Electronically excited states and theoretical spectroscopy: principles, simulations, examples, machine learning

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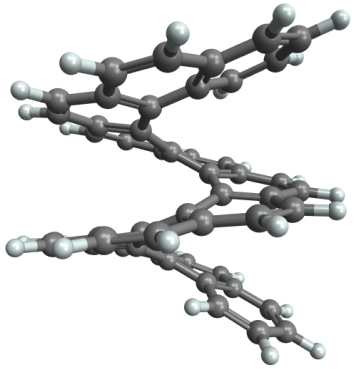
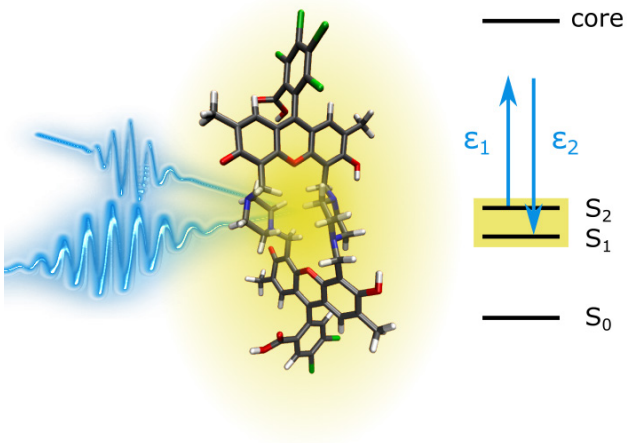
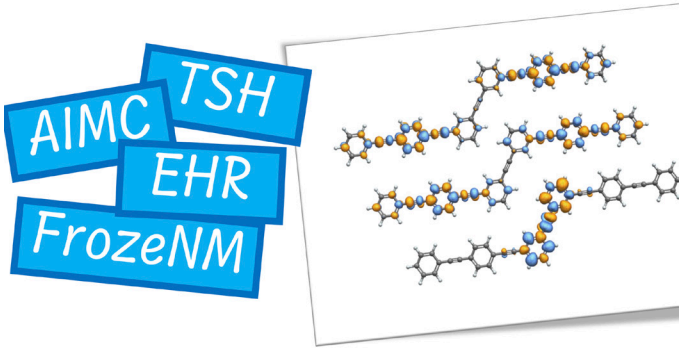




