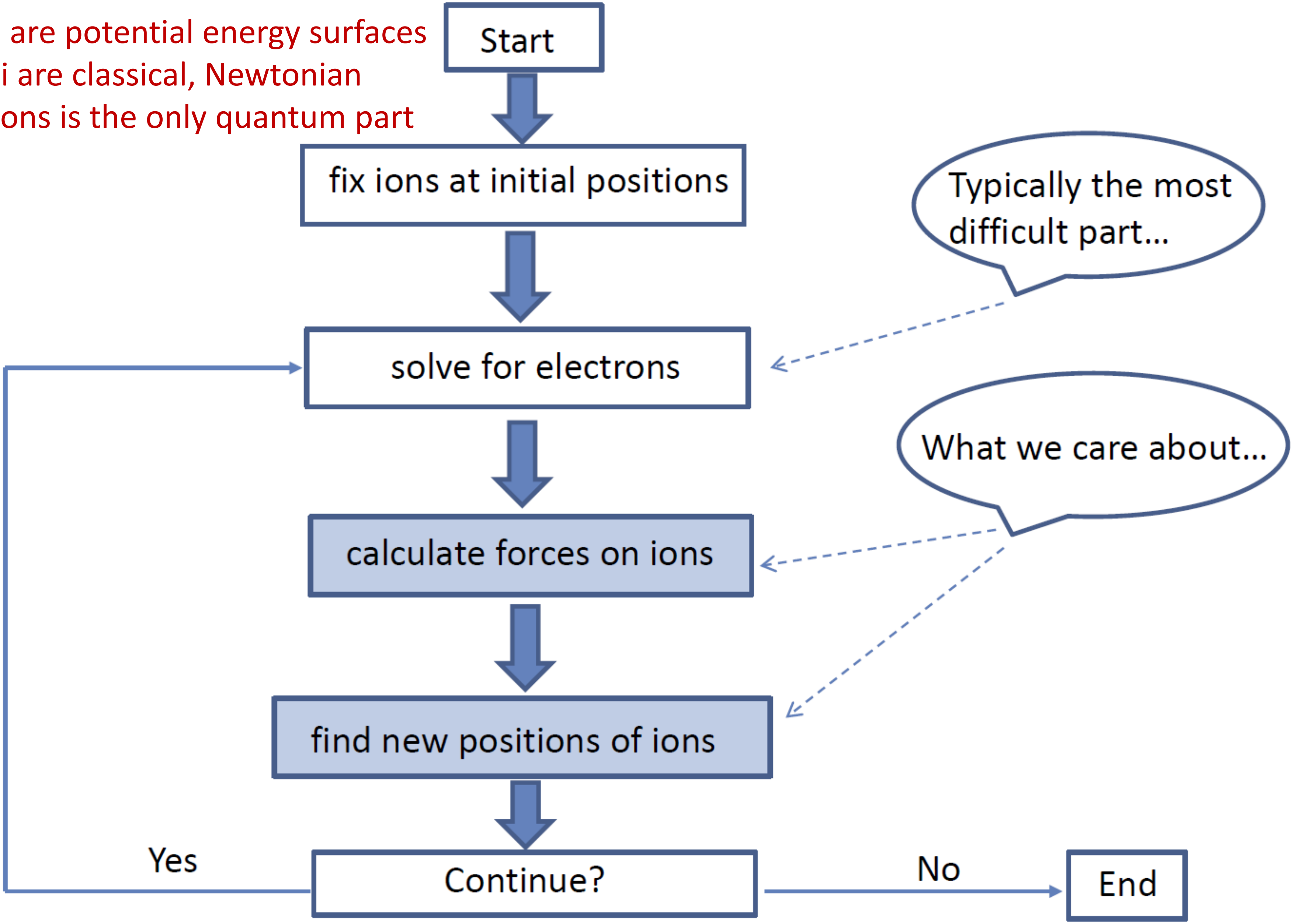
1. Self-consistency between the classical and quantum coordinates
2. Proper treatment of quantum coherence and decoherence phenomena
3. Incorporation of detailed balance (respect temperature, distribution and relaxation down!)
4. Lack of vibrational quantum effects such as tunneling, zero-point motion,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

The main message of the 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

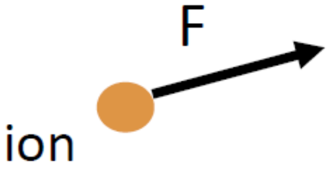
End

Typically the most difficult part…

What we care about…

Forces in adiabatic and non-adiabatic case

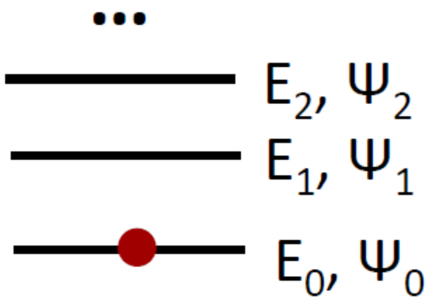
Adiabatic situation



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

Hellman-Feynman relation

Electronic States

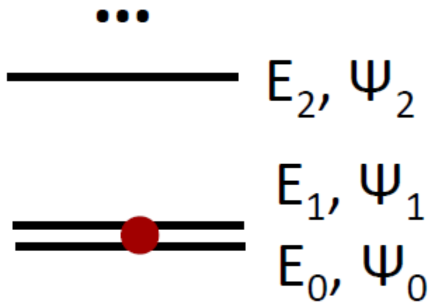


Non-adiabatic situation

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

occupation probabilities

Electronic States



The main questions when approaching large molecular systems:

I) ***What is an optimal model chemistry in terms of numerical cost/accuracy? The answer is system-specific!!!!***

II) ***What are the main 'pitfalls' for accuracy loss while modeling photoexcited dynamics?***

- ***Are we describing excited state properly? Excitons, charge transfer states, spin states, bond-breaking, etc.***
- ***Are we using appropriate non-adiabatic excited state dynamics methodology? Branching into products, coherences, etc.***
- ***What are we missing in our particular implementation? Reaching statistical averages, uncontrolled approximations, numerical issues (e.g. trivial crossings)***

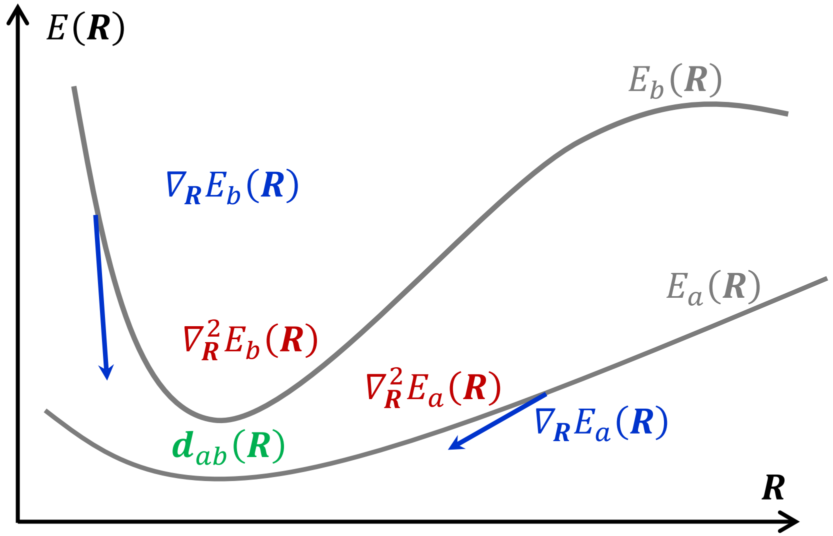
What do we need from the electronic structure calculator for a given geometry $\boldsymbol{R}$?

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

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

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.

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❑ ***KEYWORDS:***

qm_theory
scfconv
exst_method
dav_guess

Feel free to ask question on the fly…

The Electronic Structure Problem

- **A molecule composed from nuclei and electrons bound by Coulomb interactions**
- **Separate electronic (fast) from nuclei (slow) motion (adiabatic or Born-Oppenheimer approximation)**
- **Assign finite basis size (lattice) – Gaussian (Gaussian, Turbomole, Q-Chem, etc.) or plain waves (VASP, etc.) or Slater (ADF, etc.)**
- **Solve the Schrodinger equation for molecular electronic Hamiltonian:**

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{iA}\frac{Z_A}{r_{iA}} + \sum_{i>j}\frac{1}{r_{ij}}\right]\psi_e(\mathbf{r};\mathbf{R}) = E_e\psi_e(\mathbf{r};\mathbf{R})$$

Exponentially hard with respect to N-electrons

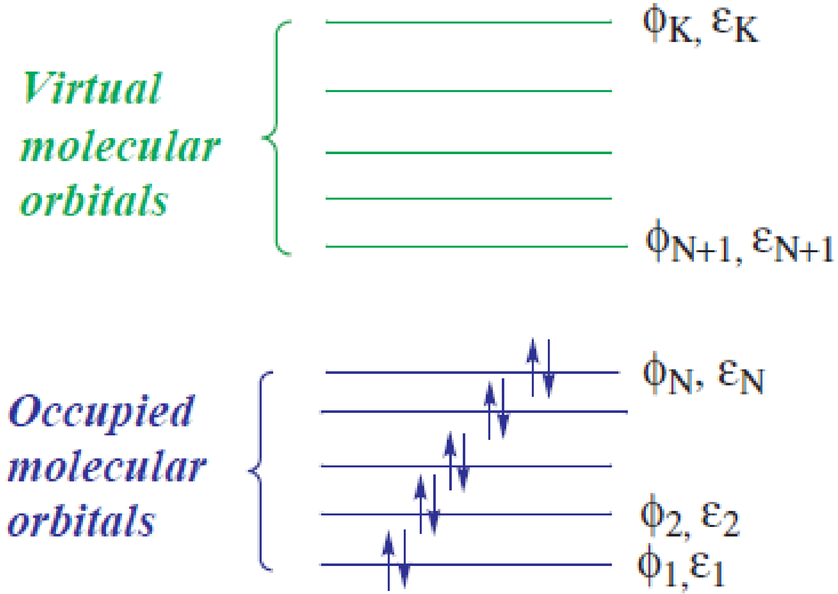
Method	***Hamiltonian***	***Wavefunction***	***Cost***
Ab initio *(e.g. HF, CAS-CI, CC-EOM)*	***Exact***	***Approximate*** *(All electronic correlations)*	***Large*** *(~10 atoms)*
Density Functional *(e.g. DFT, TDDFT)*	***Approximate, F(ρ),*** *(All electronic correlations)*	***Fixed*** *(Kohn-Sham system, mean field)*	***Significant*** *(~100 atoms)*
Semiempirical *(e.g. AM1, MNDO, INDO/S)*	***Approximate,*** *(Some electronic correlations)*	***Approximate*** *(Some electronic correlations)*	***Low*** *(~1000 atoms)*
Tight-binding *(e.g. Huckel, Frenkel, SSH)*	***Approximate,*** *(Min electronic correlations)*	***Approximate*** *(Usually uncorrelated)*	***Low*** *(~10,000 atoms)*

Hartree-Fock procedure

For simplicity, assume an even number of electrons (closed shell) and an orthogonal basis set

Looking for a solution of electronic problem, $H_e\Psi = E\Psi$ where the wavefunction is a single Slater determinant $\Psi = |\phi_1 \ldots \phi_N\rangle$ built on the (unknown) molecular orbitals

$$\phi_i(\mathbf{r}) = \sum_j^K C_{ij}\psi_j(\mathbf{r})$$



Ground state one-electron density matrix

$$\bar{\rho}_{nm} = 2\sum_a^{occ} C_{na}C^{\star}_{ma}$$

The Fock operator

$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

The Coulomb operator (V or G ~2J-K)

$$V(\bar{\rho})_{mn} = \sum_{k,l}^K \bar{\rho}_{kl}[\langle mk|nl\rangle - \frac{1}{2}\langle mn|kl\rangle]$$

The eigenvalue problem (secular equation)

$$\boxed{FC = SC\varepsilon}$$

Ground state energy $E = Tr(\bar{\rho}(F+t))$

The total energy $E + \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$

Nonlinear integro-differential equations, needs to be solved iteratively to achieve self-consistency!

Time-Dependent Density Functional Theory & Time-Dependent Hartree-Fock formalism

- ***TD equation of motion:***

$$i\frac{\partial \rho_{mn}(t)}{\partial t} = [F(\rho),\rho] - \mathcal{E}(t)[\mu,\rho]$$

$$L\xi_\nu = \Omega_\nu \xi_\nu$$

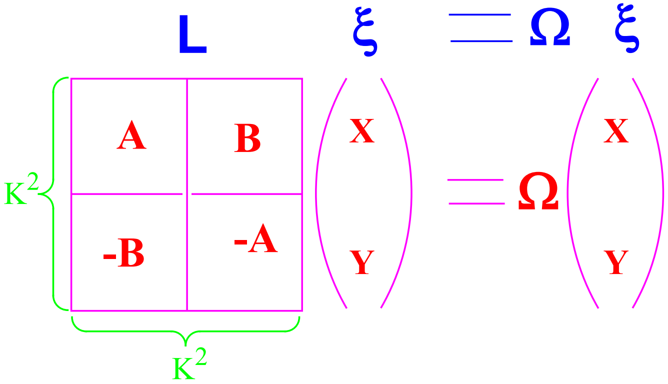
- ***Electronic normal modes or transition densities***

$$(\xi_\nu)_{ij} = \langle \Psi_\nu | c_i^+ c_j | \Psi_g \rangle$$

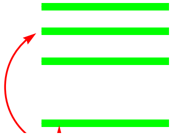
- ***Krylov space algorithms (e.g. Davidson, Lanczos)***

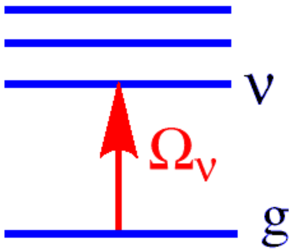
TDHF: Dirac, Pines, Bartlett, Schmitt-Rink, Jorgensen, McKoy, Fukotome ….

TDDFT: Runge, Gross, Casida, Perdew, Becke, Yang, Burke, Furche ….



A, X - CIS (particle-hole) part



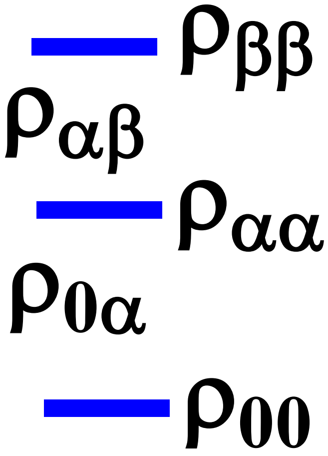


- ***Scaling of computational effort:***
  - *Time* ~N^3
  - *Memory* ~N^2

Cost/per excited state is smaller than SCF ground state effort

Computing analytic gradients and non-adiabatic couplings:

Analytic gradients for excited state potential energy surfaces (Furche/Ahlrichs)



Need excited state density matrices

10-40%

$$\rho_{\alpha\alpha} = \rho_{00} + [[\xi_\alpha^\dagger, \rho_{00}], \xi_\alpha] + Z_{\alpha\alpha}$$

F. Furche, R. Ahlrichs, J. Chem. Phys. 117, 7433 (2002)

$$LZ_{\alpha\alpha} = -[([[\rho_{00}, \xi_\alpha^\dagger], V(\xi_\alpha)] + V(\frac{1}{2}[[\xi_\alpha^\dagger, \rho_{00}], \xi_\alpha])), \rho_{00}]$$

$$Z_{\alpha\alpha} = -\sum_\beta \frac{V_{-\alpha\alpha\beta}}{\Omega_\beta}\xi_\beta$$

'Relaxed' part of excited state density matrices

S. Tretiak, V. Chernyak, J. Chem. Phys., 119, 8809(2003); S. Tretiak, S. Mukamel, Chem. Rev., 102, 3171 (2002)

Analytic calculation of non-adiabatic couplings among excited state (Tommasini/Chernyak/Mukamel/Furche)

Need transition density matrices between excited states

$$\mathbf{d}_{\alpha\beta} = \frac{\mathrm{Tr}(F^{(R)}\rho_{\alpha\beta})}{\Omega_\alpha - \Omega_\beta};$$

M. Tommasini, V. Chernyak, S. Mukamel, Int. J. Quant.Chem., 85, 225 (2001); V. Chernyak, S. Mukamel, J. Chem. Phys., 112, 3572 (2000)

$$\rho_{\alpha\beta} = [[\xi_\alpha^\dagger, \rho_{00}], \xi_\beta] + Z_{\alpha\beta}$$

5-15%

$$Z_{\alpha\beta} = \sum_\gamma \frac{V_{-\alpha\beta\gamma}}{-\Omega_\alpha + \Omega_\beta - \Omega_\gamma}\xi_\gamma$$

S. Tretiak, V. Chernyak, S. Mukamel, Int. J. Quant. Chem., 70, 711 (1998), S. Tretiak, V. Chernyak, J. Chem. Phys., 119, 8809(2003).

What RPA/CIS framework can do…

I) Pros:

- ***Numerically efficient (states, gradients, couplings)***
- ***Can describe excitons***
- ***Can describe crossings of excited states***
- ***Transparent physics of semiempirics***

II) Cons:

- ***Beware of semiempirics, semi-quantitative accuracy***
- ***Cannot describe excited/ground state crossings***
- ***Cannot describe double excitations and generally highly correlated states***
- ***Problems with energetics of spin states***
- ***Problems with open shell and bond braking***

Our plan for the lecture

PART I: Methodology and Applications

- ***Introduction: what are we taking about?***
- ***Born-Oppenheimer Approximation***
- ***Need for atomistic methods, mixed quantum-classical approach***
- ***Electronic structure theory in NEXMD***
- ***Ehrenfest dynamics***
- ***Surface Hopping methodology***
- ***Trivial crossings and decoherence effects***

PART II: Some advanced NEXMD capabilities

- ***Multi-configurational Ehrenfest with Ab Initio Multiple Cloning (MCE-AIMC)***
- ***Environmental effects***
- ***Extended Largangian excited state MD***
- ***Open shell, bond breaking***
- ***Polaritonics, molecules in the cavity***
- ***Practical aspects: spectra, rates, wavefunction analysis***

❑ ***KEYWORDS:***

natoms
bo_dynamics
exc_state_init
n_exc_states_propagate
moldyn_deriv
therm_type
therm_temperature

Feel free to ask question on the fly…

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 becomes Ehrenfest equation to propagate in the adiabatic basis

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

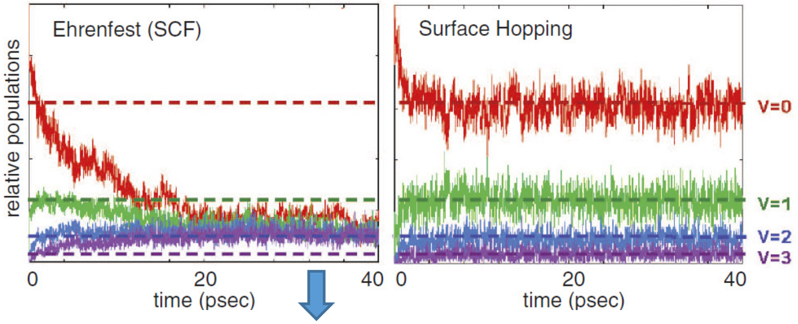
Ehrenfest Force

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)

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):

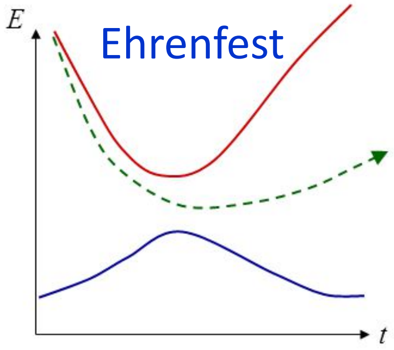
$$\hat{\boldsymbol{m}}_{\boldsymbol{R}}\ddot{\boldsymbol{R}}_t = \boldsymbol{F}_t = -\nabla_{\boldsymbol{R}} E_a(\boldsymbol{R}_t)$$

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

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

- Evaluate the probability for a “hop”:

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

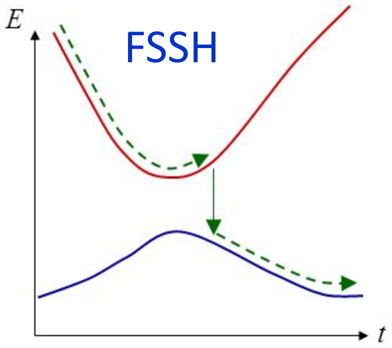


The “hop” is evaluated at every numerical step (δt):

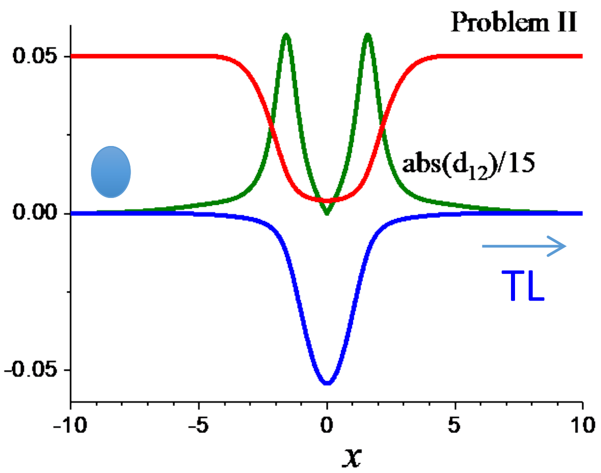
1) The probability to hop to all included states is determined. If the probability to hop to a state is negative, it is set to zero.