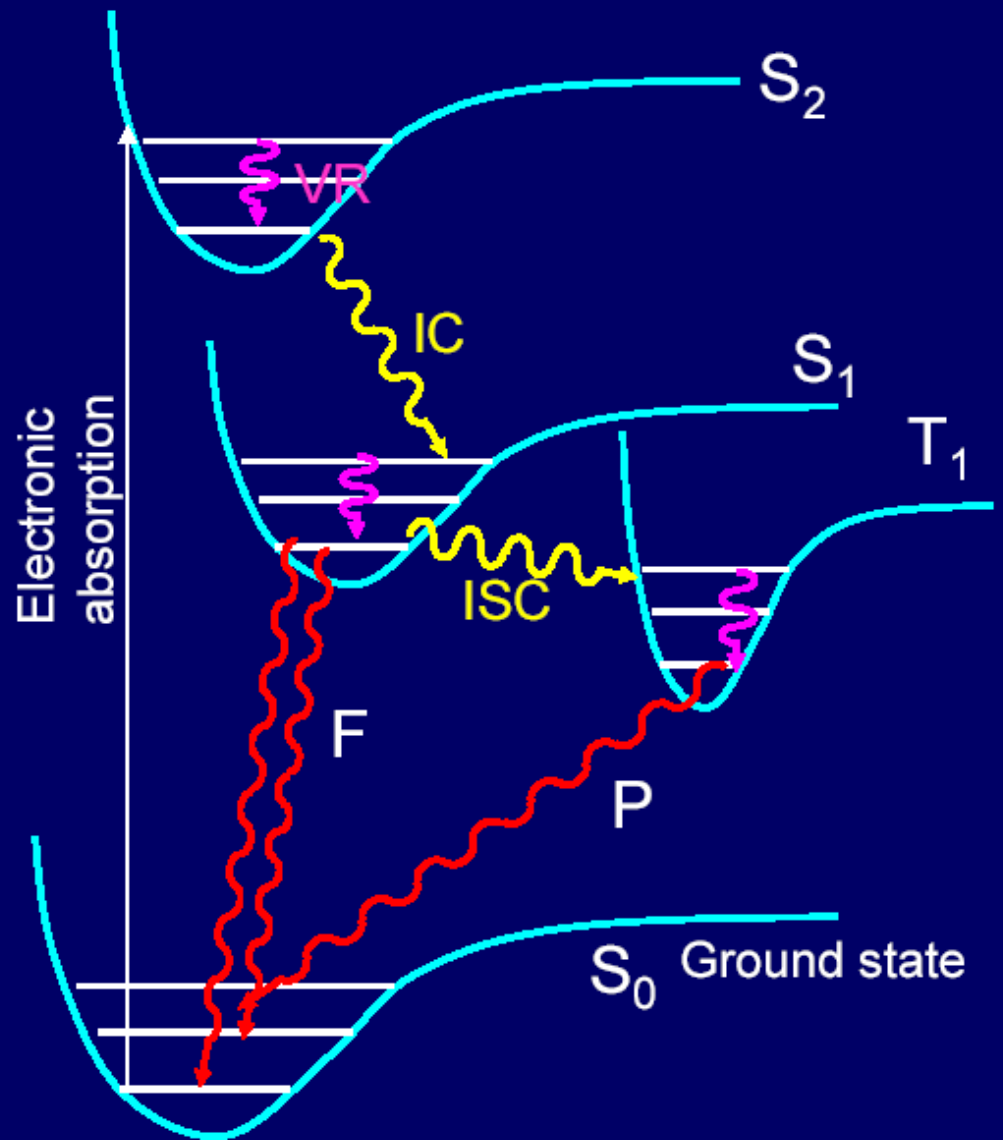
NEXMD v2.0



Outline

- General quantum-chemical approaches for excited state modeling: from handling electronic correlations to theoretical spectroscopy.
- Modeling excited state dynamics: Non-adiabatic drivers, coherences, convergence.
- Modeling of time-resolved spectroscopy: Transient-Absorption Spectroscopy of dendrimers.
- The emergence of machine learning for excited state modeling. Triplet excitations example.
- Environment-aware Hamiltonian models: machine learning for minimalistic quantum chemistry.

Properties of Absorption and Emission

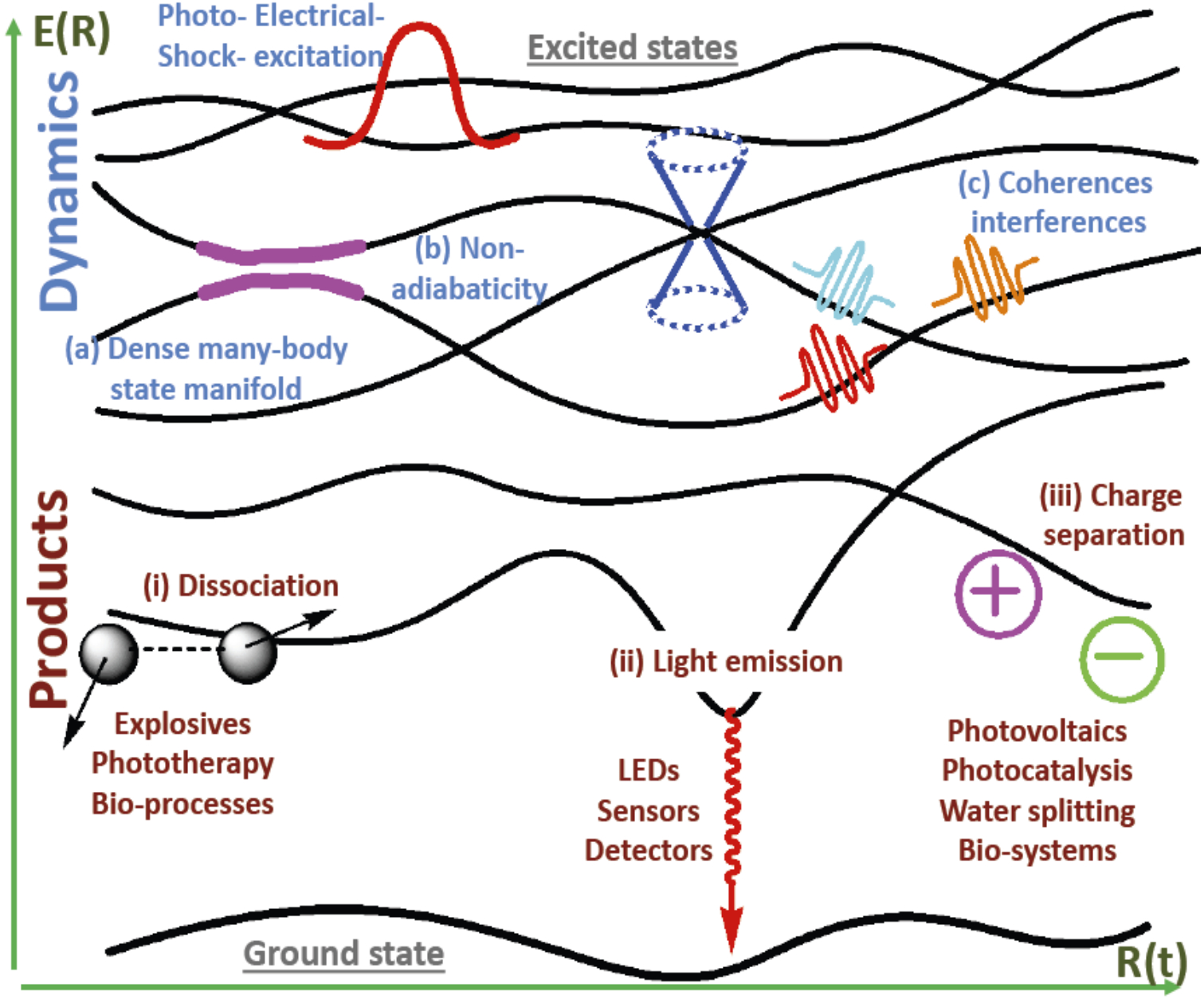


Absorption starts from the lowest vibrational level of the ground state

Fluorescence is red shifted (called Stokes shift) and is independent of excitation wavelength