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

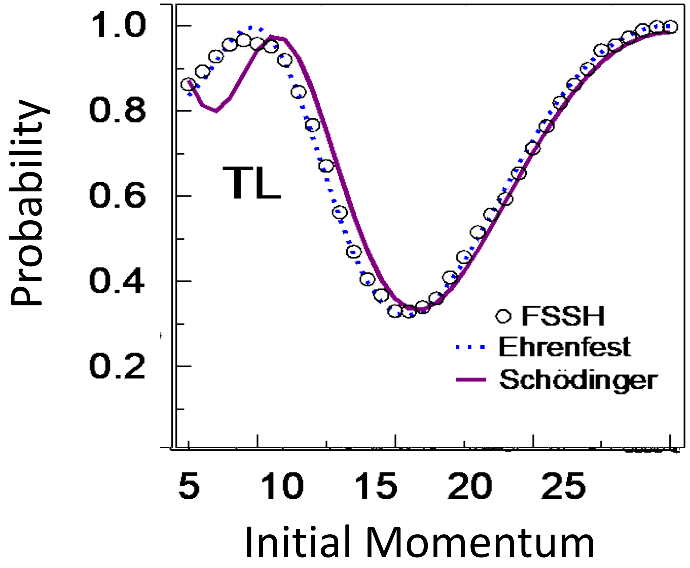
3) If a hop occurs the nuclear velocity $\dot{\boldsymbol{R}}_t$ is adjusted along the direction of the NACR $\boldsymbol{d}_{ab}(\boldsymbol{R}_t)$ such that the total energy is conserved. For hops which increase the potential energy, if there is not enough kinetic energy in this direction then the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

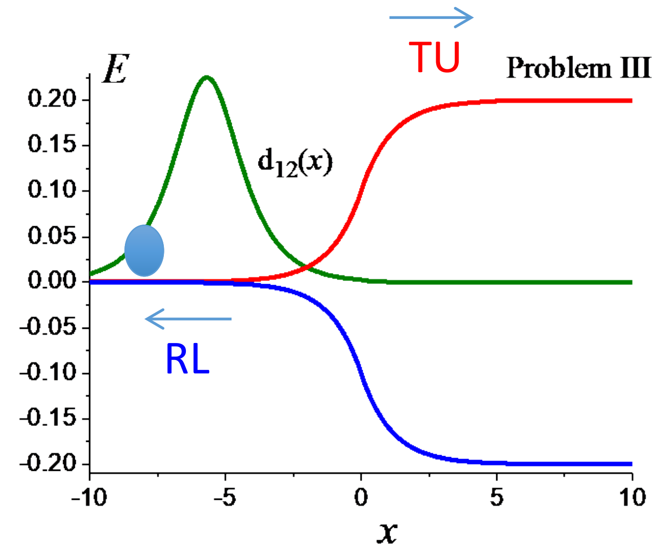


How does all this work? 3 Tully's problems

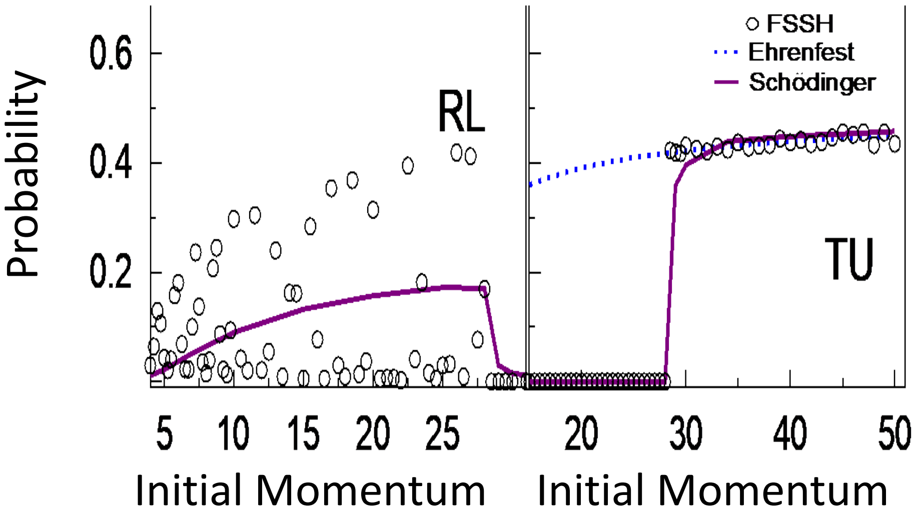


Tully's model II: Dual avoided crossing: Stueckelberg oscillations





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

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- ***Surface Hopping methodology***
- ***Trivial crossings and decoherence effects***

☐ ***KEYWORDS:***
decoher_type
dotrivial
quant_step_reduction_factor

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- ***Environmental effects***
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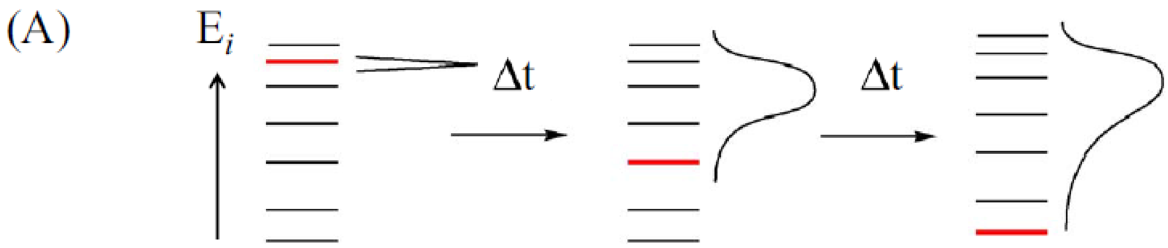
- ***Practical aspects: spectra, rates, wavefunction analysis***

Feel free to ask question on the fly…

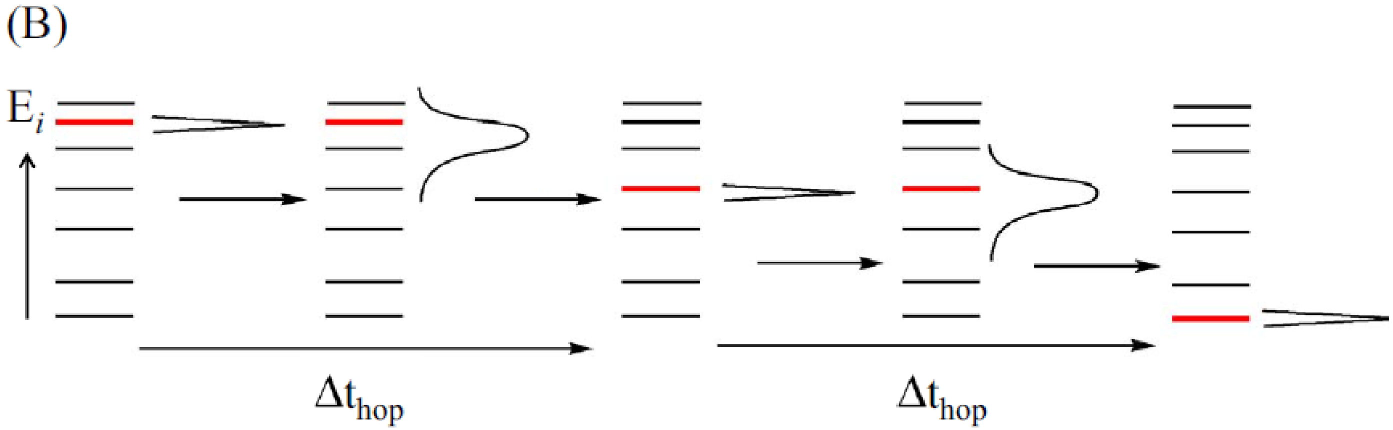
The main TSH problem: decoherence corrections

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)!

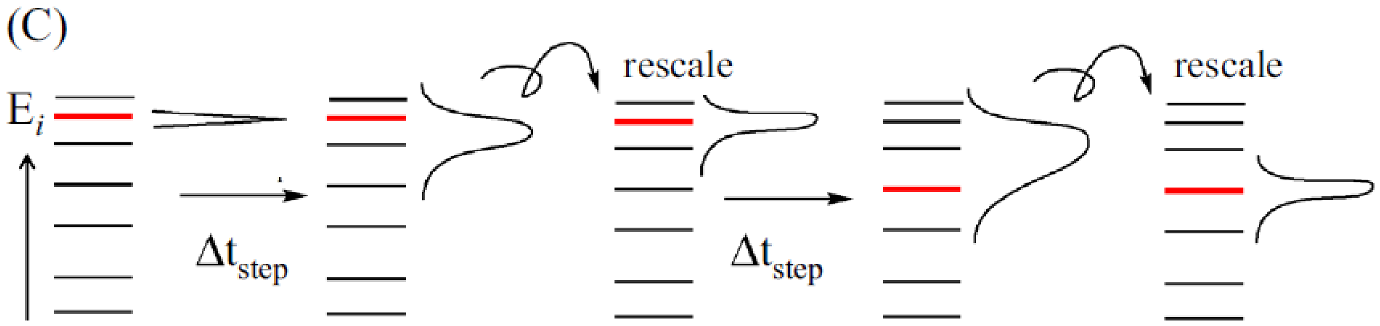
Pristine FSSH
(quantum wavepacket is left 'behind')



Empirical fix:
Instantaneous decoherence schemes



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

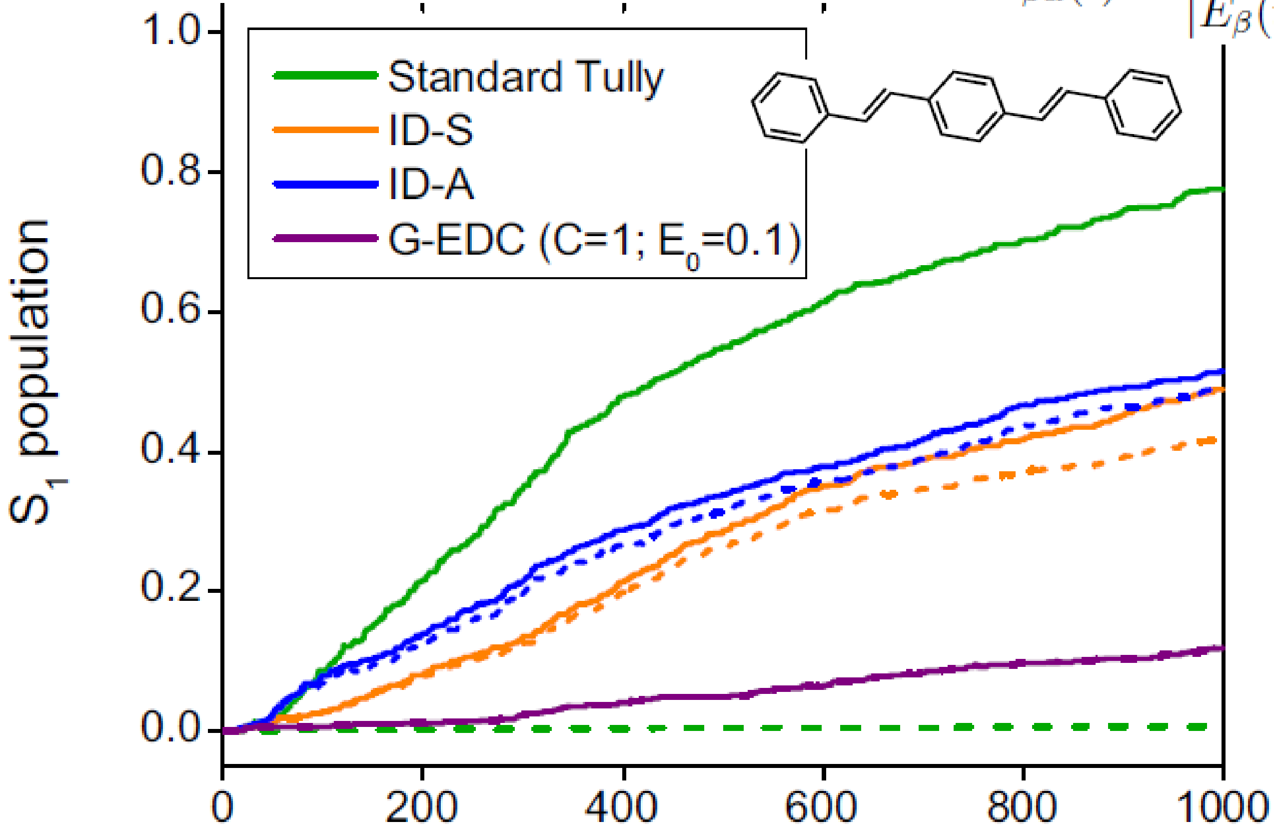


IDC-A (instantaneous decoherence at each attempted hop) is a practical fix

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)

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

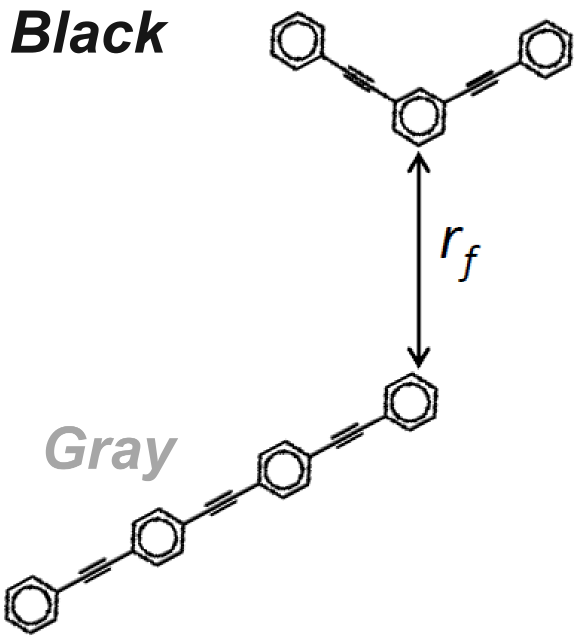
$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_\beta(t) - E_\alpha(t)|}\left(C + \frac{E_0}{E_{kin}(t)}\right)$$

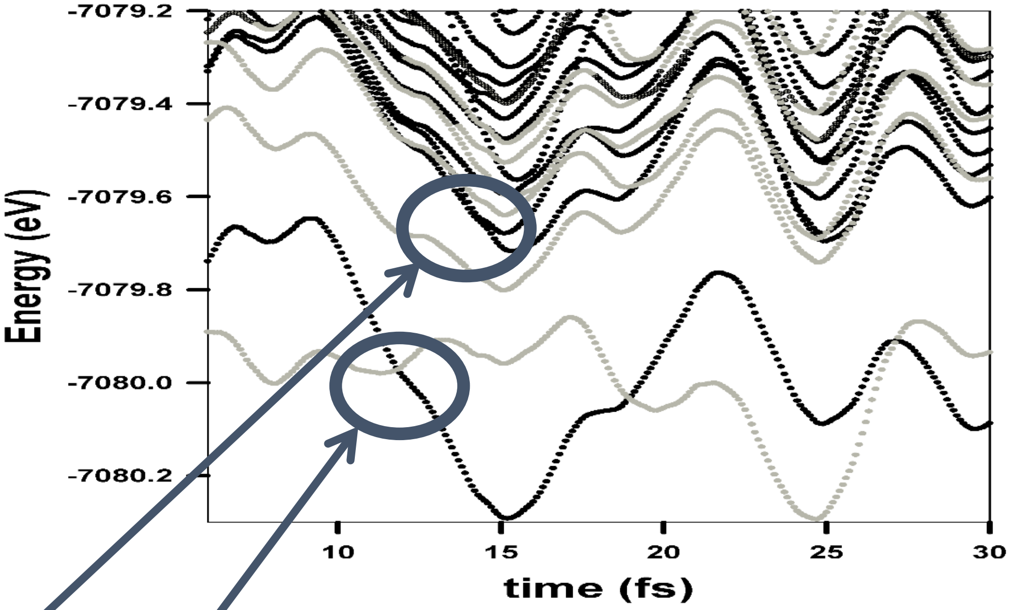


T. Nelson, S. Fernandez-Alberti, A. E. Roitberg, S. Tretiak, J. Chem. Phys., 138 224111 (2013)

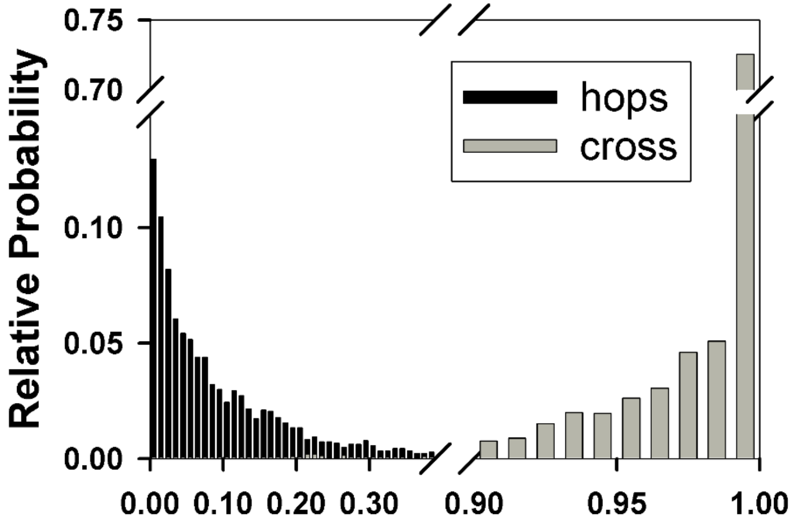
Non-obvious problem: trivial crossings

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

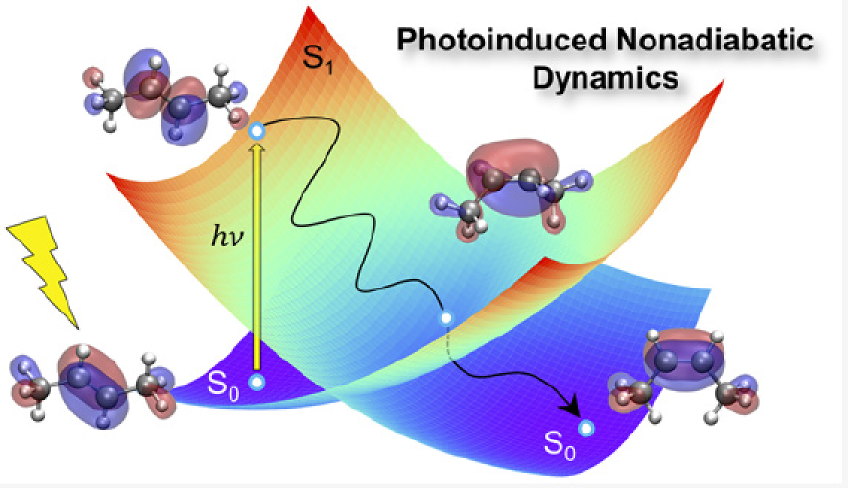


S. Fernandez-Alberti, A.E. Roitberg, T. Nelson, S. Tretiak, J. Chem. Phys. 137, 014512 (2012)

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

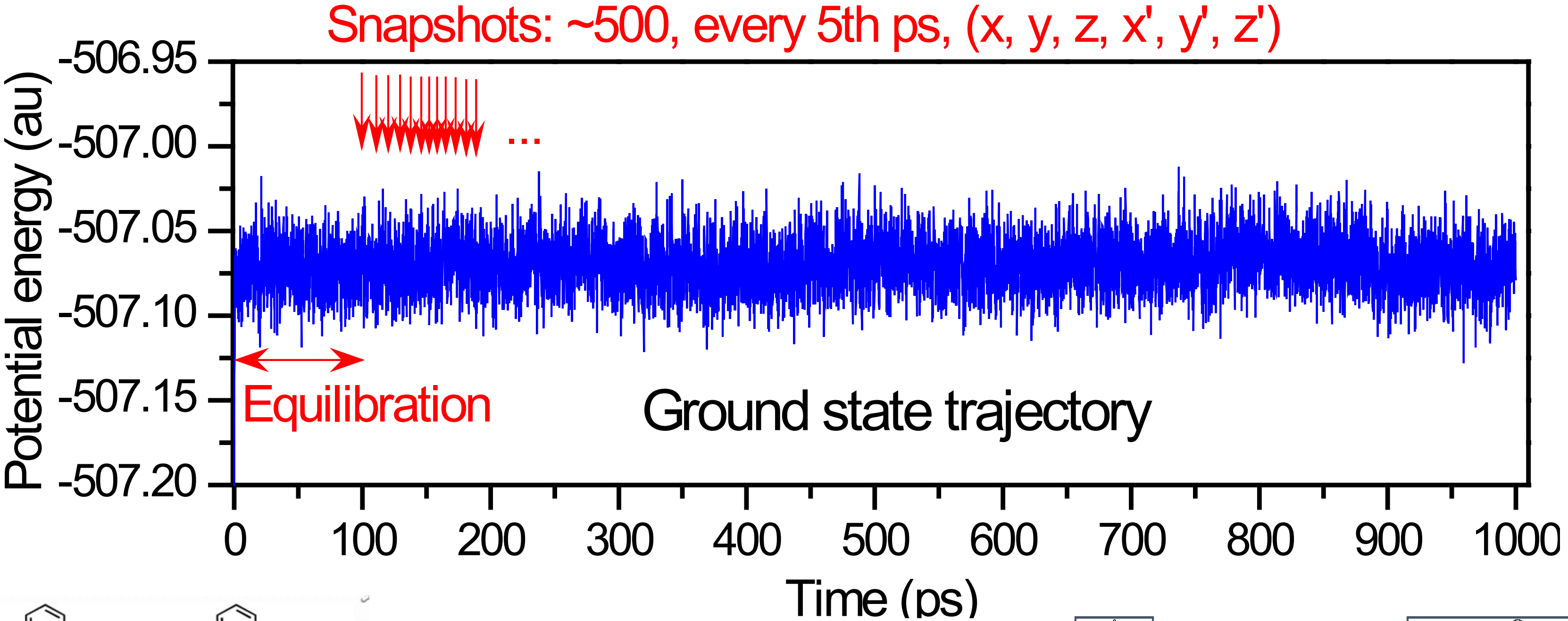
- Lack of decoherence and interferences (independent trajectory, no phase information)
- Simulations must include empirical corrections such as decoherence or trivials
- Works only in adiabatic representation (fails in diabatic basis)
- Neglects both differences in zero-point energy (ZPE) for different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

The Ugly

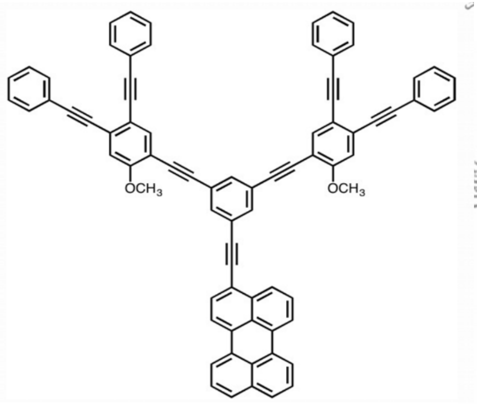
- Completely ad hoc. Impossible to derive.
- The number of variations competes with DFT

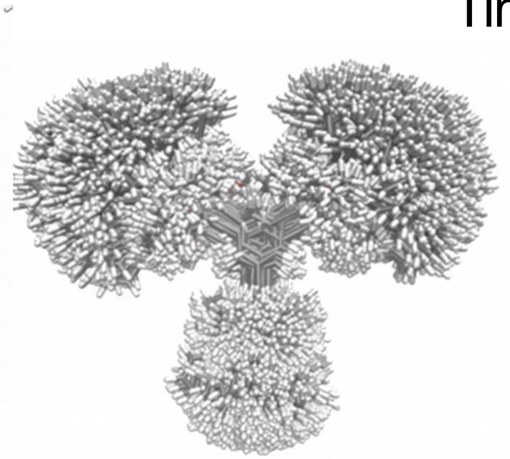
Practical implementations of surface hopping dynamics are typically done across MANY approaches ranging from tabulated PESs to semiempirical Hamiltonians to DFT and TDDFT, to MR-CI to EOM-CC to CASSCF. Codes: ANT, COBRAMM, JADE, NEWTON-X, SHARC, Turbomole, NWChem, Q-Chem, PIXAID, Libra, NEXMD, CPMD,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

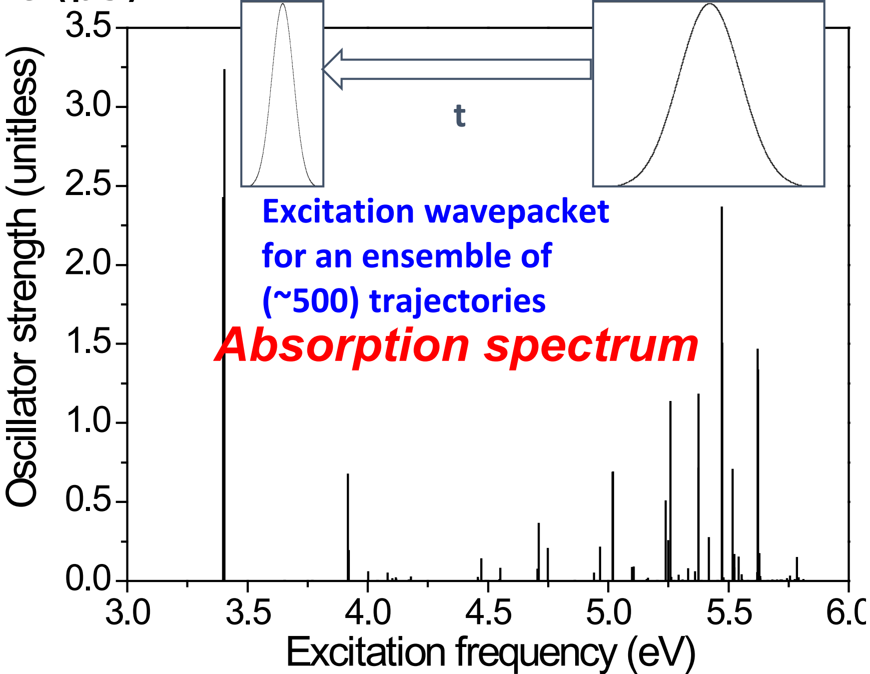
Conformational sampling for dynamics



Snapshots: ~500, every 5th ps, (x, y, z, x', y', z')





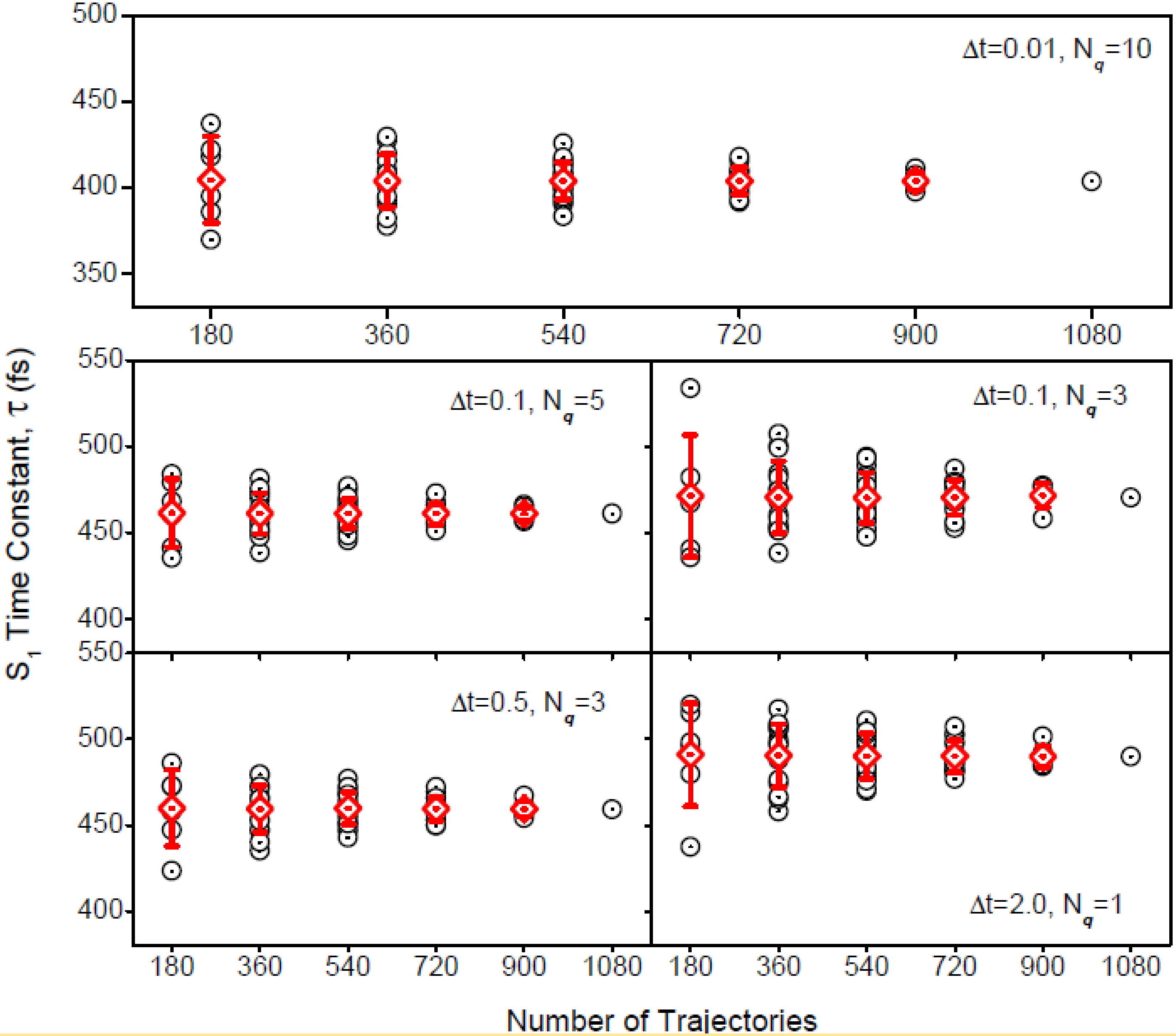


Excitation wavepacket for an ensemble of (~500) trajectories

Absorption spectrum

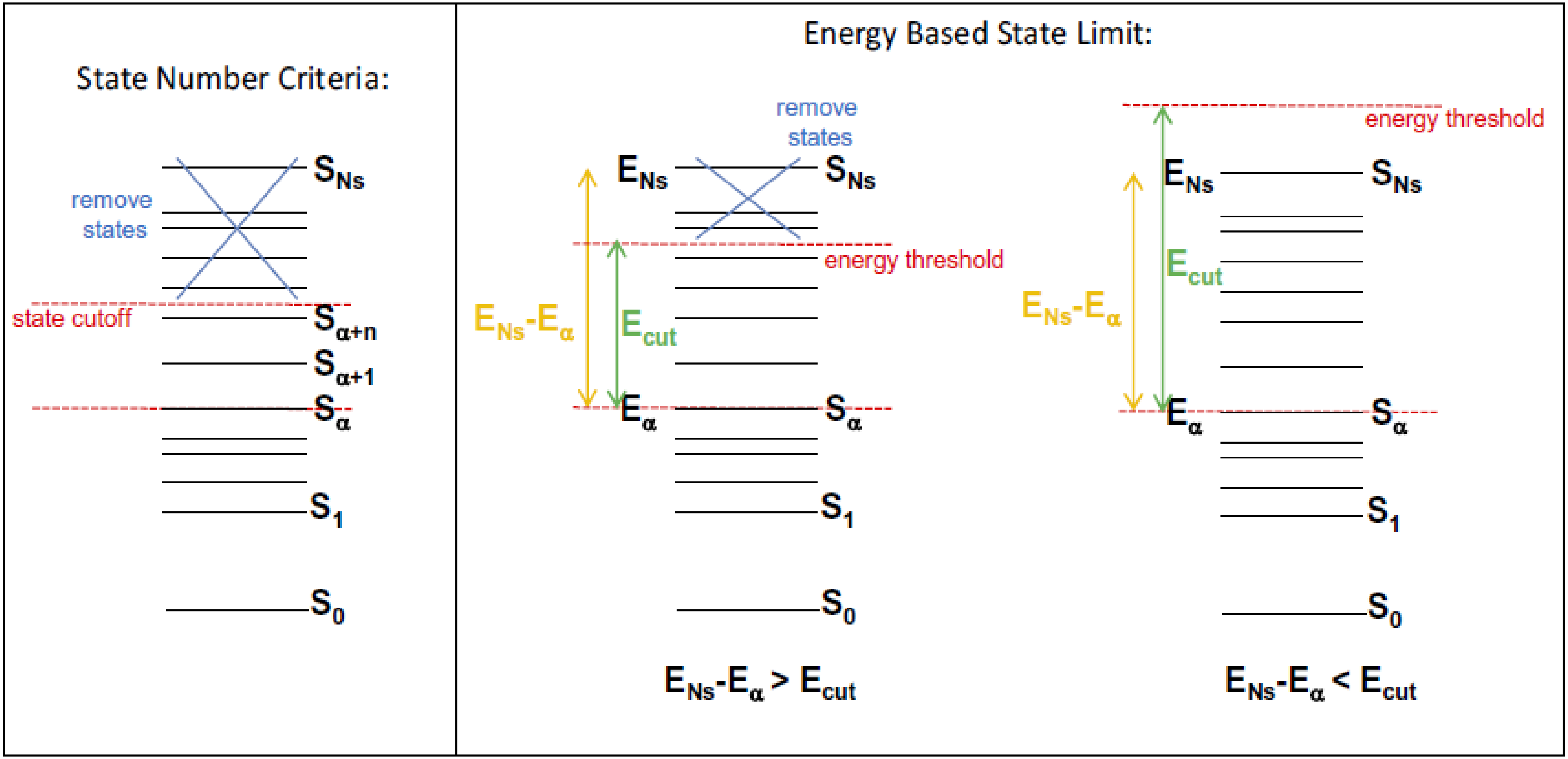
T. Nelson, S. Fernandez-Alberti, V. Chernyak, A.E. Roitberg, S. Tretiak, J. Phys. Chem. B 115, 5402 (2011); Nelson, S.F. Alberti, A. E. Roitberg, S. Tretiak, Acc. Chem. Res., 47, 1155 (2014)

How many trajectories are enough?



T. Nelson, S. Fernandez-Alberti, V. Chernyak, A.E. Roitberg, S. Tretiak, J. Chem. Phys., 136 054108 (2012)

On-the-fly limiting of essential excited states

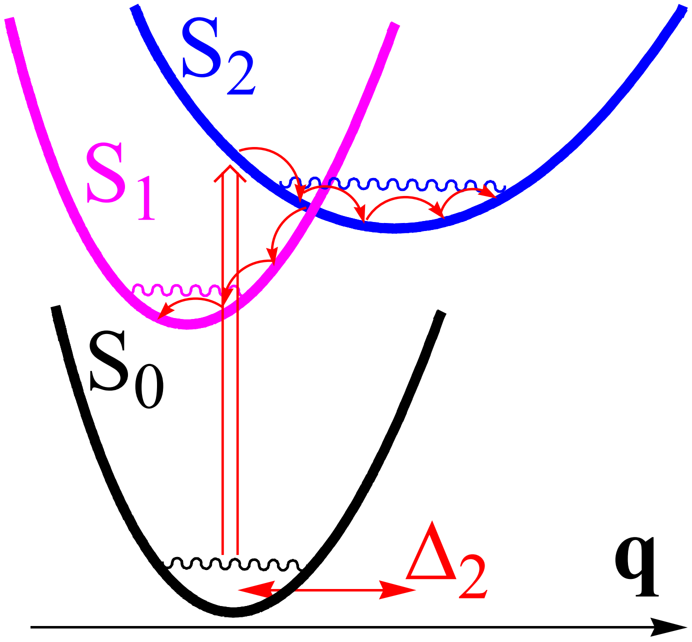


Potential computational saving factor x2-100, depending on the excited state density

T. Nelson, A. Naumov, S. Fernandez-Alberti, S. Tretiak, Chem. Phys., 84-90 (2016)

For molecular systems one needs to go beyond Classical Path Approximation

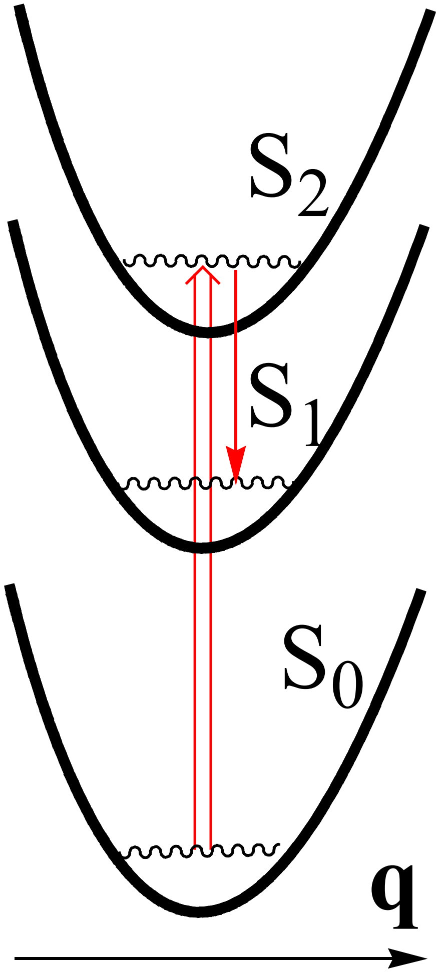
Use true excited state PES



4 fs and 63 fs
bi-exponential fit

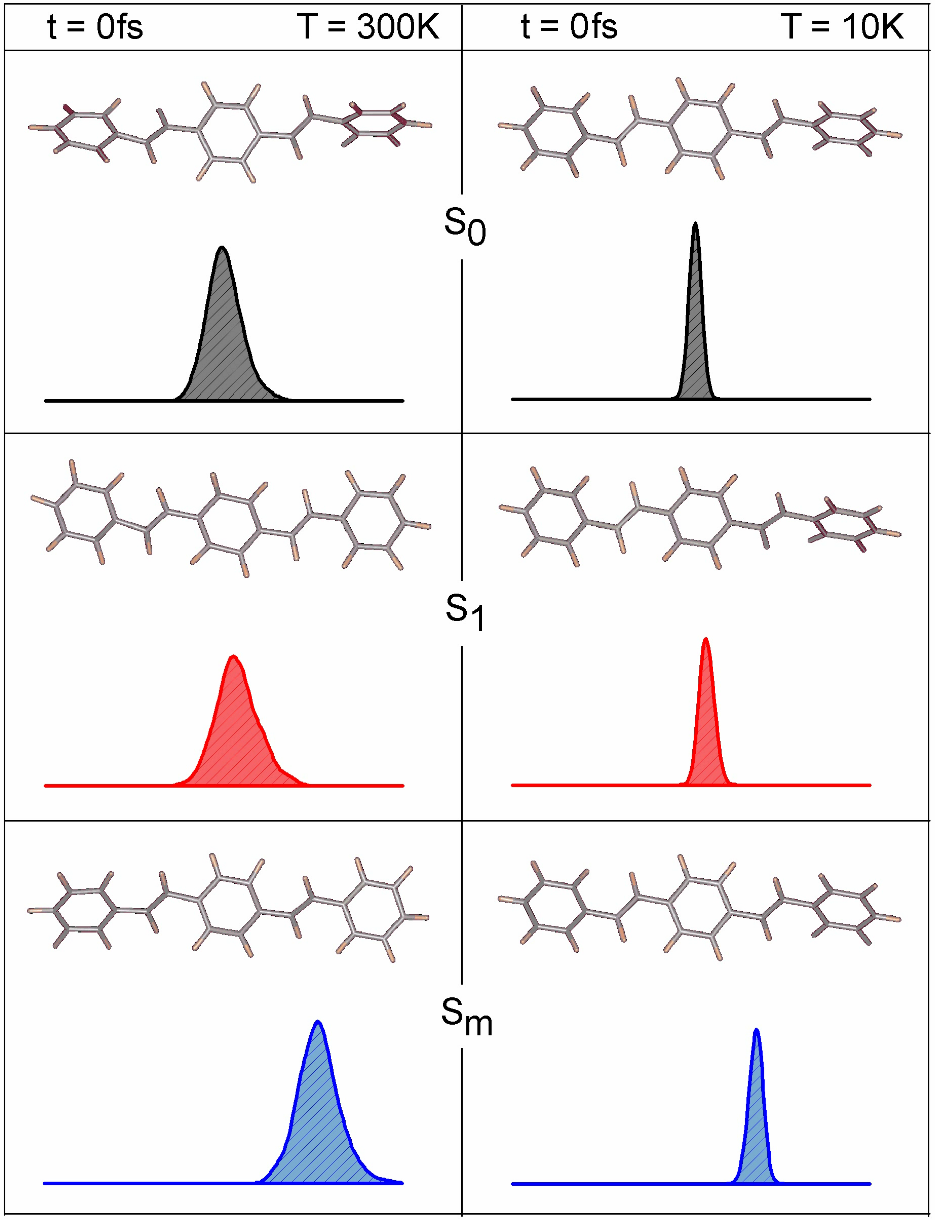
- ***Excited state vibrational relaxation brings states closer facilitating hops***;
- **Excited state trajectories lead to/away from the level crossing regions**

Use ground state PES



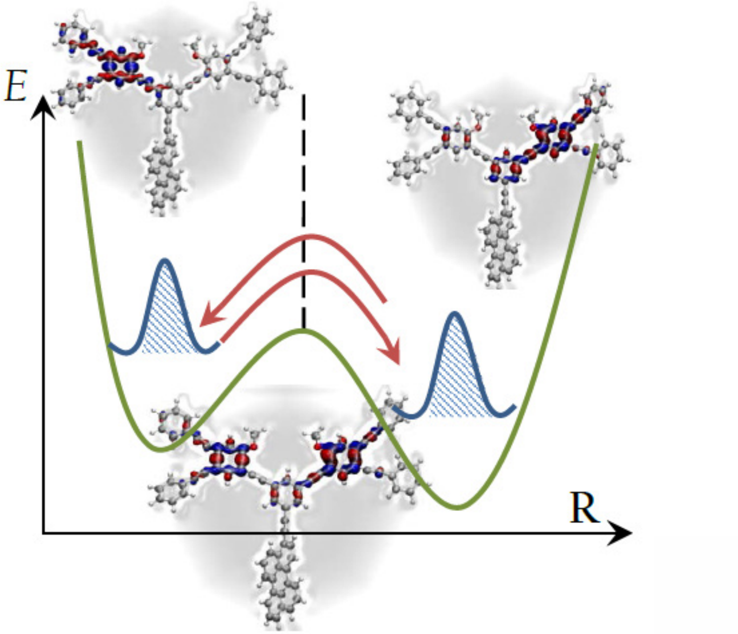
380 fs exponential fit

Wavepacket Evolution

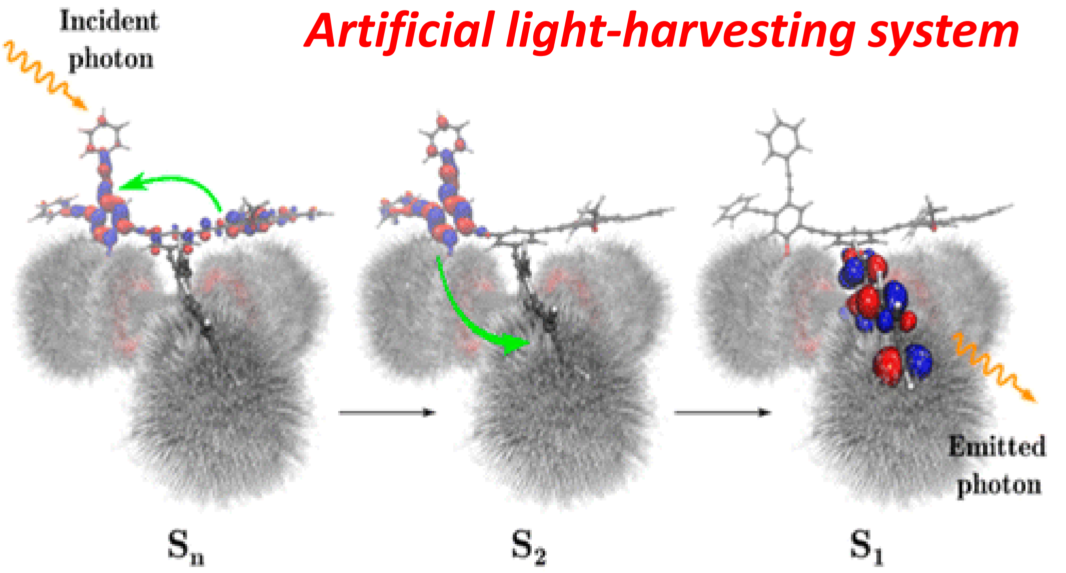


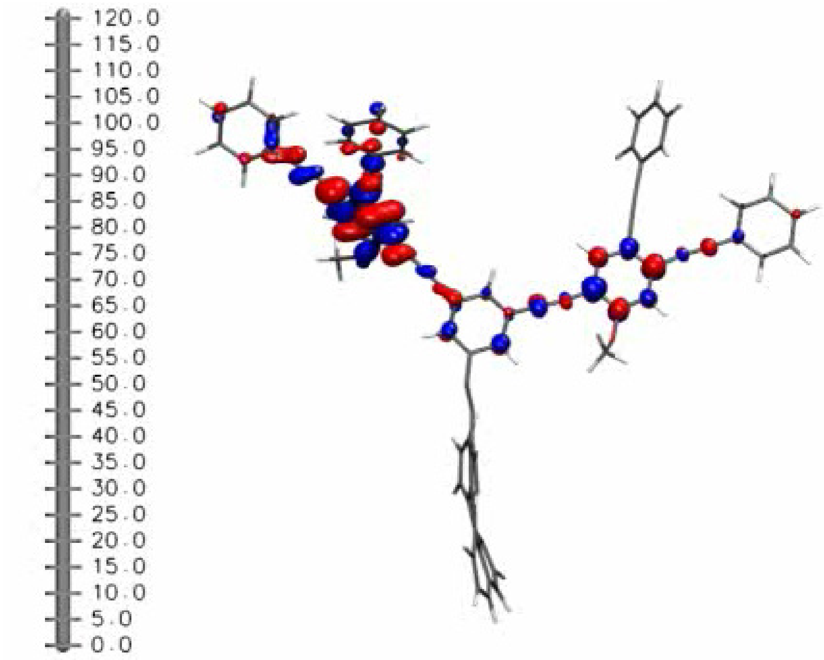
energy

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)

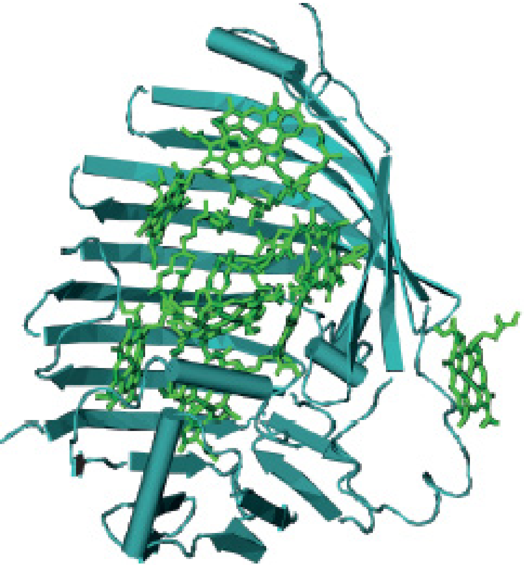
The notion of electron-vibrational coherence