The lifetime of phosphorescence is much longer than that of fluorescence

Photoexcited dynamics

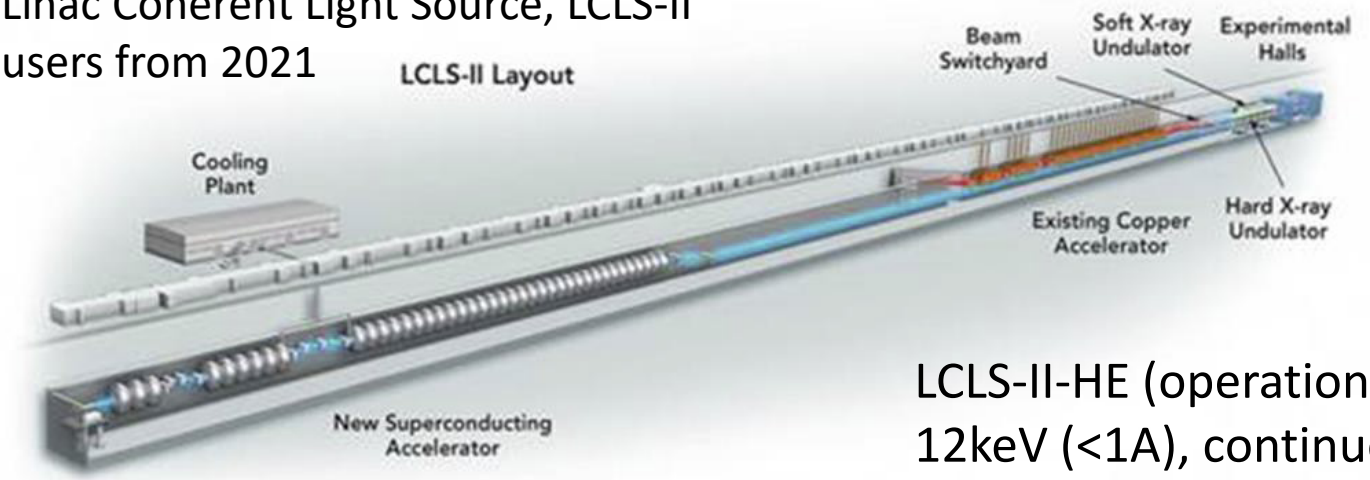


Excited state relaxation timescales:

- ❑ Phosphorescence decay ~ 1ms
- ❑ Fluorescence decay ~ 1ns
- ❑ Intersystem crossing ~ 1μs
- ❑ Nonradiative relaxation ~ 10ps
- ❑ Conical inter-section ~ 100fs

Probing time and space: X-Ray lasers

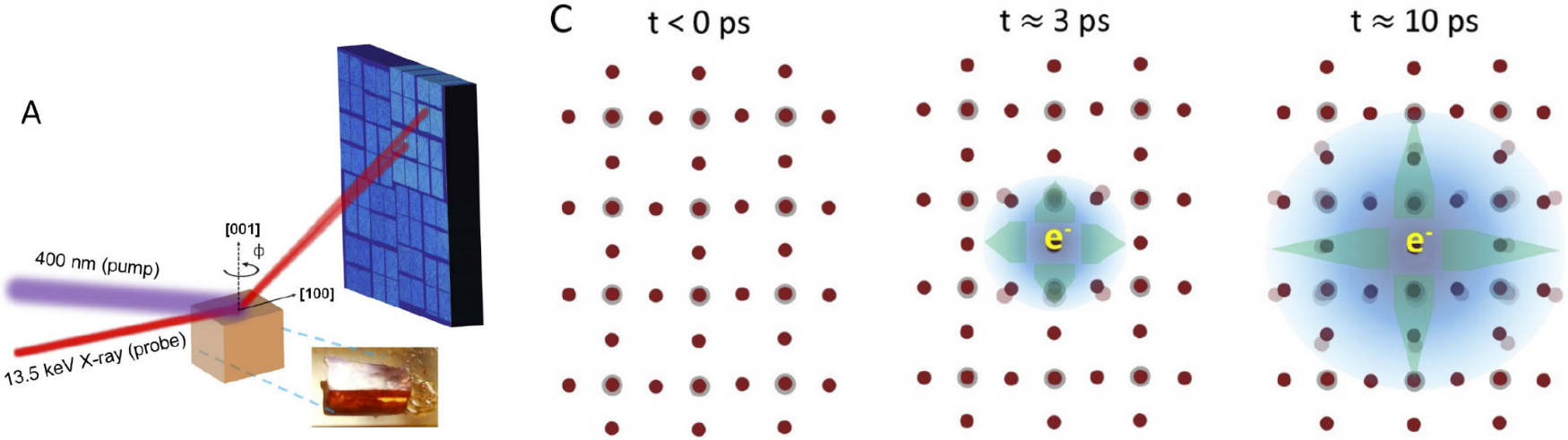
Linac Coherent Light Source, LCLS-II users from 2021



X-ray wavelengths extend down to the atomic scale, while x-ray pulse durations now lie in the femtosecond range.

LCLS-II-HE (operational from 2024): beyond 12keV (<1A), continuous pulse train (1 MHz).