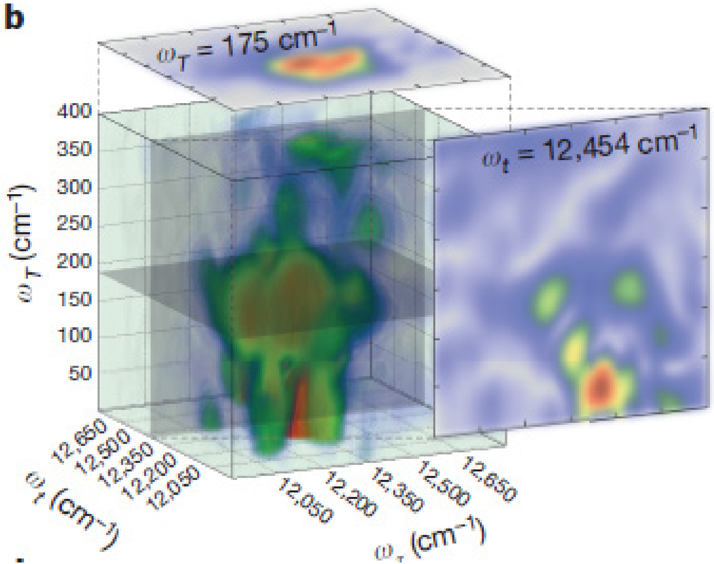
REVIEW

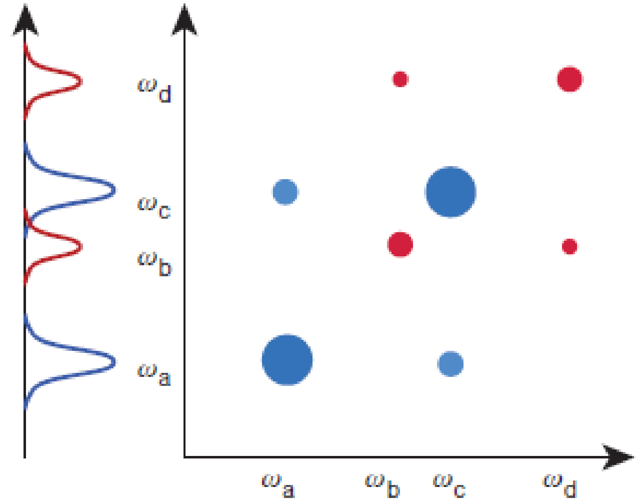
doi:10.1038/nature21425

Using coherence to enhance function in chemical and biophysical systems

Gregory D. Scholes[1], Graham R. Fleming[2], Lin X. Chen[3,4], Alán Aspuru-Guzik[5], Andreas Buchleitner[6], David F. Coker[7], Gregory S. Engel[8], Rienk van Grondelle[9], Akihito Ishizaki[10], David M. Jonas[11], Jeff S. Lundeen[12], James K. McCusker[13], Shaul Mukamel[14], Jennifer P. Ogilvie[15], Alexandra Olaya-Castro[16], Mark A. Ratner[17], Frank C. Spano[18], K. Birgitta Whaley[19,20] & Xiaoyang Zhu[21]

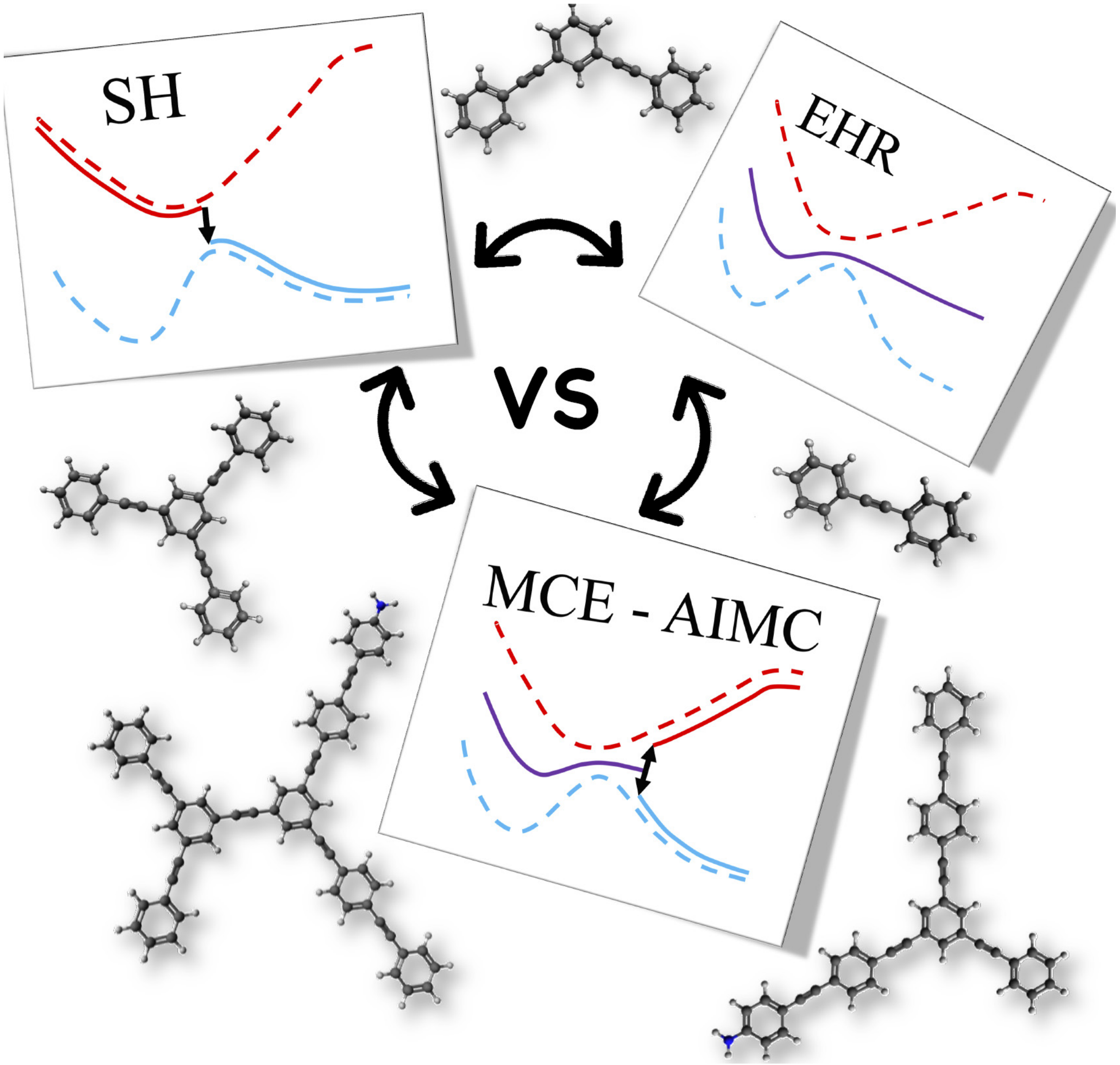




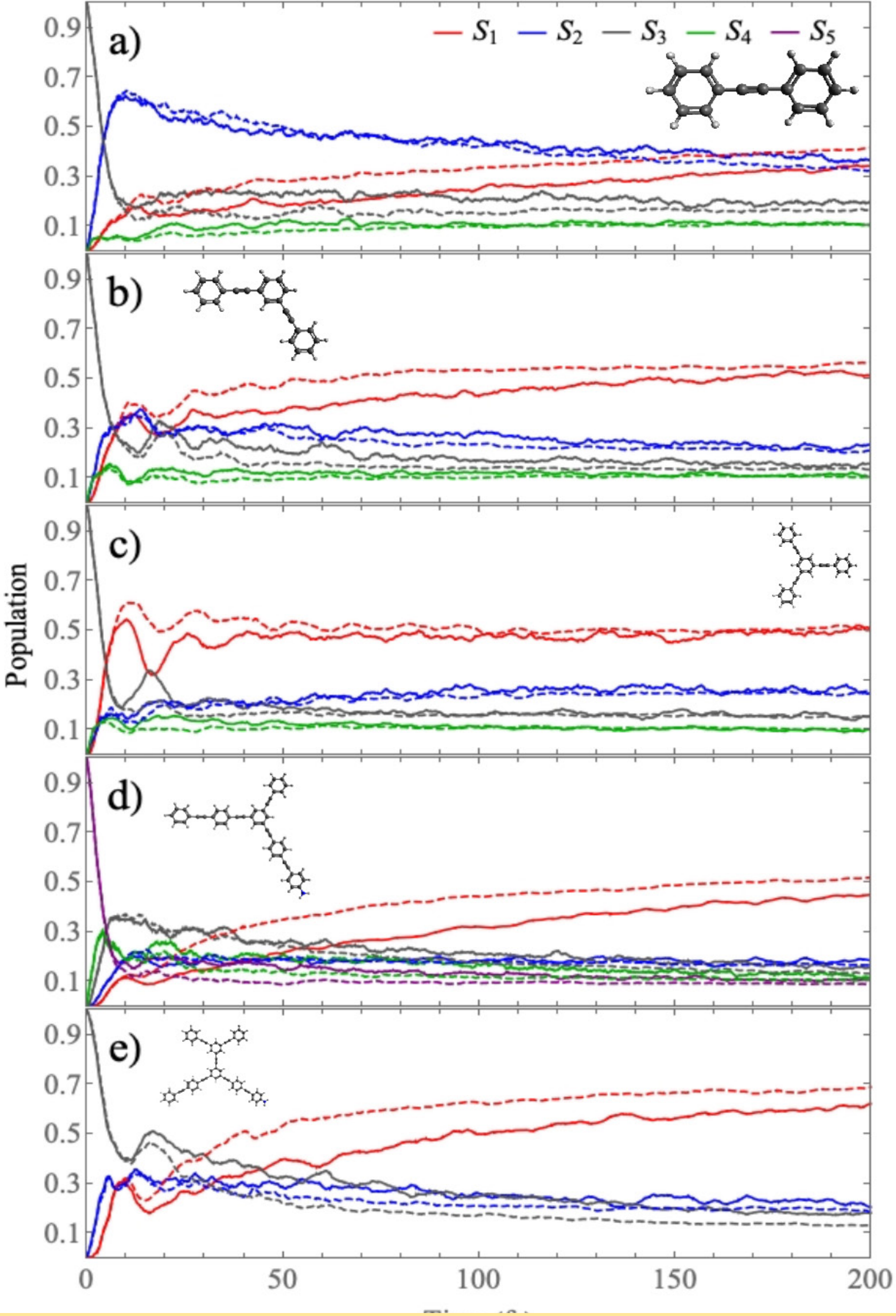


Box 2 Figure | **How to read a 2D spectrum.**

SH vs Ehr vs AIMC-MCE



V.M. Freixas, A.J. White, T. Nelson, D.V. Makhov, D. Shalashilin, S. Fernandez-Alberti, S. Tretiak, J. Phys. Chem. Lett. Perspective, 12, 2970 (2021)



SH vs Ehr vs AIMC-MCE

I. Population evolution

Decay rates generally follow $k_{SH} > k_{MCE\text{-}AIC} > k_{Ehr}$

SH rates strongly depend on the type of decoherence corrections

Decay rates are MUCH MORE sensitive to electronic structure methods used (due to gaps)

II. Coherences

As manifested by 'wiggles' in population or gap or other observables:

Ehr - the strongest coherence (vibronic wavepacket cannot decohere in mean field),

SH – the weakest coherence (independent trajectories, no vibronic wavepacket!)

AIMC – in between SH and Ehr

V.M. Freixas, A.J. White, T. Nelson, D.V. Makhov, D. Shalashilin, S. Fernandez-Alberti, S. Tretiak, J. Phys. Chem. Lett. Perspective, 12, 2970 (2021)

Questions?

Our plan for the lecture

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- ***Polaritonics, molecules in the cavity***
- ***Practical aspects: spectra, rates, wavefunction analysis***

☐ ***KEYWORDS:***

NAMD_type='aimc

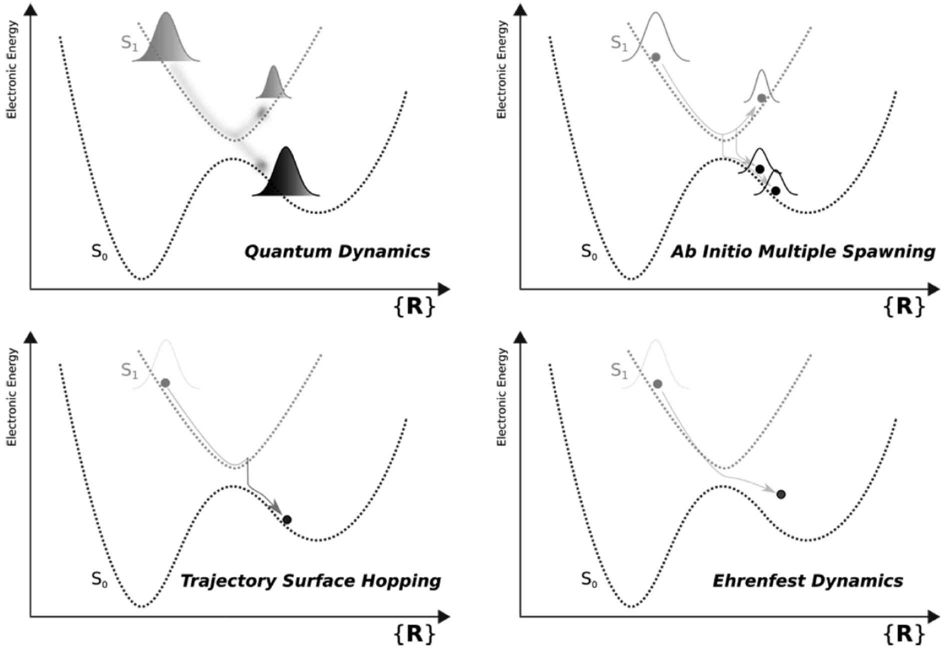
AIMC_max_clone

nclones0

Feel free to ask question on the fly…

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.

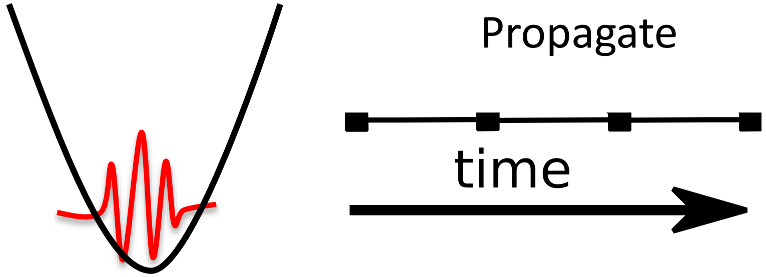
Note: Most of world computer power in materials modeling is spent on MD applications vs. electronic structure simulations.

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.



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

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.*

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

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

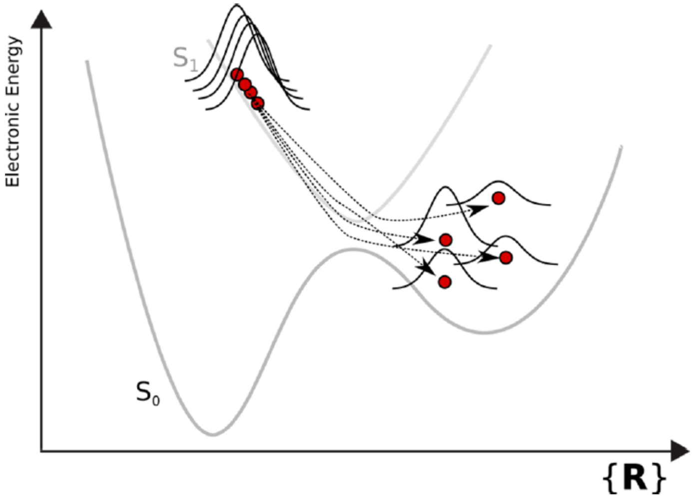
$$\dot{\widehat{\boldsymbol{\alpha}}} = -2\widehat{\boldsymbol{\alpha}} \cdot \widehat{\boldsymbol{m}_{\boldsymbol{R}}}{}^{-1} \cdot \widehat{\boldsymbol{\alpha}} - \frac{1}{2}\nabla_{\boldsymbol{R}}(\nabla_{\boldsymbol{R}} E(\boldsymbol{R}_t))$$

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

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

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 $d^{(n)}(t)$

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

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

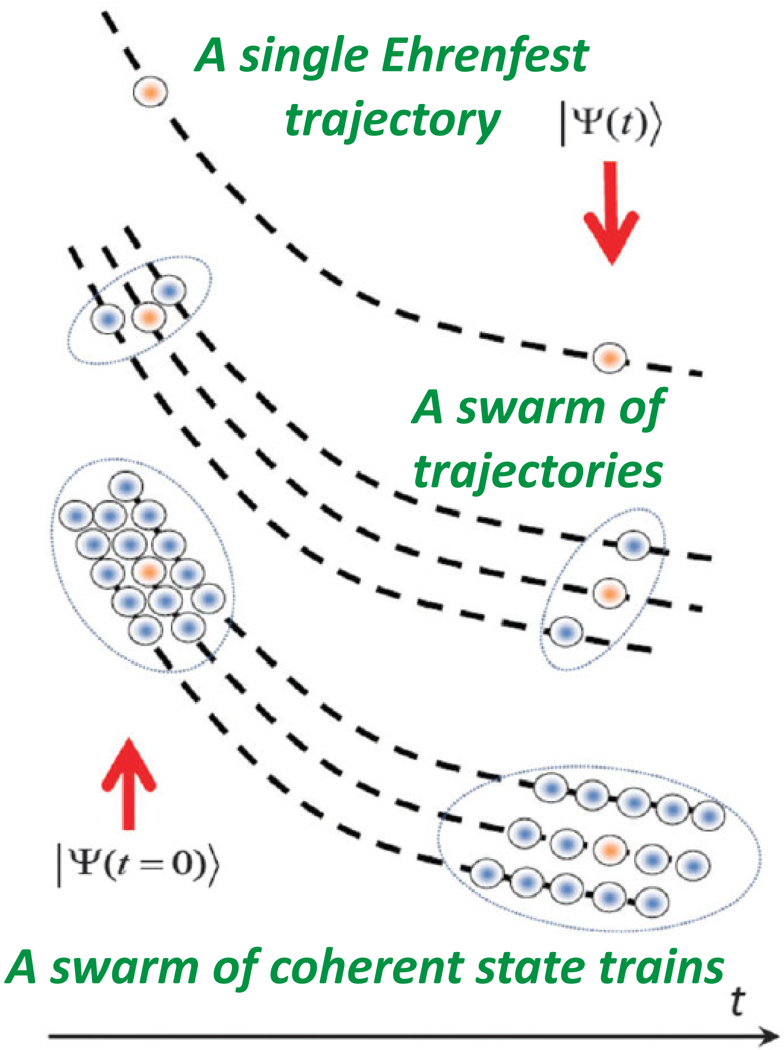
$$\chi^{(n)}(\boldsymbol{R}_t,\boldsymbol{P}_t,\boldsymbol{R},t) = \exp\left[\frac{i}{\hbar}[\gamma_t + \boldsymbol{P}_t\cdot(\boldsymbol{R}-\boldsymbol{R}_t) + \ (\boldsymbol{R}-\boldsymbol{R}_t)\cdot\hat{\boldsymbol{\alpha}}\cdot(\boldsymbol{R}-\boldsymbol{R}_t)]\ \right]$$

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



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 $\phi_a(\boldsymbol{r})$

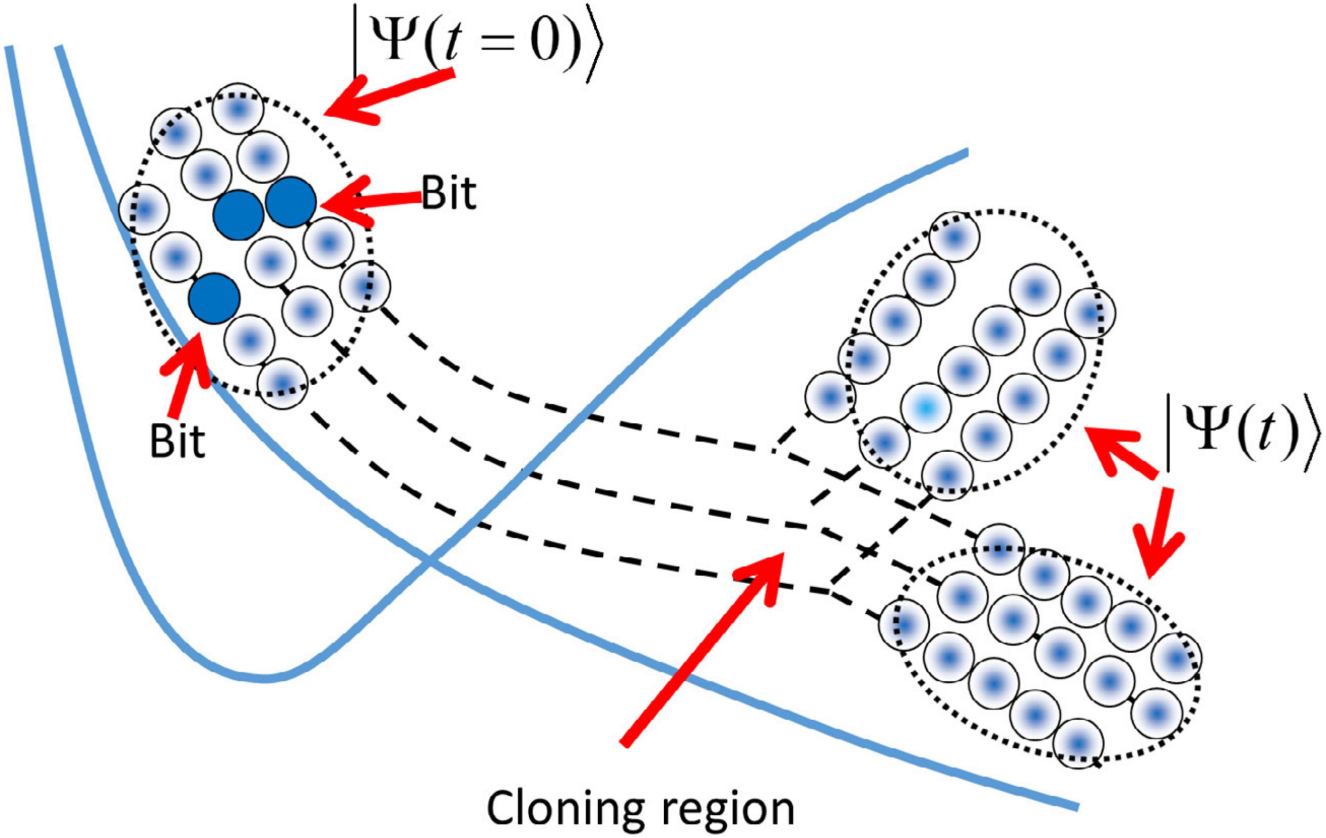
Phys. Chem. Chem. Phys. 18, 10028 (2016)

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)