Visualization of polaronic effects in halide perovskites



B. Guzelturk, T. Winkler, T. Van de Goor, M. D. Smith, S. A. Bourelle, S. Feldmann, M. Trigo, S. Teitelbaum, H-G. Steinruck, G. A. de la Pena, R. Alonso-Mori, D. Zhu, T. Sato, H. I. Karunadasa, M. F. Toney, F. Deschler, A. M. Lindenberg, Nature Materials (2021, https://doi.org/10.1038/s41563-020-00865-5)

Spectroscopy (very incomplete list)

A MAJOR experimental tool to get information about the material:

- Electronic uv-vis spectroscopy: optical properties , electronic states;

- Time- and frequency- resolved nonlinear spectroscopies: dynamics of electronic system; rates, transport of energy and charges;

- Vibrational spectroscopy (Raman and IR): nuclei degrees of freedom and their dynamics

- Terahertz spectroscopy: dynamics of charges and low frequency vibrations;

- NMR (Nuclei Magnetic Resonance): structural information;

- EPR (Electron Paramagnetic Resonance) and ESR (Electron Spin Resonance) spectroscopy: spin dynamics in systems with unpaired electrons;

- PES (Photoemission Spectroscopy), also known as photoelectron spectroscopy: binding of electrons to material;

- XPS (X-ray photoelectron spectroscopy): elemental analysis of surface composition;

- STS (Scanning Tunneling Spectroscopy): density of electrons in a sample as a function of their energy;

- Etc.

General quantum-chemical approaches for excited state modeling: from handling electronic correlations to theoretical spectroscopy

General considerations

- Our material is composed from nuclei and electrons bound by Coulomb interactions
- Separate electronic (fast) from nuclei (slow) motion (adiabatic or Born-Oppenheimer approximation)
- Electronically excited state: any solution of the Schrodinger equation below but higher than the lowest energy solution (ground state)
- Solve the Schrodinger equation for molecular electronic Hamiltonian:

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

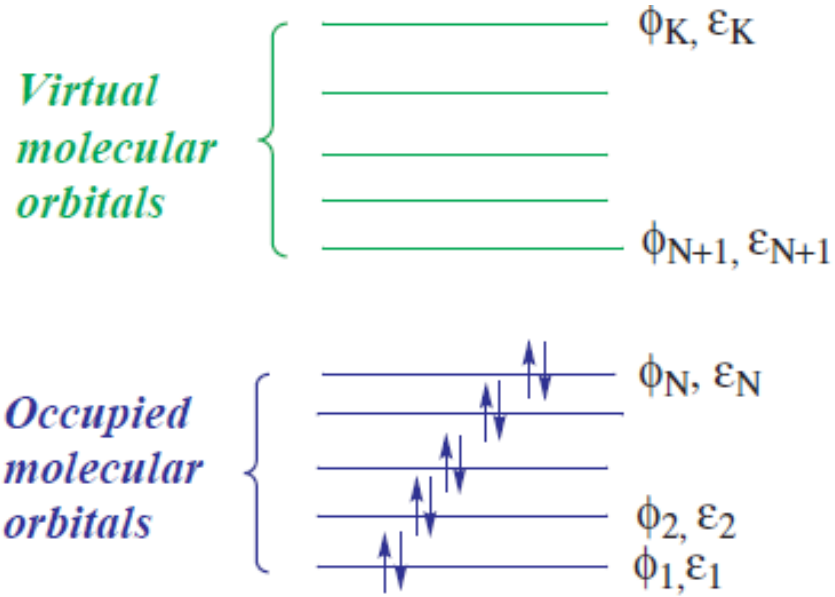
Method	*Hamiltonian*	*Wavefunction*	*Cost*
Ab initio ***(e.g. HF, CAS-CI, CC-EOM)***	***Exact***	***Approximate*** ***(All electronic correlations)***	***Large*** ***(~10 atoms)***
Density Functional ***(e.g. DFT, TDDFT)***	***Approximate, F(ρ),*** ***(All electronic correlations)***	***Fixed*** ***(Kohn-Sham 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/DFT procedure

For simplicity, assume an even number of electrons (closed shell)

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)

$$FC = SC\varepsilon$$

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!

A basic approach CIS (or Tamm-Dancoff)

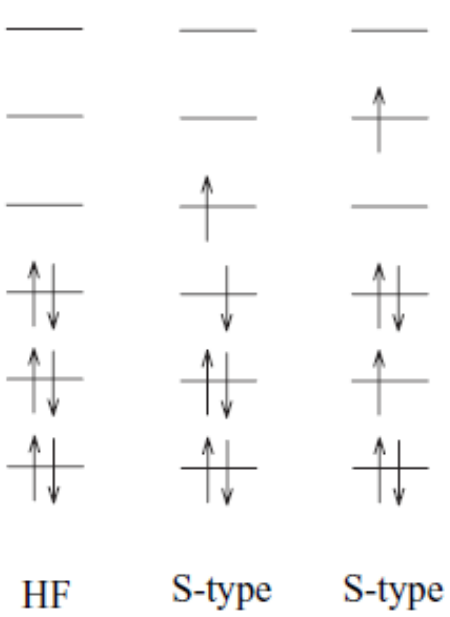
Build the wavefunction as a superposition of singly excited determinants (these are orthogonal to the HF reference state)

$$\Psi_k = \sum_{i}^{\text{occupied}} \sum_{a}^{\text{virtual}} c_{iak} \Psi_i^a$$

	Ψ_{HF}	Ψ_i^a
Ψ_{HF}	E_{HF}	0
Ψ_i^a	0	***CIS matrix A*** dense

diagonalization ⟹

	Ψ_{HF}	Ψ_i^a
Ψ_{HF}	E_{HF}	0
Ψ_i^a	0	E_1 ⋱ E_Ω



E_1, E_2, … are energies of excited states at the CIS level

Bottom line: relatively simple approach accounting for some electronic correlations (e.g., excitonic effects). Performance semiempirical CIS varies (ZINDO is usually accurate). Ab initio CIS is not accurate – transition energies are significantly shifted to the blue.

More accurate wavefunction approaches

Spin-Flip Equation-of-Motion Coupled-Cluster Electronic Structure Method for a Description of Excited States, Bond Breaking, Diradicals, and Triradicals

ANNA I. KRYLOV*

VOL. 39, NO.

Higher order CI methods (e.g. CISD)

Coupled Cluster (CC) methods (e.g. EOM-CCSD)

Ground state models:

SCF : $\Psi=\Phi_0=|\varphi_1 \ldots \varphi_n\rangle$

MP2 : SCF + T_2 by PT

CCSD: $\Psi=\exp(T_1+T_2)\,\Phi_0$

CCSD(T): CCSD + T_3 by PT

CCSDT: $\Psi=\exp(T_1+T_2+T_3)\,\Phi_0$

.....

Excited state models:

$\Psi_{ex}=R_1\,\Psi_0$ **(CIS)**

CIS + R_2 by PT **[CIS(D)]**

$\Psi_{ex}=(R_1+R_2)\Psi_0$ **(EOM-CCSD)**

$\Psi_{ex}=(R_1+R_2+R_3)\Psi_0$ **(EOM-CCSDT)**

.....

FCI: $\Psi=(1+T_1+T_2+\ldots+T_n)\Phi_0$ - exact!