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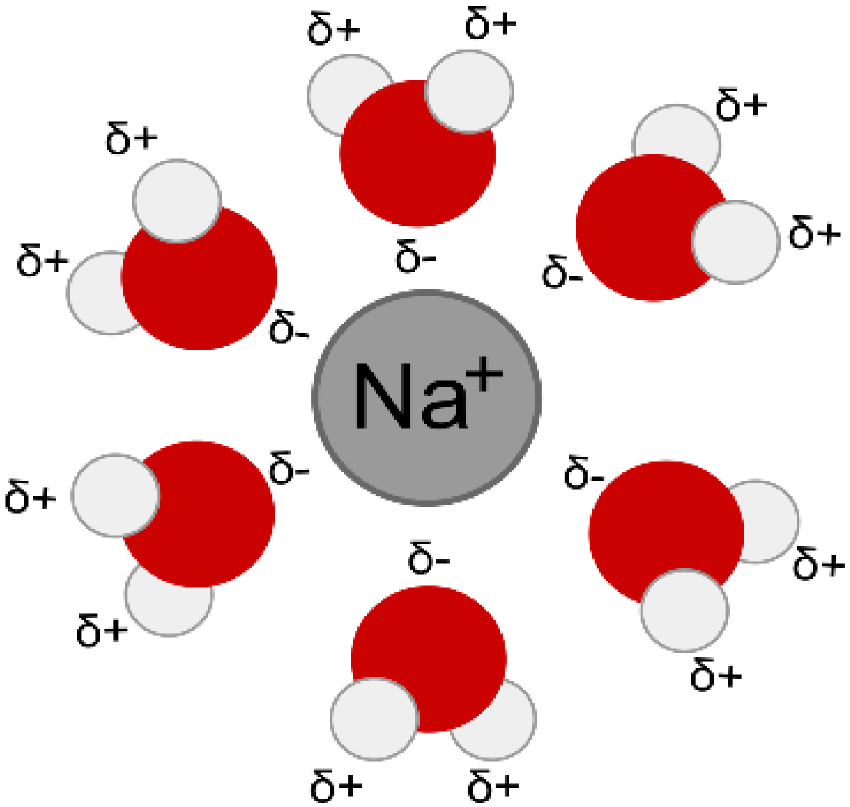
☐ ***KEYWORDS:***

solvent_model
potential_type
ceps
EF

Feel free to ask question on the fly…

Anatomy of solution



- Electronic polarizability
  - Induced dipole
  - Usually a smaller effect
  - Instantaneous

- Dipole orientation
  - Permanent dipole
  - Usually a larger effect
  - Dielectric relaxation

Martin, R. L., Hay, P. J., Pratt, L. R. *J. Phys. Chem. A* **1998** 102, 3565

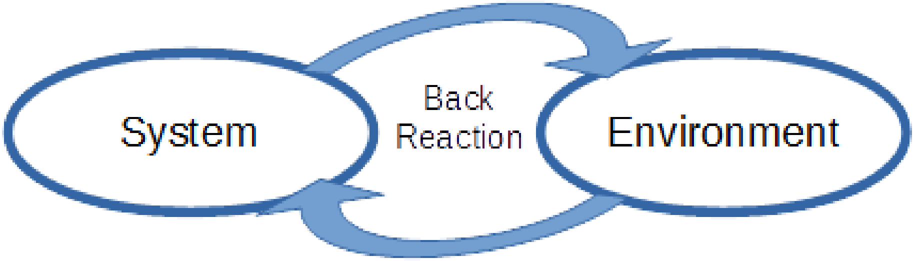
Solvation models for excited state calculations

Single electron density of electronically excited state *n*: $|n\rangle\langle n|$

Single electron density of adiabatic transition from electronic ground state to *n*: $|0\rangle\langle n|$

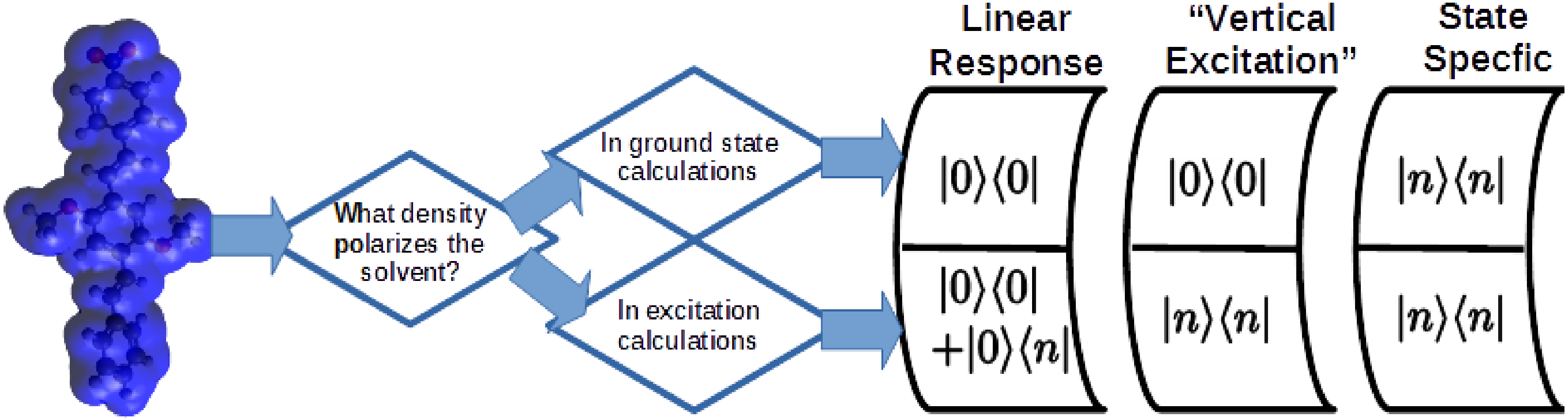
Reaction Field

$$\vec{F} = \frac{\epsilon - 1}{2\epsilon + 1}\frac{\vec{\mu}}{R^3}$$


System

Back Reaction

Environment


What density polarizes the solvent?

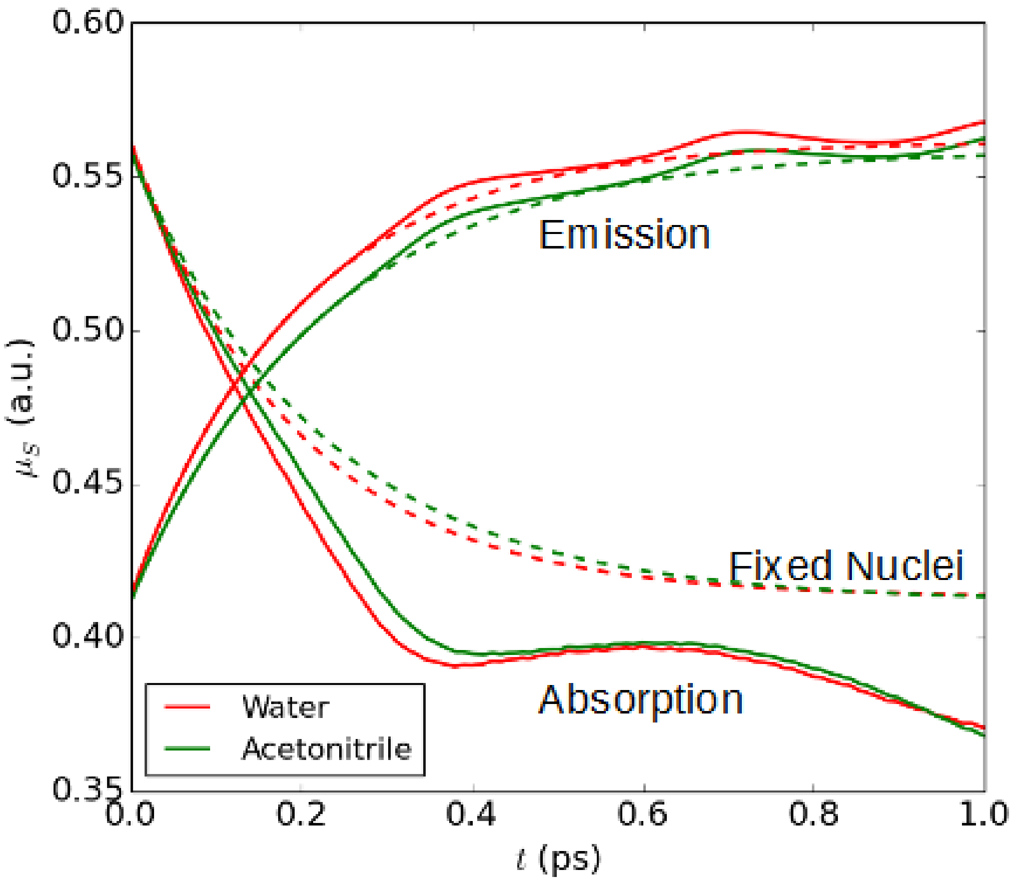
	Linear Response	"Vertical Excitation"	State Specfic
In ground state calculations	$\vert 0\rangle\langle 0\vert$	$\vert 0\rangle\langle 0\vert$	$\vert n\rangle\langle n\vert$
In excitation calculations	$\vert 0\rangle\langle 0\vert + \vert 0\rangle\langle n\vert$	$\vert n\rangle\langle n\vert$	$\vert n\rangle\langle n\vert$

Analytic gradients

J. A. Bjorgaard, V. Kuzmenko, K. Velizhanin, S. Tretiak, J. Chem. Phys. 142, 044103. (2015)
J. A. Bjorgaard, K. Velizhanin, S. Tretiak, J. Chem. Phys. 143, 054305 (2015)

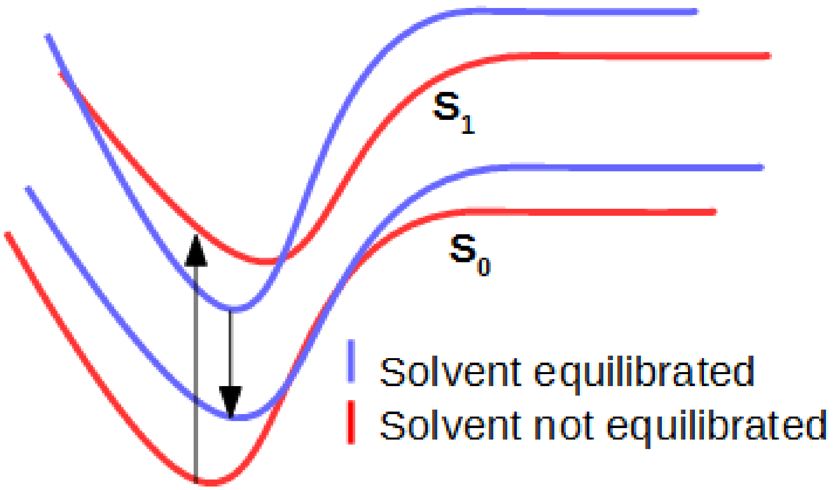
C. A. Guido, G. Scalmani, B. Mennucci, D. Jacquemin, J. Chem. Phys. 146, 204106 (2017)

Non-equilibrium solvation in NEXMD



Evolution of the solvent dipole

Using a fixed cavity here (Onsager model)



At each time step, update from the previous reaction field

$$R_M(t+\Delta t) = e^{-\Delta t/\tau_L} R(t).$$

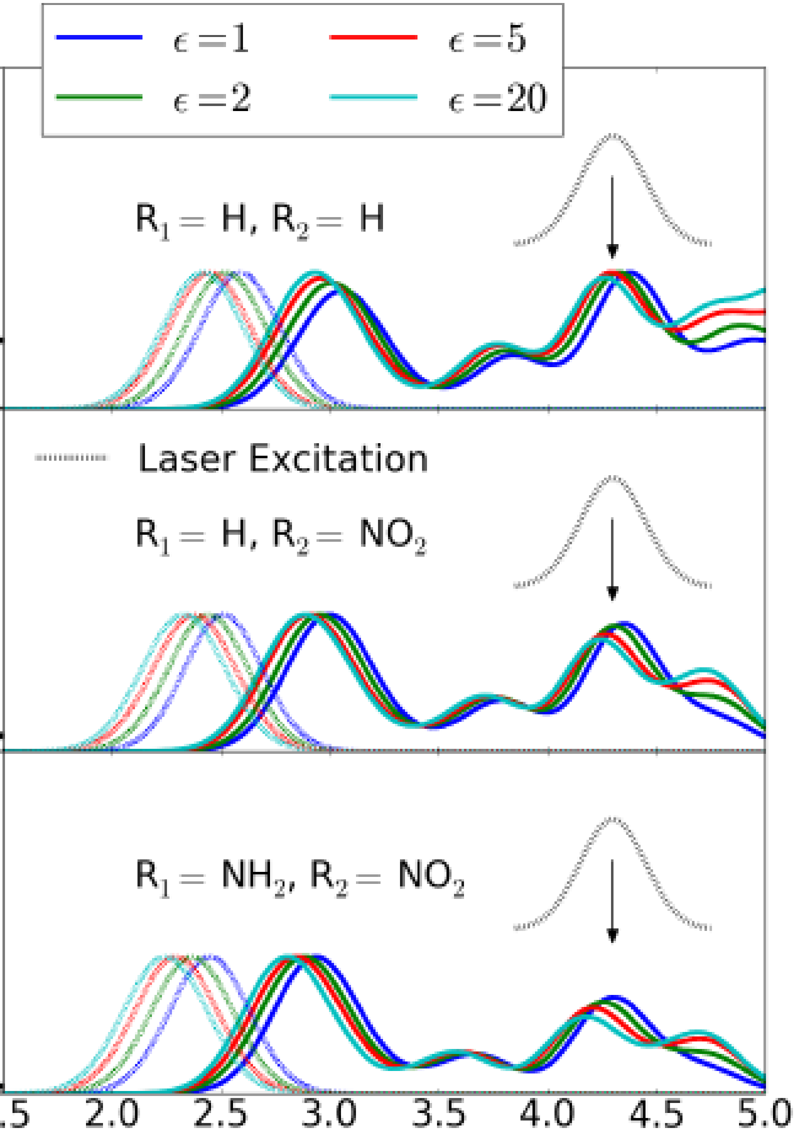
Assume a constant potential across each time step

$$R_I(t+\Delta t) = \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty}(1 - e^{-\frac{\Delta t}{\tau_L}})V(t)$$

J. A. Bjorgaard, K. Velizhanin, S. Tretiak,
J. Chem. Phys. 144, 154104 (2016)

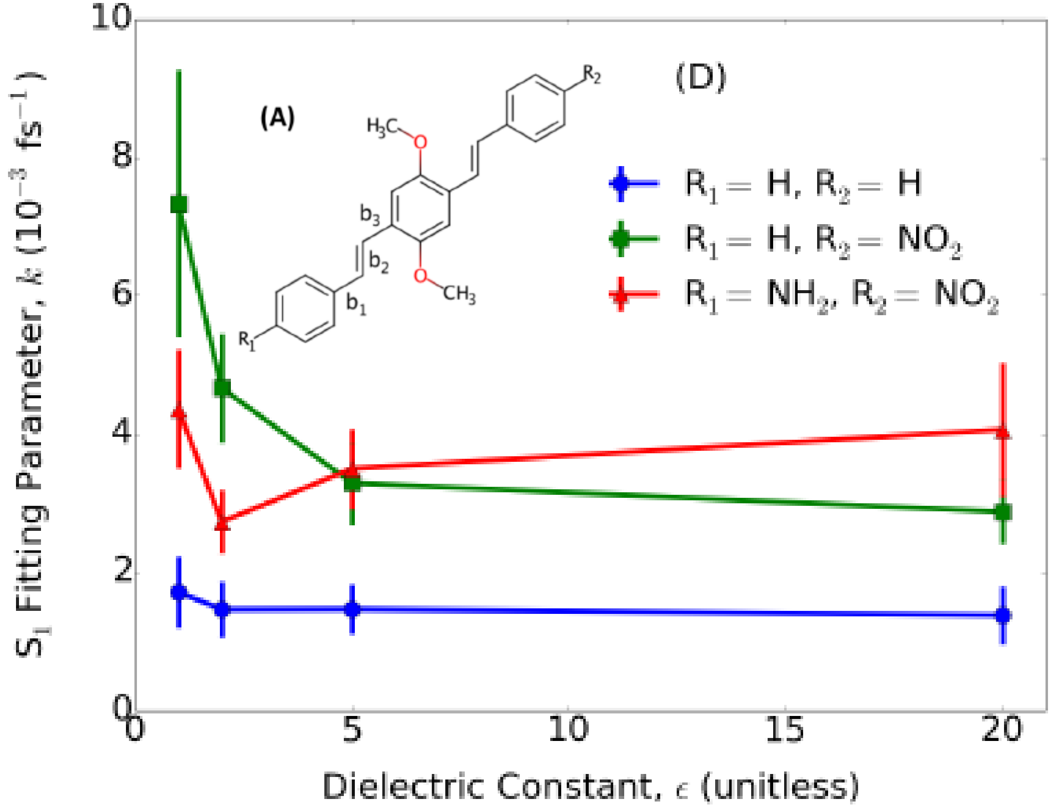
F. Ding, D. B. Lingerfelt, B. Mennucci, X. Li,
J. Chem. Phys. 142, 034120 (2015)

LR solvent non-adiabatic dynamics



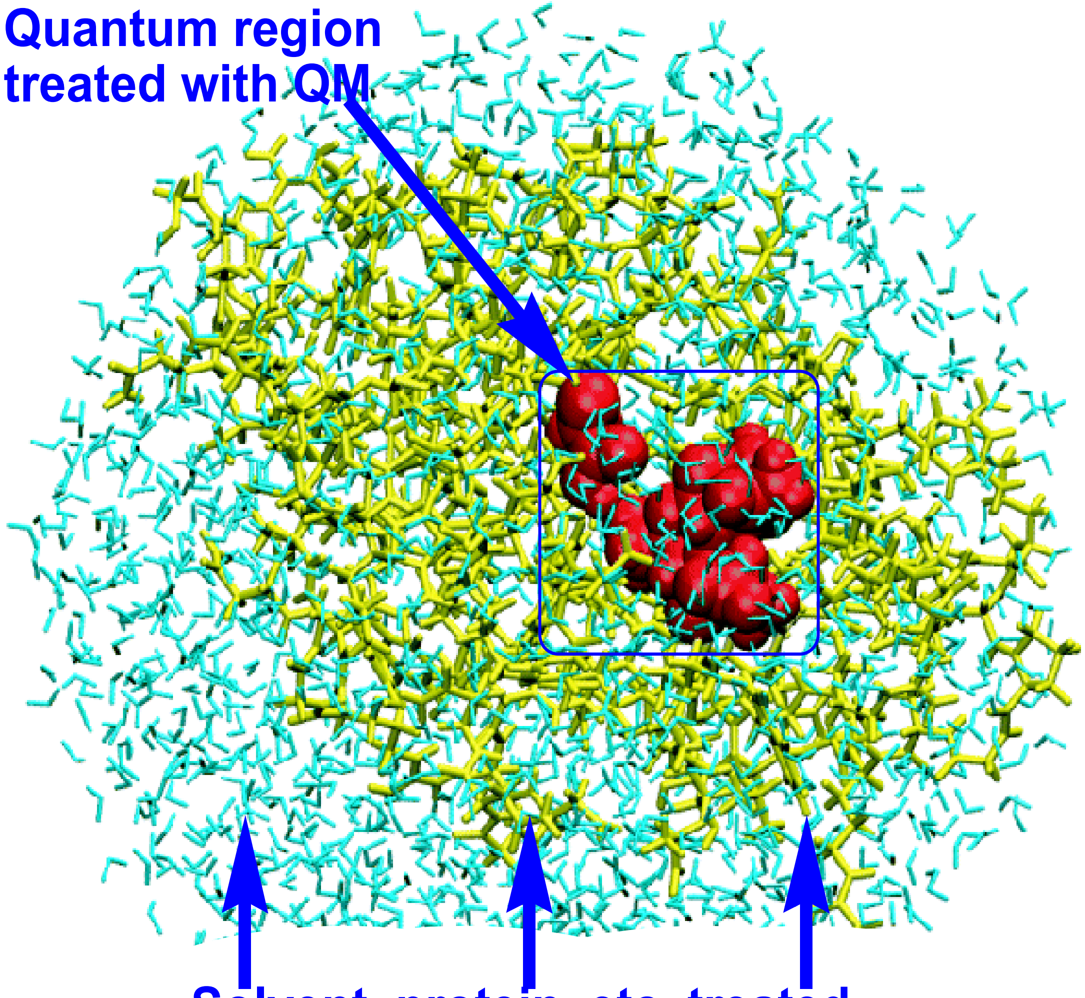
$$\mathbf{d}_{\alpha\beta} = \frac{\langle \phi_\alpha(\mathbf{r};\mathbf{R}) | \nabla_\mathbf{R} H | \phi_\beta(\mathbf{r};\mathbf{R}) \rangle}{E_\beta - E_\alpha}$$

$$H = H_{\text{vac}} + H_{\text{sol}}$$



A. E. Sifain, J. A. Bjorgaard, T.R. Nelson, B.T. Nebgen, A.J. White, B. J. Gifford, O.V. Prezhdo, S. Fernandez-Alberti, A.E. Roitberg, S. Tretiak J. Chem. Theory Comput., 14, 3955 (2018)

QM/MM framework



Quantum region treated with QM

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

QM/MM interactions MM effect on QM: van-der-Waals spheres and polarization/charges; QM effect on MM: polarization through the excited state density matrix ρ^{ex}_{ij}

Note that ρ^{gr}_{ij} is used in the ground state QM/MM dynamics (e.g., AMBER Tools/AMBER). So conceptually excited state QM/MM is straightforward and attractive.

Currently being developed in A. Roitberg group

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☐ ***KEYWORDS:***
density_predict

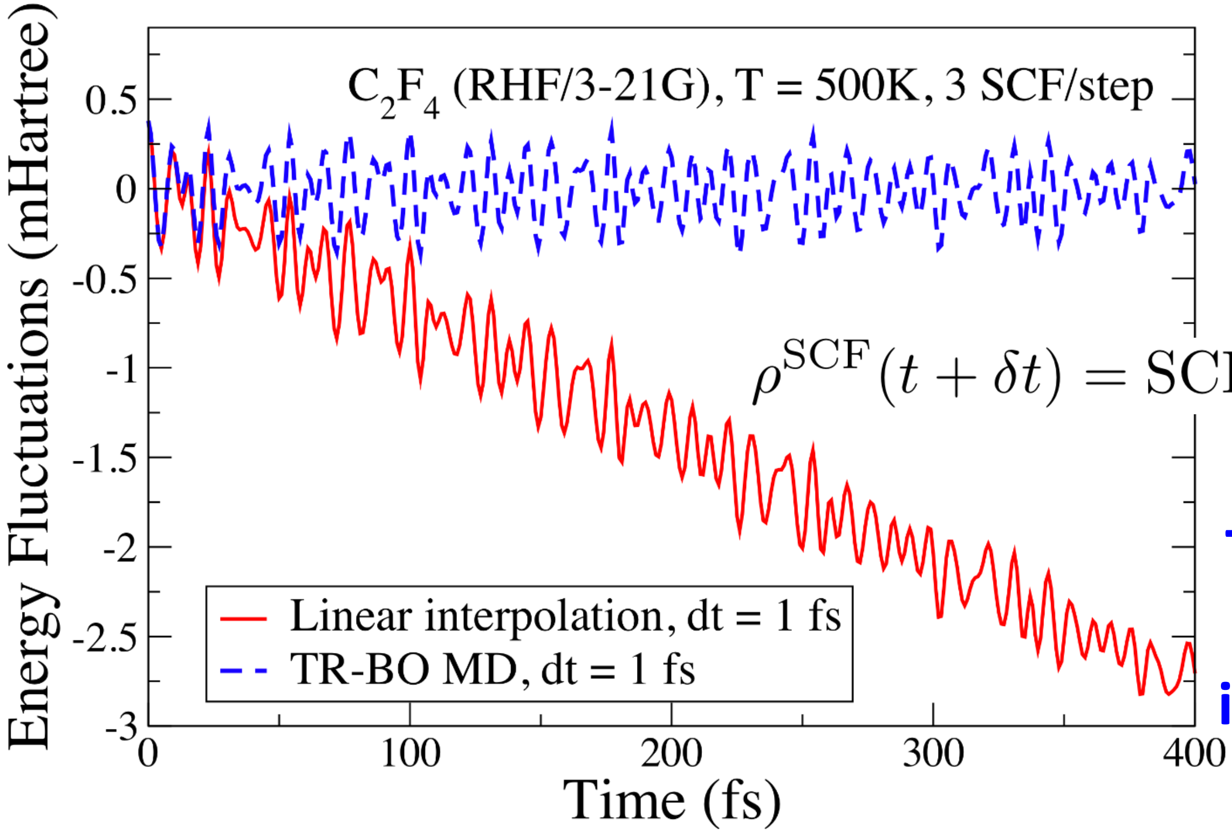
Feel free to ask question on the fly…

Problems with ab initio BOMD

$$\mathcal{L}^{\mathrm{BO}}(\mathbf{R},\dot{\mathbf{R}}) = \frac{1}{2}\sum_I M_I \dot{R}_I^2 - U(\mathbf{R},\rho^{\mathrm{SCF}}) \qquad M_I\ddot{\mathbf{R}}_I = -\frac{\partial U(\mathbf{R},\rho^{\mathrm{SCF}})}{\partial R_I}$$

Broken time-reversibility → **Unstable trajectories with energy drift**

Impose time-reversibility
or use “exact” forces?



$$\rho^{\mathrm{SCF}}(t+\delta t) = \mathrm{SCF}\left[2\rho^{\mathrm{SCF}}(t) - \rho^{\mathrm{SCF}}(t-\delta t)\right]$$

The next generation QMD allows both without the iterative SCF optimization!

Extended Lagrangian excited states

$$\mathcal{L}^{\mathrm{ES}}(\mathbf{R}, \dot{\mathbf{R}}) = \frac{1}{2}\sum_k M_k \dot{R}_k^2 - U[R; D] - \Omega[R; D, \xi]$$

$$\mathcal{L}^{\mathrm{XES}}(\mathbf{R}, \dot{\mathbf{R}}, P, \dot{P}, \zeta, \dot{\zeta})$$

$$= \mathcal{L}^{\mathrm{ES}}(\mathbf{R}, \dot{\mathbf{R}}) + \frac{\mu_{\mathrm{gs}}}{2} Tr[\dot{P}^2] - \frac{\mu_{\mathrm{gs}}\omega_{\mathrm{gs}}^2}{2} Tr[(D - P)^2]$$

$$+ \frac{\mu_{\mathrm{es}}}{2} Tr[\dot{\zeta}^2] - \frac{\mu_{\mathrm{es}}\omega_{\mathrm{es}}^2}{2} Tr[(\xi - \zeta)^2]$$

The Euler−Lagrange equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}^{\mathrm{XES}}}{\partial \dot{\mathbf{R}}}\right) = \frac{\partial \mathcal{L}^{\mathrm{XES}}}{\partial \mathbf{R}}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}^{\mathrm{XES}}}{\partial \dot{P}}\right) = \frac{\partial \mathcal{L}^{\mathrm{XES}}}{\partial P}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}^{\mathrm{XES}}}{\partial \dot{\xi}}\right) = \frac{\partial \mathcal{L}^{\mathrm{XES}}}{\partial \xi}$$

Ground state density matrix P is an extended dynamical variable to the Born-Oppenheimer Lagrangian that follows the ground state through a harmonic oscillator centered around the evolving ground state D. ζ is the corresponding variable to the excited state transition density ξ

μ_{gs} , μ_{es} , ω_{gs} and ω_{es} are the fictitious electronic mass and frequency parameters of the extended harmonic oscillators for the ground state (gs) and the excited state (es).

J. A. Bjorgaard, D. Sheppard, S. Tretiak, A. Nicklasson, J. Chem. Theory Comput., 14, 799 (2018)

Extended Lagrangian excited states

Vanishing mass -> decoupled Euler−Lagrange equations $\mu_{\mathrm{gs}} \to 0$ and $\mu_{\mathrm{es}} \to 0$,

$$\ddot{P} = \omega_1^{\,2}(D - P)$$

$$\ddot{\zeta} = \omega_2^{\,2}(\xi - \zeta)$$

$$M_k \ddot{R}_k = -\frac{\partial U[\mathbf{R};\, D]}{\partial R_k} - \frac{\partial \Omega[\mathbf{R};\, D,\, \xi]}{\partial R_k}$$

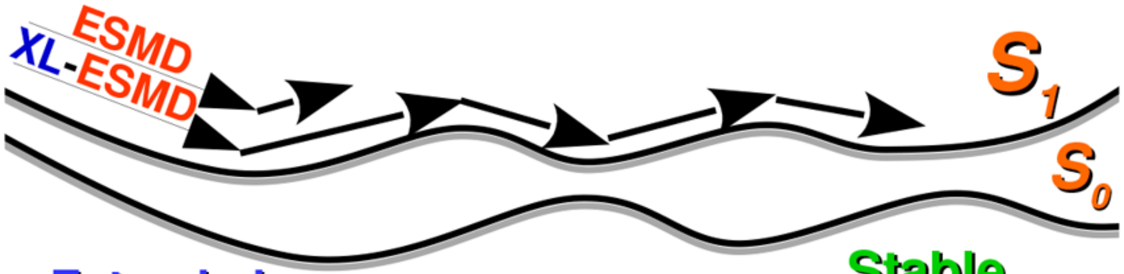
A modified Verlet integration scheme with small amount of dissipation

$$P(t+\delta t) = 2P(t) - P(t-\delta t) + \delta t^2 \ddot{P}(t) + \alpha \sum_{k=0}^{K_{\max}} c_k P(t - k\delta t)$$

$$\zeta(t+\delta t) = 2\zeta(t) - \zeta(t-\delta t) + \delta t^2 \ddot{\zeta}(t) + \alpha \sum_{k=0}^{K_{\max}} c_k \zeta(t - k\delta t)$$

$$D(t+\delta t) = \mathcal{SCF}[\mathbf{R}(t+\delta t), P(t+\delta t)] \quad \xi(t+\delta t) = \mathcal{RPA}[\mathbf{R}(t+\delta t), D(t+\delta t), \zeta(t+\delta t)]$$

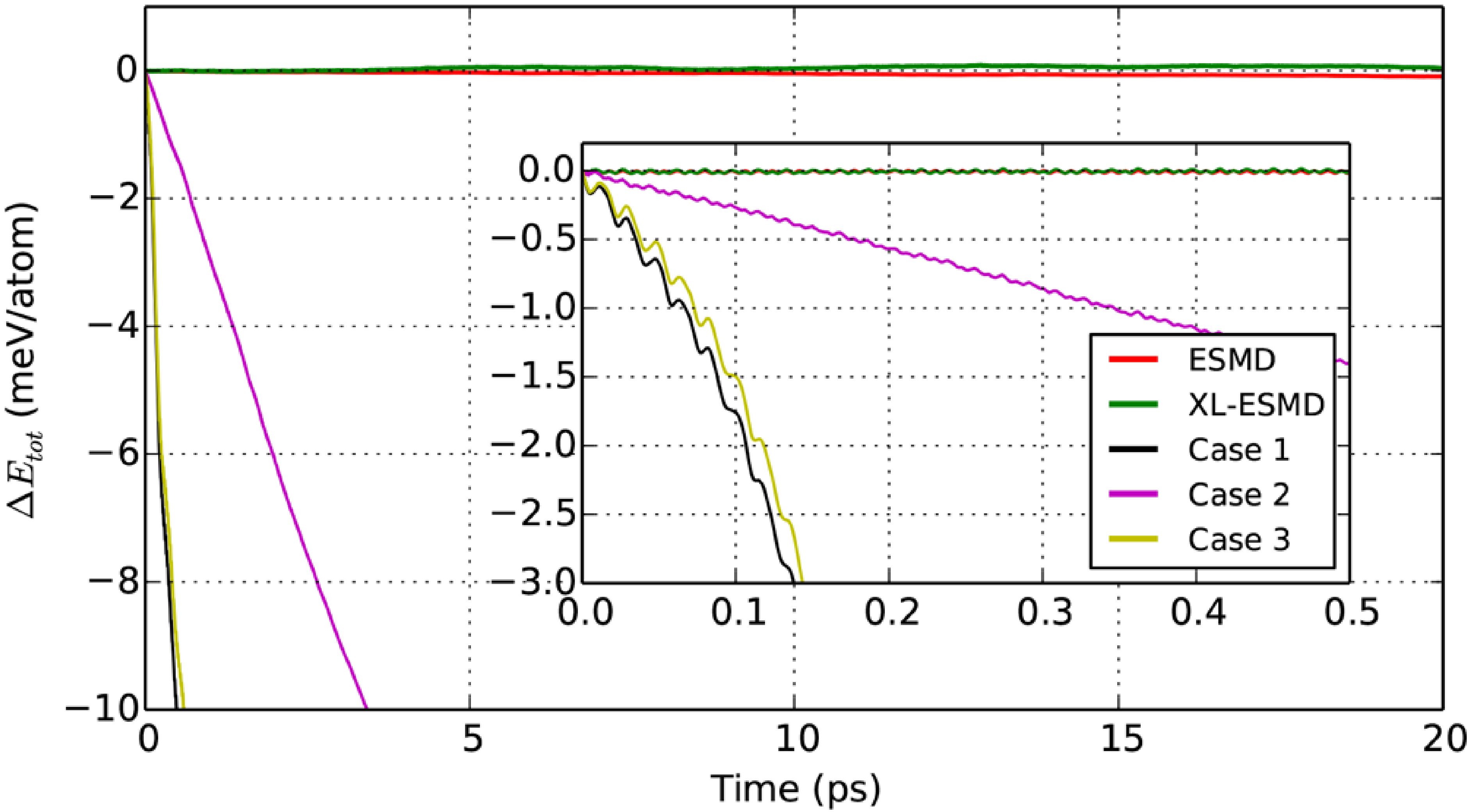
P(t+δt) and ζ(t+dt) provide accurate approximations to D(t+δt) and ξ(t+δt) up to δt^2



Extended Lagrangian BOMD + **Excited State MD** = **Stable Acclerated ESMD**

J. A. Bjorgaard, D. Sheppard, S. Tretiak, A. Nicklasson, J. Chem. Theory Comput., 14, 799 (2018)

XL-ESMD adiabatic dynamics tests



Long story short: $N_{SCF}=2$ and $d_{ES}=10^{-4}$ eV work well vs general non-XL $d_{SCF}=10^{-8}$ eV and $d_{ES}=10^{-7}$ eV

J. A. Bjorgaard, D. Sheppard, S. Tretiak, A. Nicklasson, J. Chem. Theory Comput., 14, 799 (2018)

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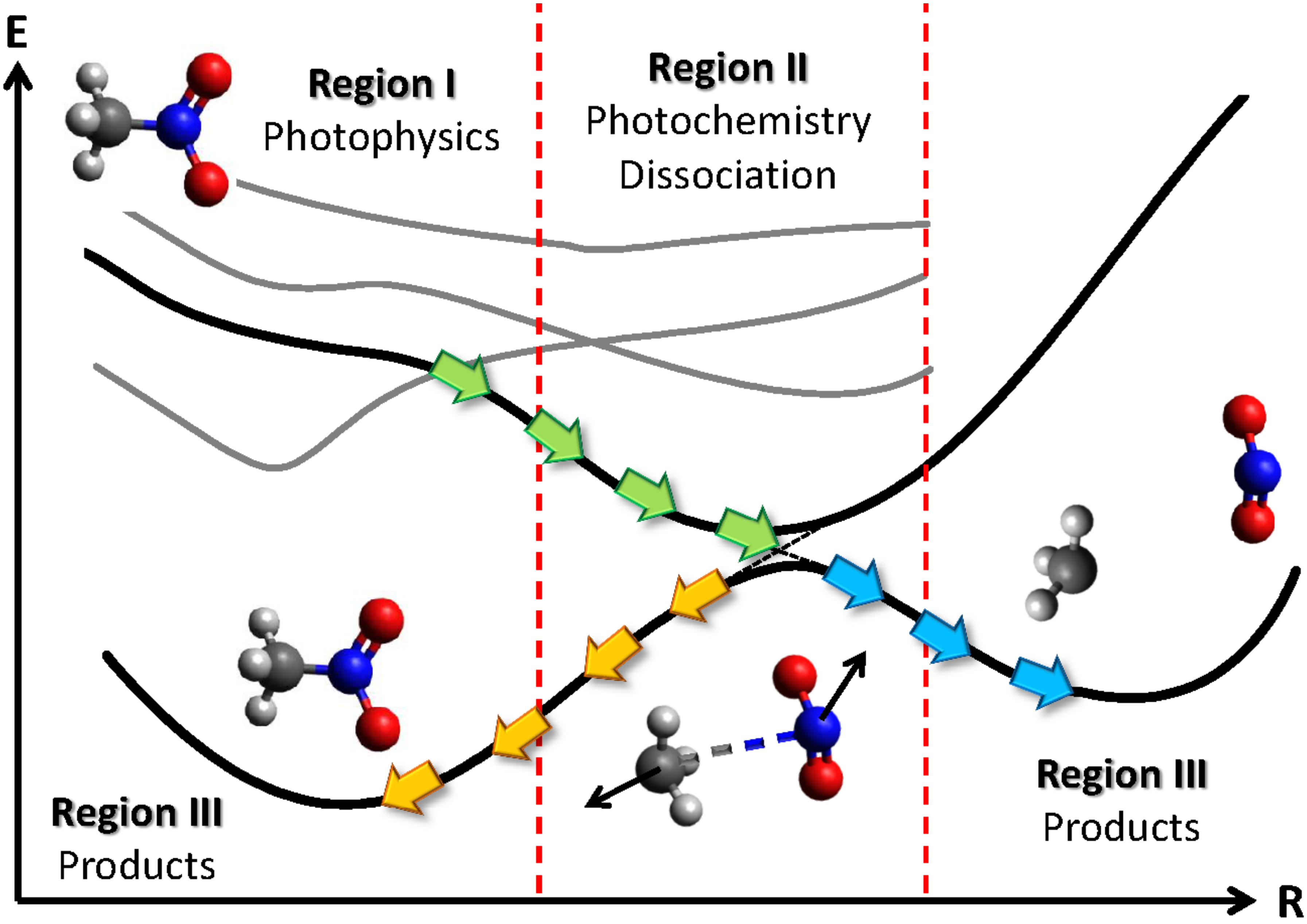
❑ ***KEYWORDS:***

Uhf = ‘True’
shop2gs
hop2gs_crit
hop2gs_method

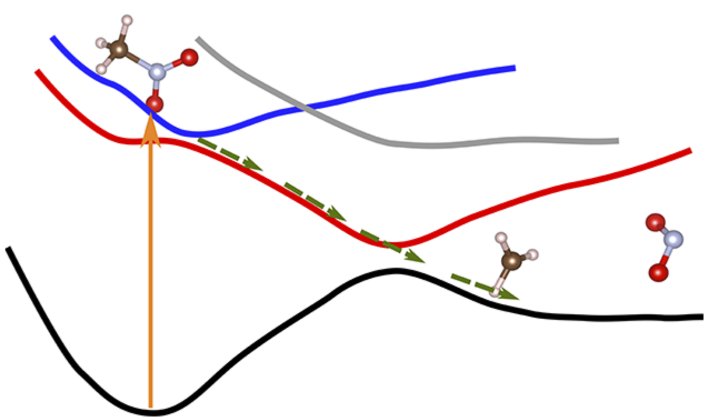
Feel free to ask question on the fly…

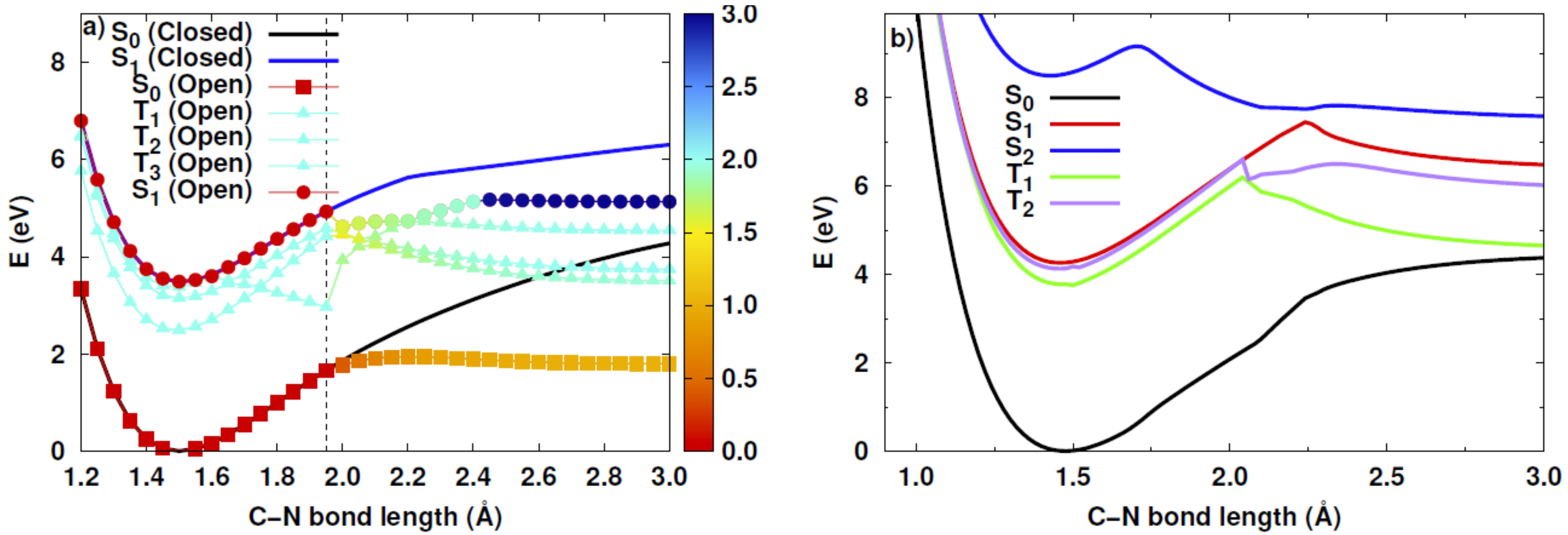
Open shell implementation is needed



Beware for severe limitations for open shells

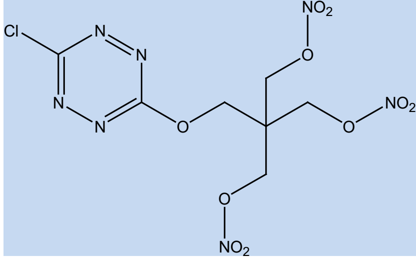
- RPA/CIS cannot properly describe excited to ground state crossing;
- Unrestricted spin approaches typically underestimate dissociation barriers;
- ΔE<1.0 eV means successful **Cis-Trans** isomerization.

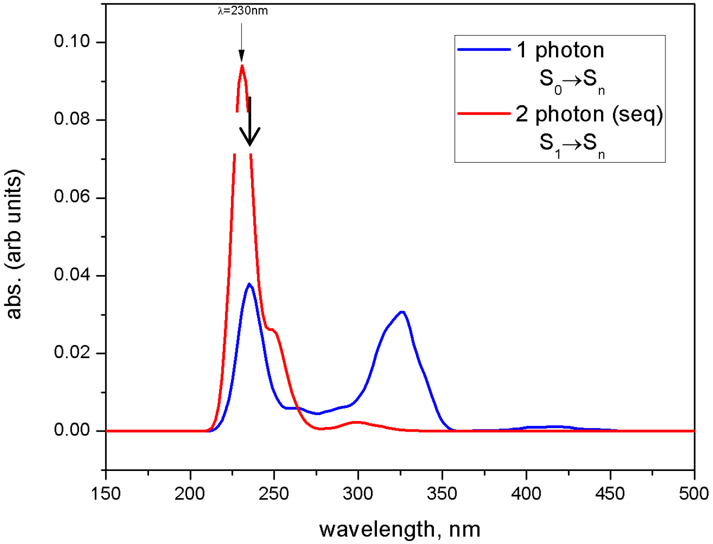


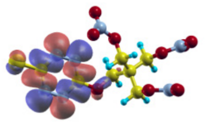
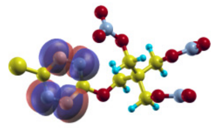
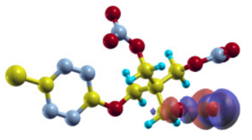
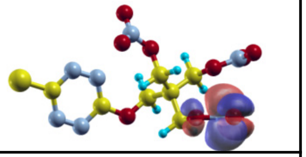
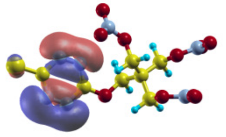
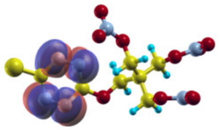


Y. Zhang, L. Li, S. Tretiak, and T. Nelson, J. Chem. Theory Comput. 14, 2053 (2020)

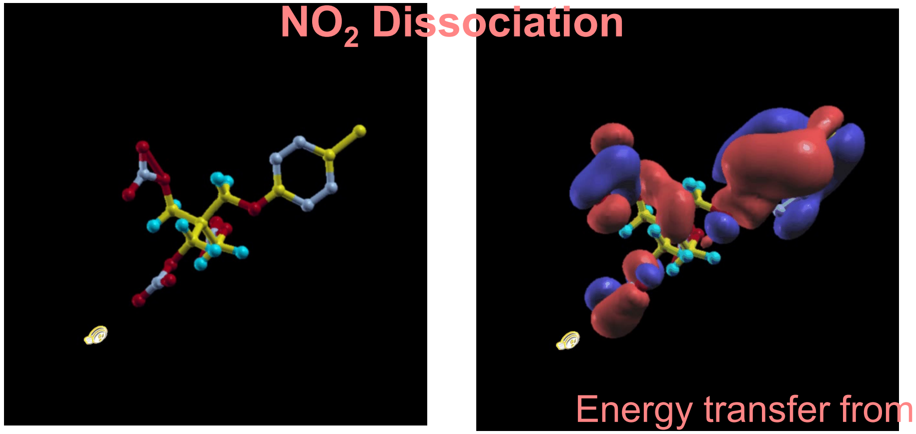
Functionalized Tetrazine-Cl





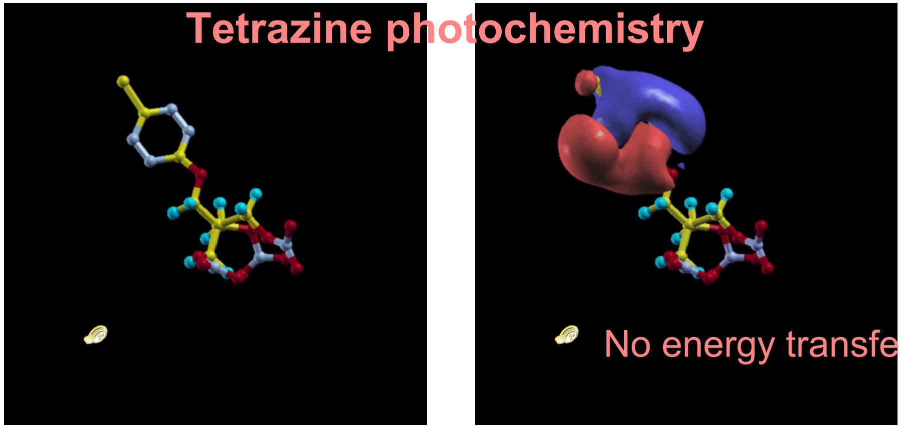
	HOMO	LUMO
S_1 (420nm)		
S_5 (275nm) NO_2 dark states		
S_{29} (230nm) Initial state		

NO_2 Dissociation



Energy transfer from tetrazine to NO_2

Tetrazine photochemistry



No energy transfer

M.T. Greenfield, S.D. McGrane, C.A, Bolme, J.A. Bjorgaard, T.R. Nelson, S. Tretiak, R.J. Scharff, J. Phys. Chem. C, 119, 4846 (2015)

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- ***Electronic structure theory in NEXMD***
- ***Ehrenfest dynamics***
- ***Surface Hopping methodology***
- ***Trivial crossings and decoherence effects***

PART II: Some advanced NEXMD capabilities

- ***Multi-configurational Ehrenfest with Ab Initio Multiple Cloning (MCE-AIMC)***
- ***Environmental effects***
- ***Extended Largangian excited state MD***
- ***Open shell, bond breaking***
- ***Polaritonics, molecules in the cavity***
- ***Practical aspects: spectra, rates, wavefunction analysis***

☐ ***KEYWORDS:***

usc = .true.

lmcoup

Ephoton

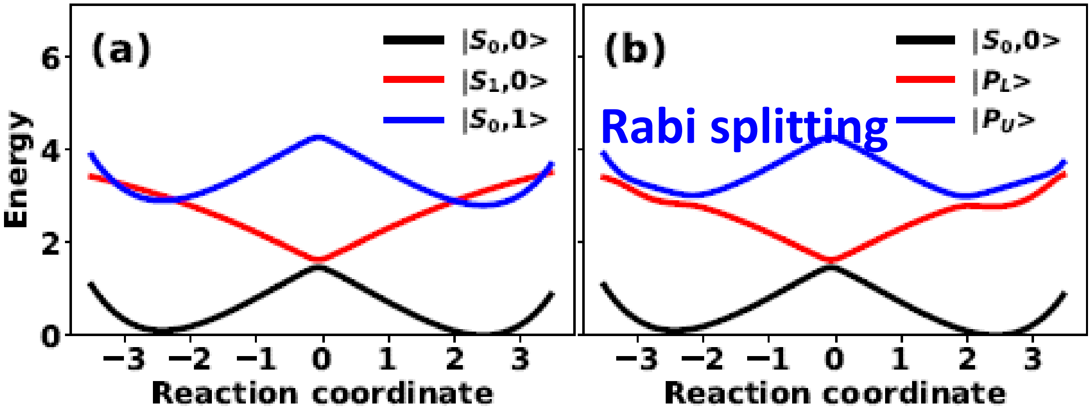
Feel free to ask question on the fly…

Coupling NEXMD with light: Jaynes-Cummings (JC) & Tavis-Cummings (TC) models

$$\hat{H}_{JC} = \omega_c a^\dagger a + \Omega(\mathbf{R})\sigma^\dagger\sigma - g(\mathbf{R})(a^\dagger\sigma + a\sigma^\dagger)$$

Cavity photon   Molecular excitation   Coupling $\mu(\mathbf{R}) \cdot \mathbf{E}$

Strong coupling = the coupling between light and matter is strong compared to the damping, but is small compared to both excitation and photon energies



Rabi splitting

Upper and lower polaritonic bands

$$|P_L\rangle = \sin\theta|S_0, N_c+1\rangle + \cos\theta|S_1, N_c\rangle$$

$$|P_U\rangle = \cos\theta|S_0, N_c+1\rangle - \sin\theta|S_1, N_c\rangle$$

$$E_\pm(\mathrm{R}) = \frac{\Omega(\mathrm{R}) + \omega_c}{2} \pm \sqrt{\frac{\Delta^2(\mathrm{R})}{4} + g^2(\mathrm{R})N_c}$$

$$\Delta(\mathrm{R}) = \Omega(\mathrm{R}) - \omega_c$$

Rabi splitting

$$\Omega_r(\mathrm{R}) = 2\sqrt{\Delta^2(\mathrm{R})/4 + g^2(\mathrm{R})N_c}$$

TC model = *M* identical two-level emitters that interact strongly with a lossless cavity mode.

The total number of excitations is constant $\hat{N} = a^\dagger a + \sum_i^M \sigma_i^\dagger \sigma_i$

E. T. Jaynes and F. W. Cummings, Proc. IEEE 51, 89 (1963).

Rabi splitting $\Omega_r(\mathrm{R}) = 2\sqrt{\Delta^2(\mathrm{R})/4 + g^2(\mathrm{R})N_c M}$

Mapping light-matter interactions into quantum chemistry

The rotating wave approximation (RWA) neglects the fast oscillating terms

$$\hat{H}_{tot} = \sum_{i=1}^{N} \Omega_i(\mathrm{R}) c_i^\dagger c_i + \omega_c a^\dagger a + \sum_{i=1}^{N} g_i(\mathrm{R})(c_i^\dagger a + c_i a^\dagger)$$

$$H = \begin{bmatrix} \omega_c & g_1 & \cdots & g_N \\ g_1 & \Omega_1(\mathrm{R}) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ g_N & 0 & \cdots & \Omega_N(\mathrm{R}) \end{bmatrix} \quad \Psi_K = \sum_{i=0}^{N} \beta_i^K |\psi_i\rangle \quad |\psi_0\rangle = |S_0, 1\rangle \quad |\psi_i\rangle = |S_i, 0\rangle$$

N+1 polaritonic states

Excited states NAMD simulations require analytic calculations of excited state gradients and derivative couplings (derived for RPA-like approaches, aka TDDFT, CIS)

$$F_a^K = -\langle \Psi_K | \nabla_a \hat{H} | \Psi_K \rangle \qquad \frac{\partial \mu_i}{\partial \mathrm{R}_a} = \sum_{\mu\nu} \left[\frac{\partial \langle \mu | \mathrm{R} | \nu \rangle}{\partial \mathrm{R}_a} \xi_{i,\nu\mu} + \langle \mu | \mathrm{R} | \nu \rangle \frac{\partial \xi_{i,\nu\mu}}{\partial \mathrm{R}_a} \right]$$

$$\mathrm{d}_{KL} = \langle \Psi_K | \nabla_{\mathrm{R}} \Psi_L \rangle = \frac{\langle \Psi_K(t) | \hat{H}^{\mathrm{R}} | \Psi_L(t) \rangle}{E_L(t) - E_K(t)}$$

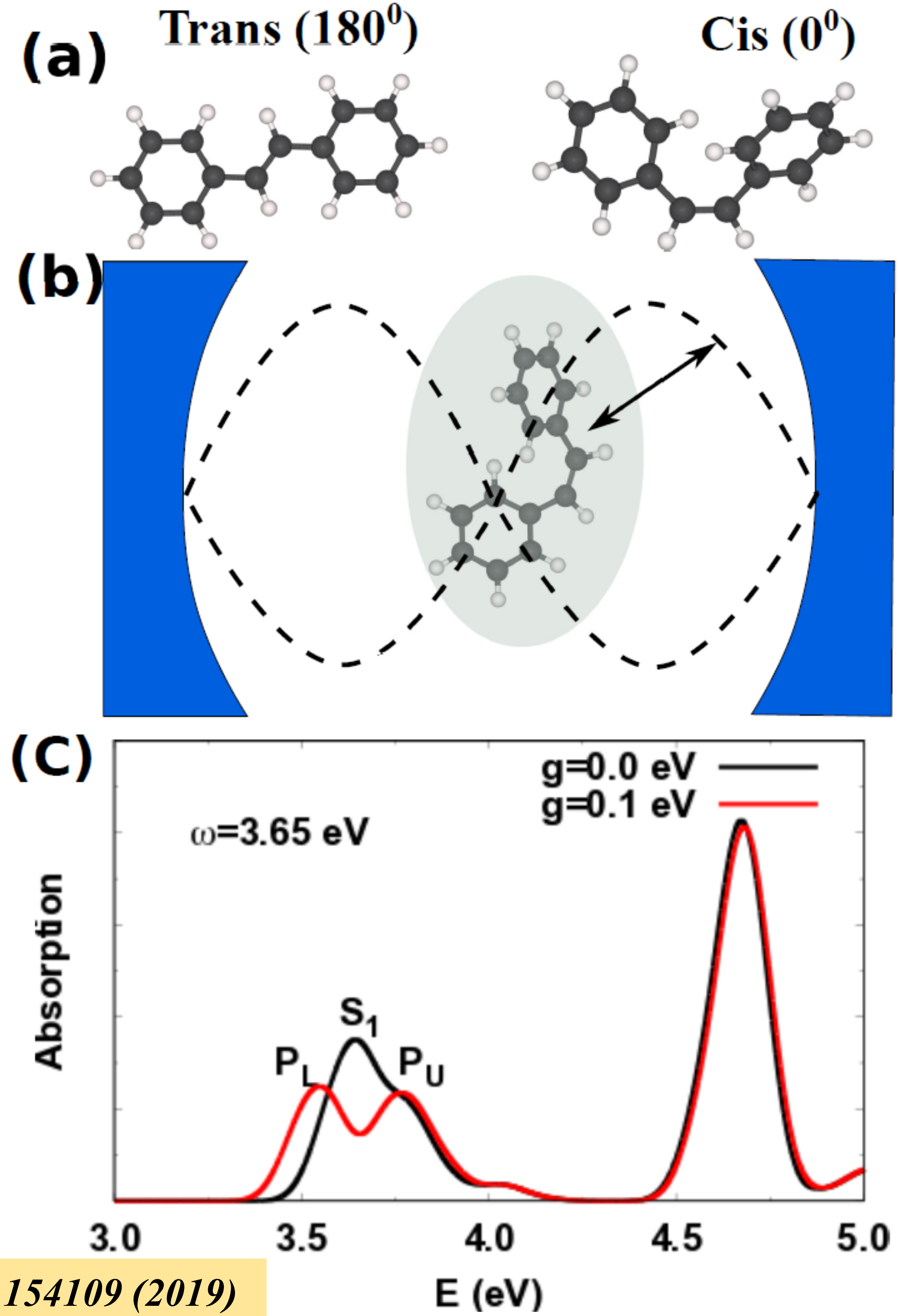
Now we can do polaritonic NAMD!!

Y. Zhang, T. Nelson, S. Tretiak J. Chem. Phys. 151, 154109 (2019)

Example: Controlling photochemistry in a cavity

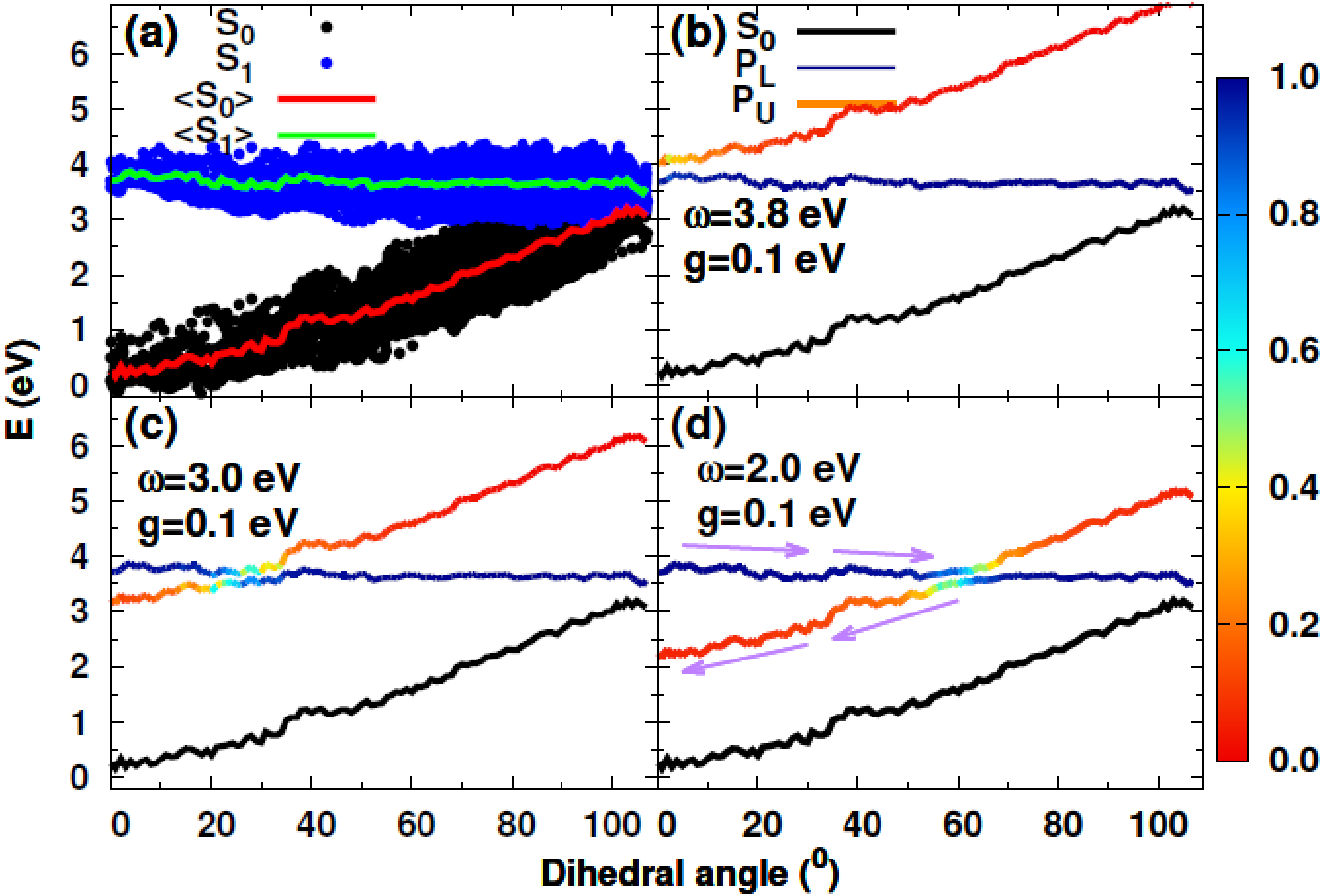
Cis-Trans isomerization of stilbene in a cavity

Calculated absorption spectrum **Cis-**isomer, appearance of P_U and P_L polationic branches.



Y. Zhang, T. Nelson, S. Tretiak J. Chem. Phys. 151, 154109 (2019)

Modification of excited state potential energy surfaces for Cis-isomer



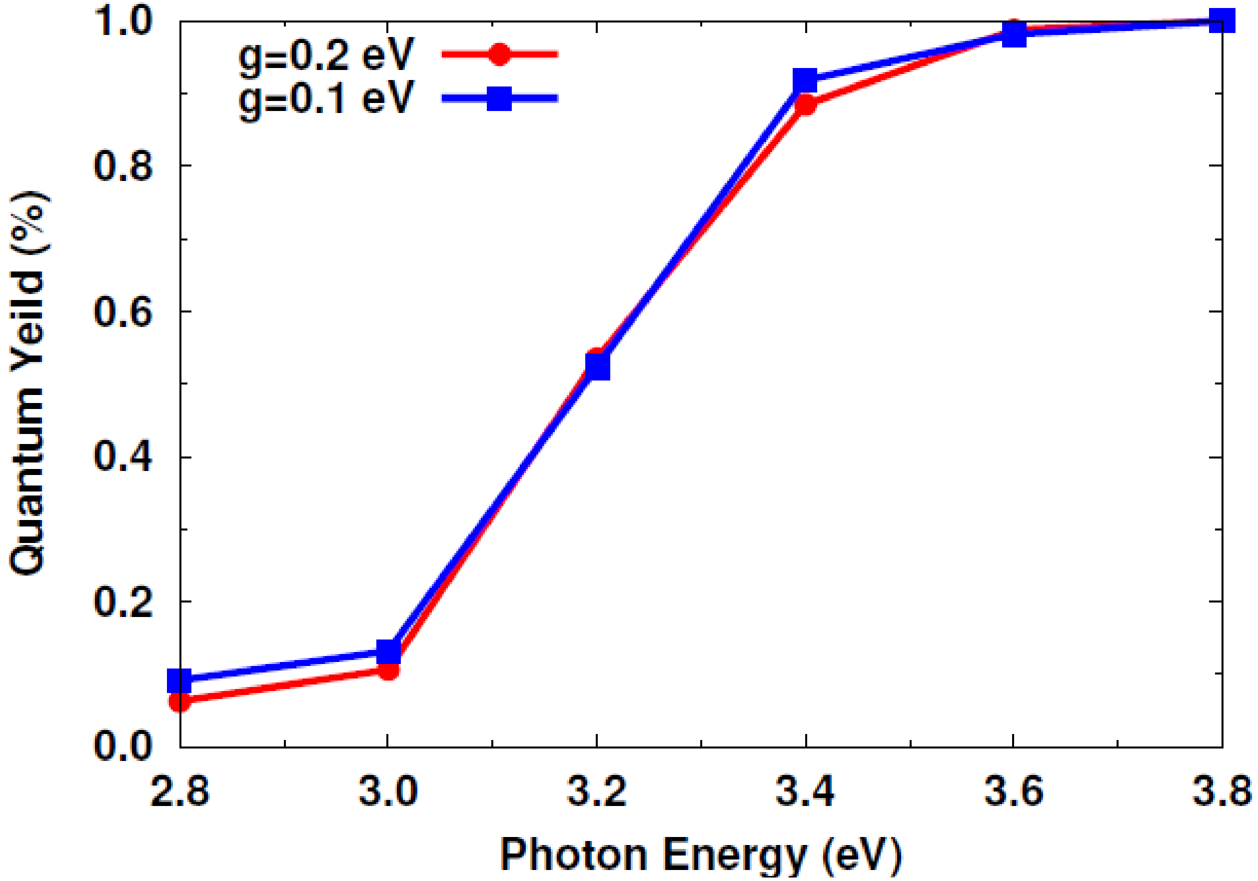
Y. Zhang, T. Nelson, S. Tretiak J. Chem. Phys. 151, 154109 (2019)

Cis-Trans isomerization quantum yield, the NAMD results

The non-adiabatic trajectories start at P_U state of **Cis-**isomer.

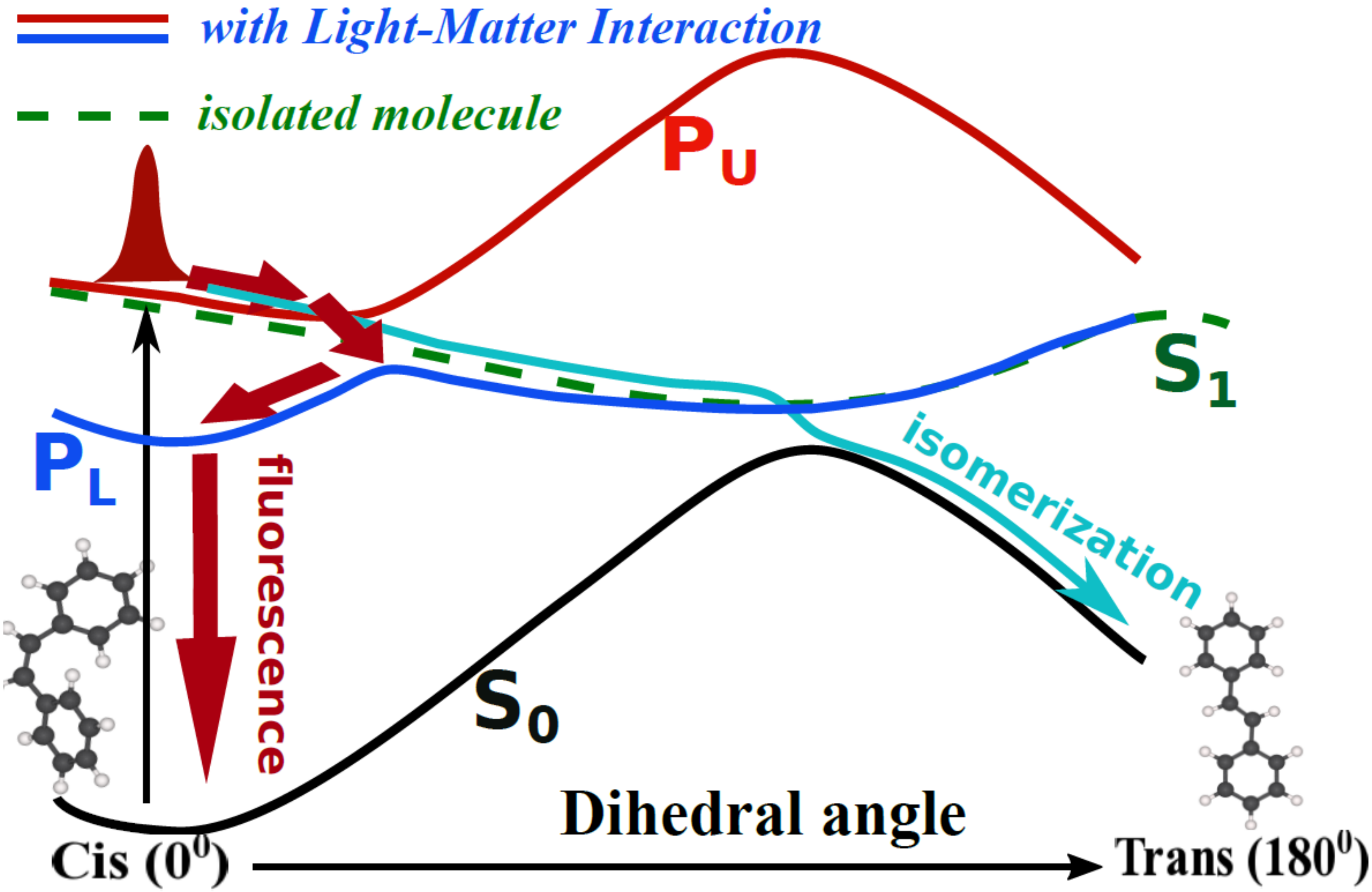
Transfer to P_L polaritonic branch potentially takes it away from the crossing.

$\Delta E < 1.0$ eV means successful **Cis-Trans** isomerization.



Y. Zhang, T. Nelson, S. Tretiak J. Chem. Phys. 151, 154109 (2019)

Take home message: polatitonics is a way to modify molecular PES



Our plan for the lecture

PART I: Methodology and Applications

- *Introduction: what are we taking about?*
- *Born-Oppenheimer Approximation*
- *Need for atomistic methods, mixed quantum-classical approach*
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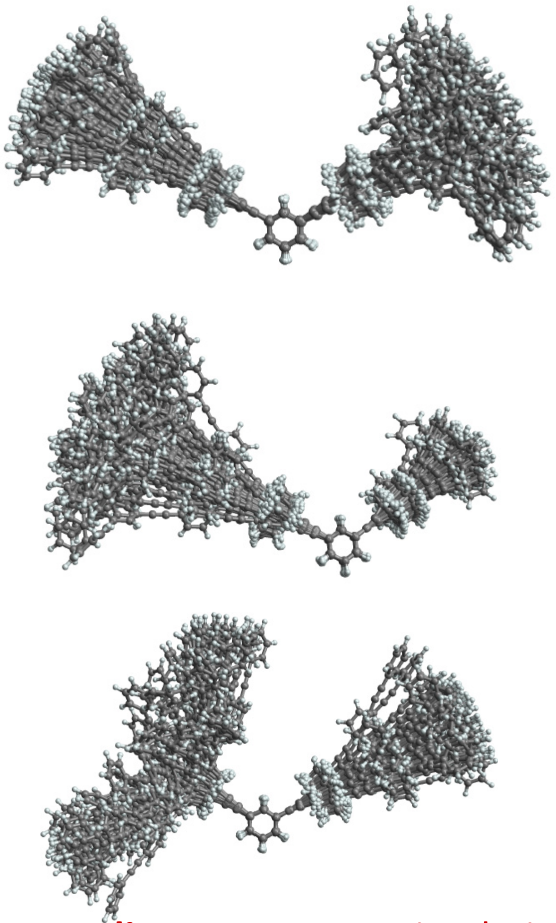
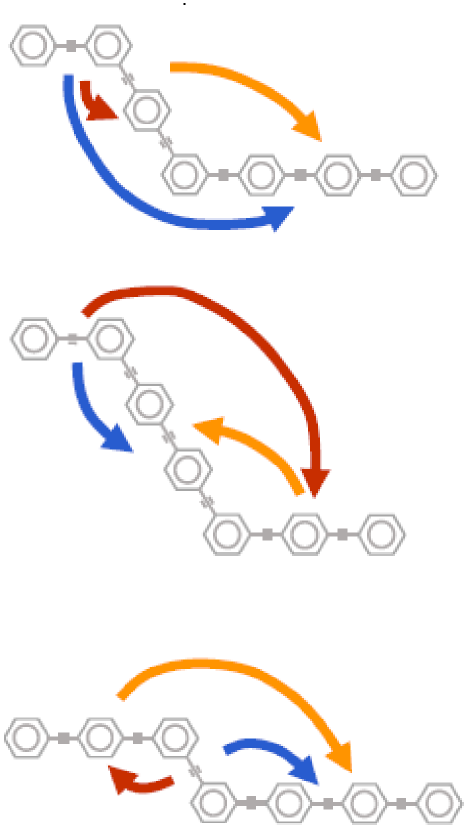
☐ ***KEYWORDS:***
getexcited.py

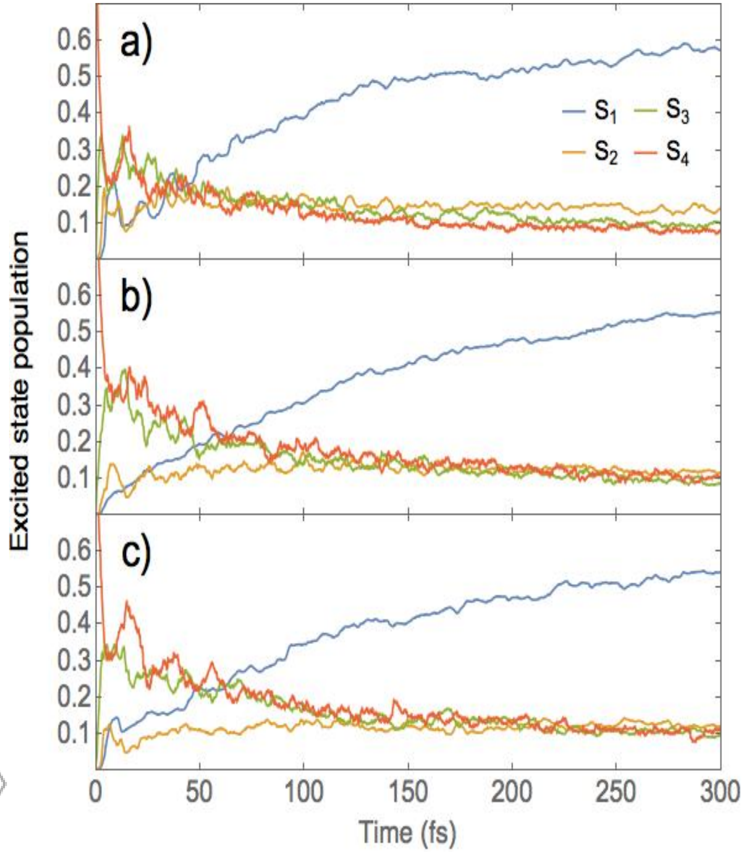
Feel free to ask question on the fly…

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).





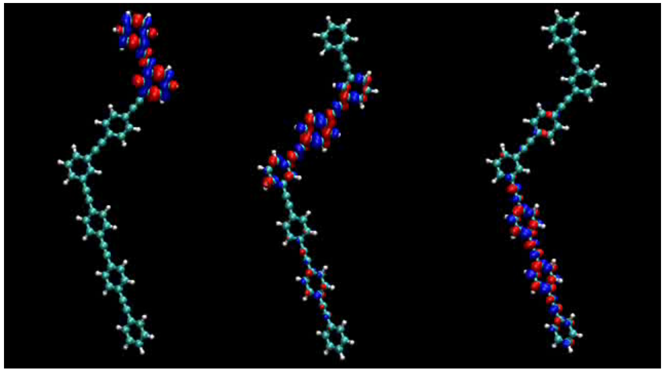


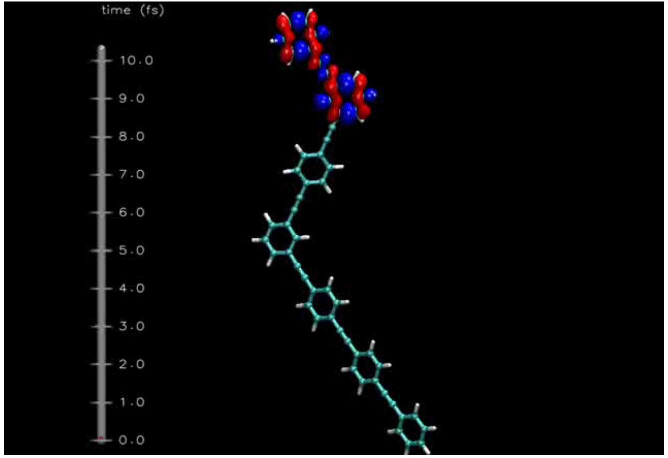
Bottom line: MCE-AIMC simulations suggest that energy moves in space most efficiently when all 3 processes are co-directional. There are notable electron-vibrational coherences appearing as beating across the entire trajectory ensemble (these are absent if surface hopping).

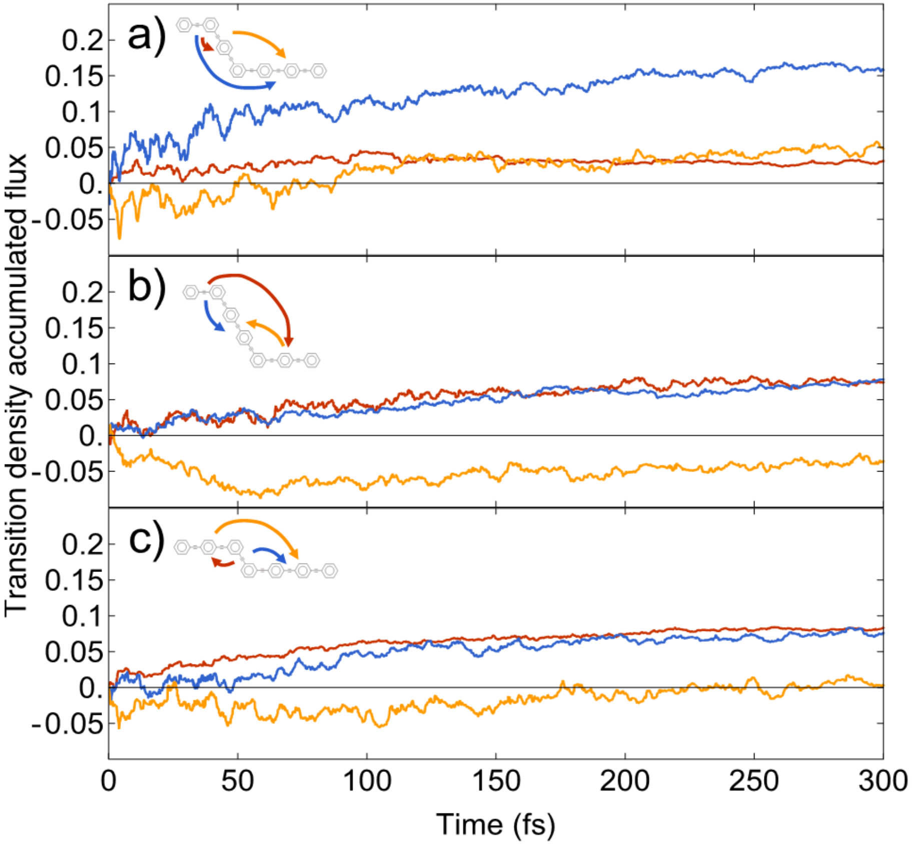
J. Chem. Phys., 150, 124301 (2019)

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

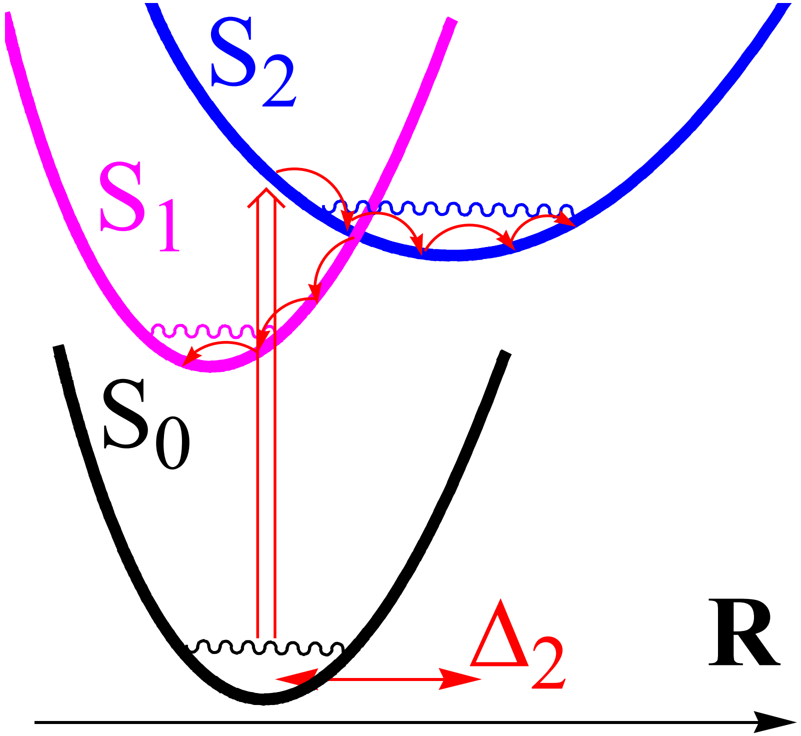
$$\rho_{I,X}^{(n)} = \frac{\sum_{i\in X} \left(\rho_I^{(n)}\right)_{i,i}^{2}}{\sum_{i} \left(\rho_I^{(n)}\right)_{i,i}^{2}}$$

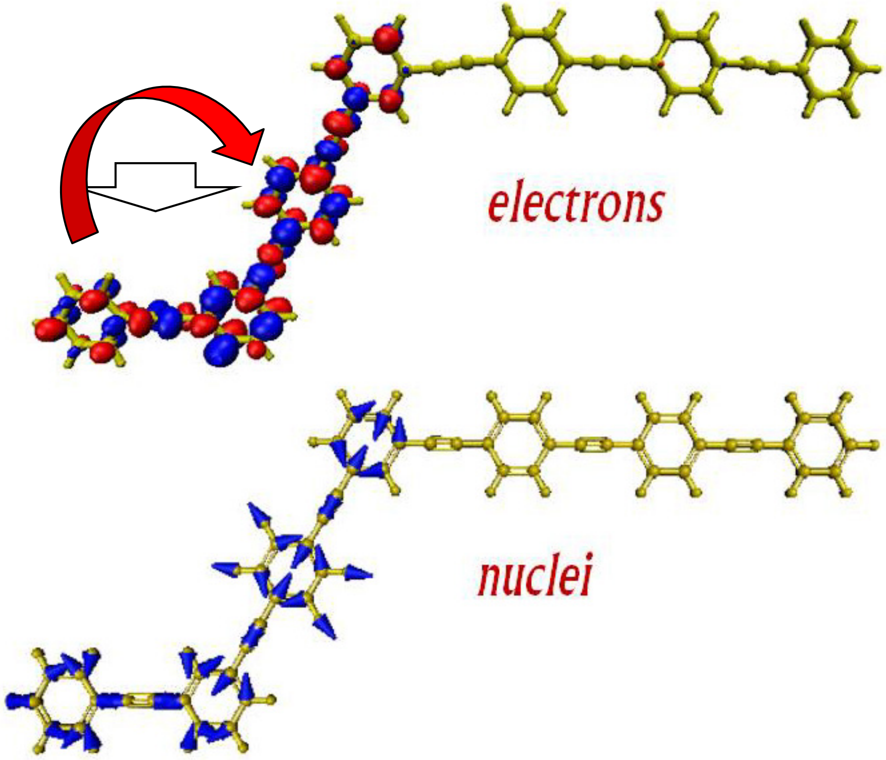
Occupation of X-segment

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

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

Analyses of non-adiabatic coupling vector and relation to the state-specific excited state vibrations





- **NEXMD can calculate Instantaneous and equilibrium normal modes for specific excited states;**
- **One has advanced options to FREEZE selective coordinates and conduct NAMD with reduced number of vibrational degrees of freedom (FrozeNM algorithm).**

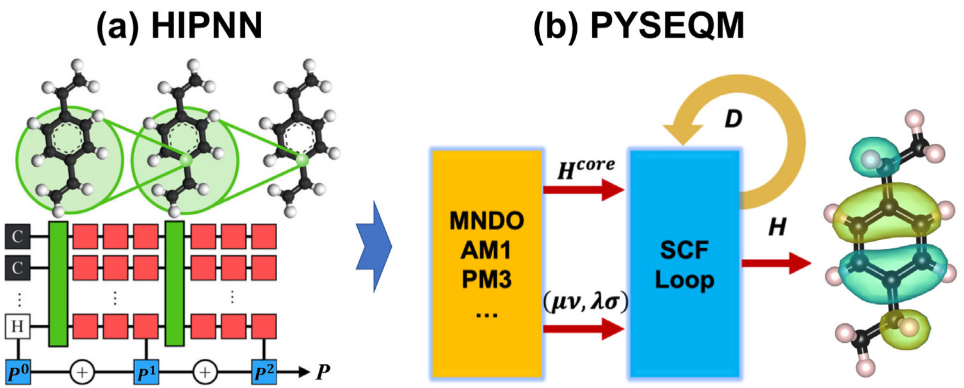
H. Negrin-Yuvero, V. M. Freixas, B. Rodriguez-Hernandez, G. Rojas-Lorenzo, S. Tretiak, A. Bastida and S. Fernandez-Alberti J. Chem. Theory Comput. 16, 7289 (2020)

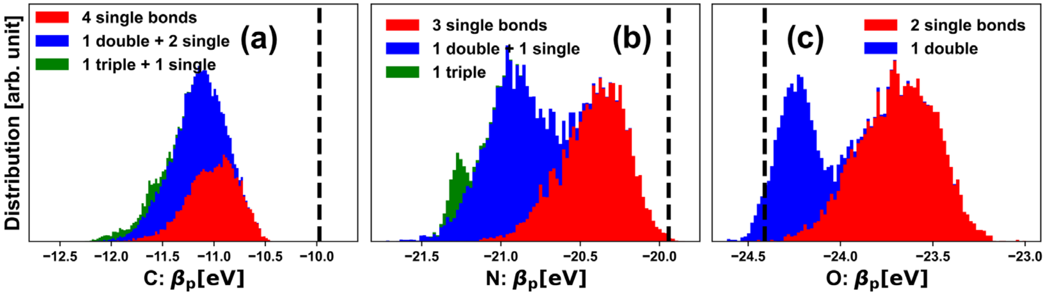
Next step: pyTorch Semi-Empirical Package (PySeQM) https://github.com/lanl/PYSEQM

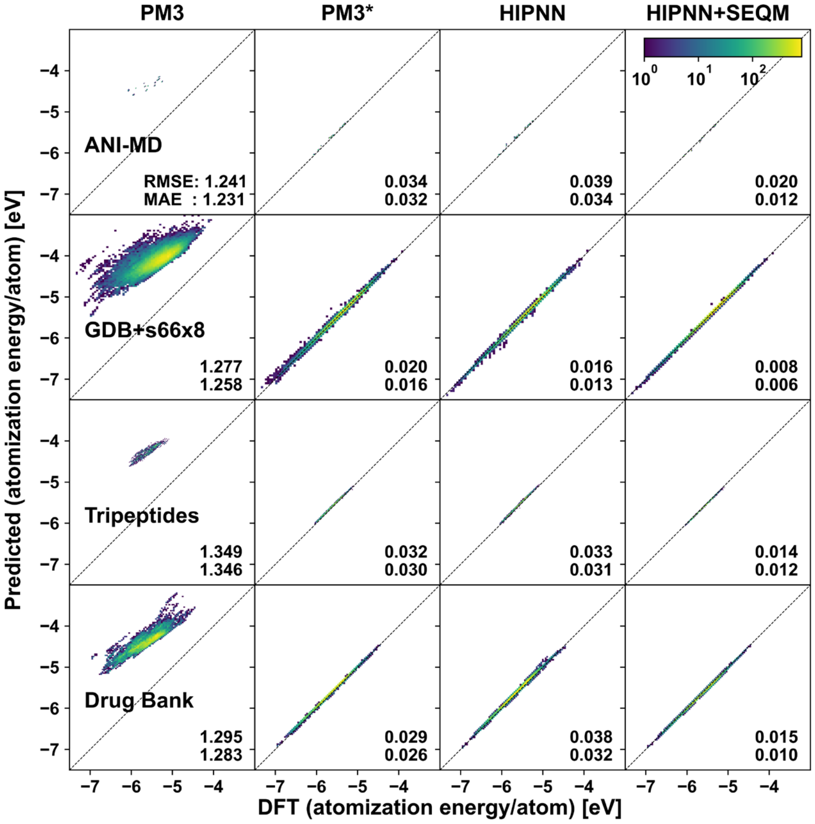
- **Features:**
  - **Specifically tailored for machine learning (ML) applications**
  - PyTorch-based: efficient automatic differentiation/backpropagation
  - AM1/PM3 with future models (PM6, OM2, OM3,…) to be added
  - Ultra fast ground state Molecular Dynamics on GPU
  - SP2 for rapid density matrix determination
  - Extended Lagrangian method for rapid MD propagation
- **Batched Processing for ML Applications**
  - cuSolver for Batched Diagonalization
  - Batched Matrix Construction
  - Batched SCF Convergence
- **The code is released for public in 2020, collaborations are welcome.**

G. Zhou, B. Nebgen, N. Lubbers, A.M.N. Niklasson, S. Tretiak, J. Chem. Theory Comput. 16, 4951 (2020)

Path forward: pyTorch Semi-Empirical Package (PySeQM) https://github.com/lanl/PYSEQM





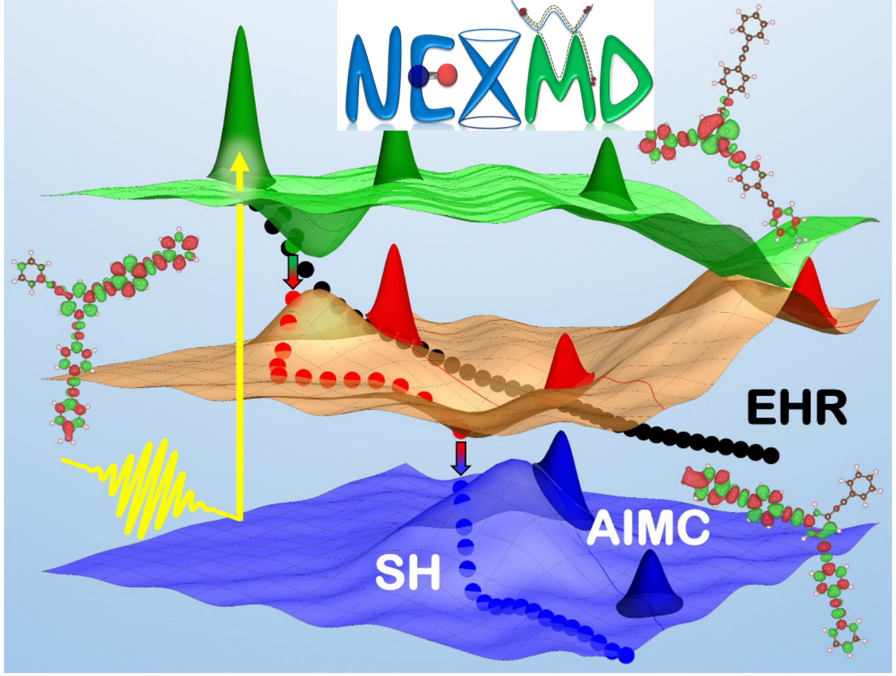


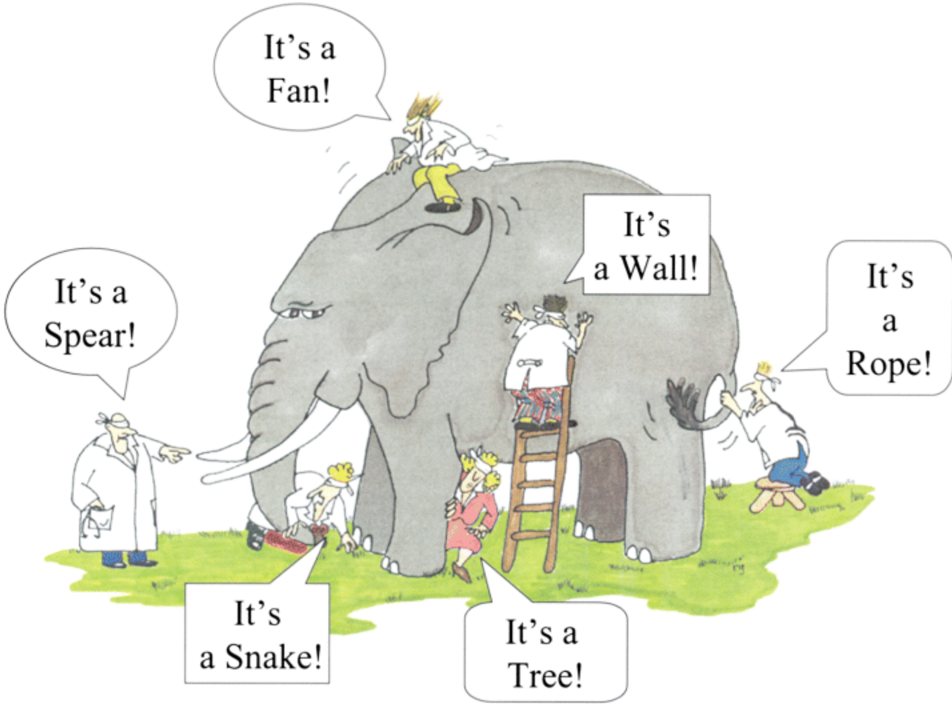
❖Future plans

- ML for ground state Hamiltonian (use of Hellmann-Feynman to avoid back propagation through SCF iterations);
- Excited states (RPA/CIS)
- ML Hamiltonian for excited state PES toward photodynamics

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?***





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Code and applications

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Solvent, XL-ESMD

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Dmitry Makhov (UK, Leeds)

Machine Learning

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Kipton Barros (LANL)
Nick Lubbers (LANL)
Guoqing Zhou (USC)

Experiment: many!

LDRD

Los Alamos
NATIONAL LABORATORY

NNSA

Thank you!

Questions?