Time-dependent methods

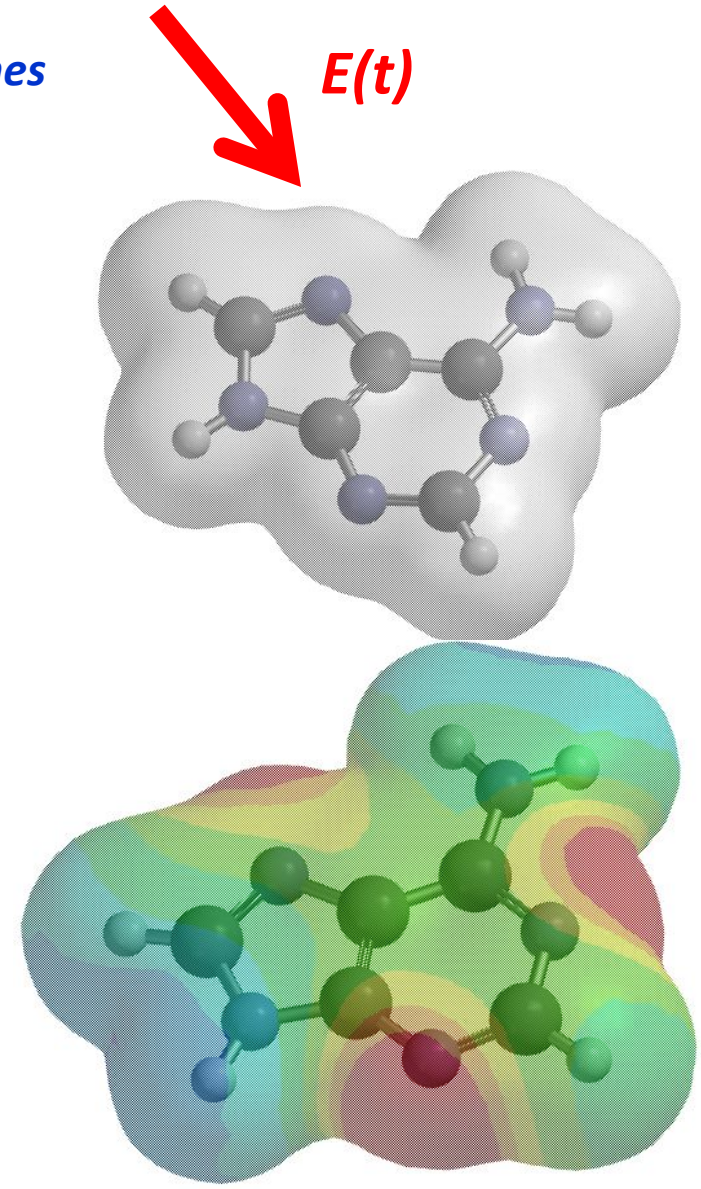
From HF reference state: ***time-dependent Hartree-Fock (TDHF) or Random Phase Approximation (RPA), sometimes approximated by CIS or Tamm-Dancoff approach***

From DFT Kohn-Sham reference state: ***time-dependent Density Functional Theory (TDDFT), sometimes approximated by Tamm-Dancoff approach***

General idea: introduce a weak perturbation (time-dependent electric field) and write equation of motion for a single-electron density matrix (Hamilton-Liouville's form):

$$i\frac{d\rho}{dt} = \{H_T, \rho\}$$

- Due to field the density will be oscillating;
- Excited electronic states will appear as resonant frequencies of these oscillations, i.e. peaks in the Fourier transform of the long trajectory;
- Beside time domain (time-dependent trajectories), excited state properties can be found directly in the frequency-domain by diagonalizing a specific matrix (operator), e.g., CIS matrix.

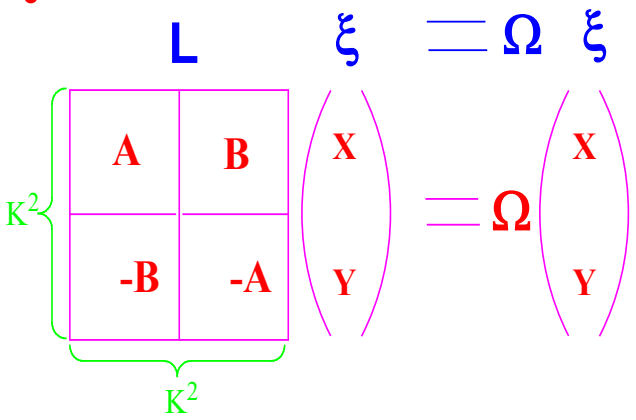


Mathematical aspects….

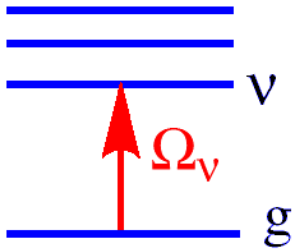
➢ *TD equation of motion:*

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

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



A, X - CIS (particle-hole) part



➢ *Electronic normal modes or transition densities*

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

➢ *Krylov subspace algorithms (e.g. Davidson, Lanczos)*

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

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

➢ **Scaling of computational effort:**

- ***Time*** **~N³**
- ***Memory*** **~N²**

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

What about spectroscopy?

If we will neglect vibronic effects, to compute absorption spectra one needs transition frequencies and transition densities. The latter can be used to calculate transition dipole moments and oscillator strengths related to the absorption of individual electronic states

Transition dipole moments

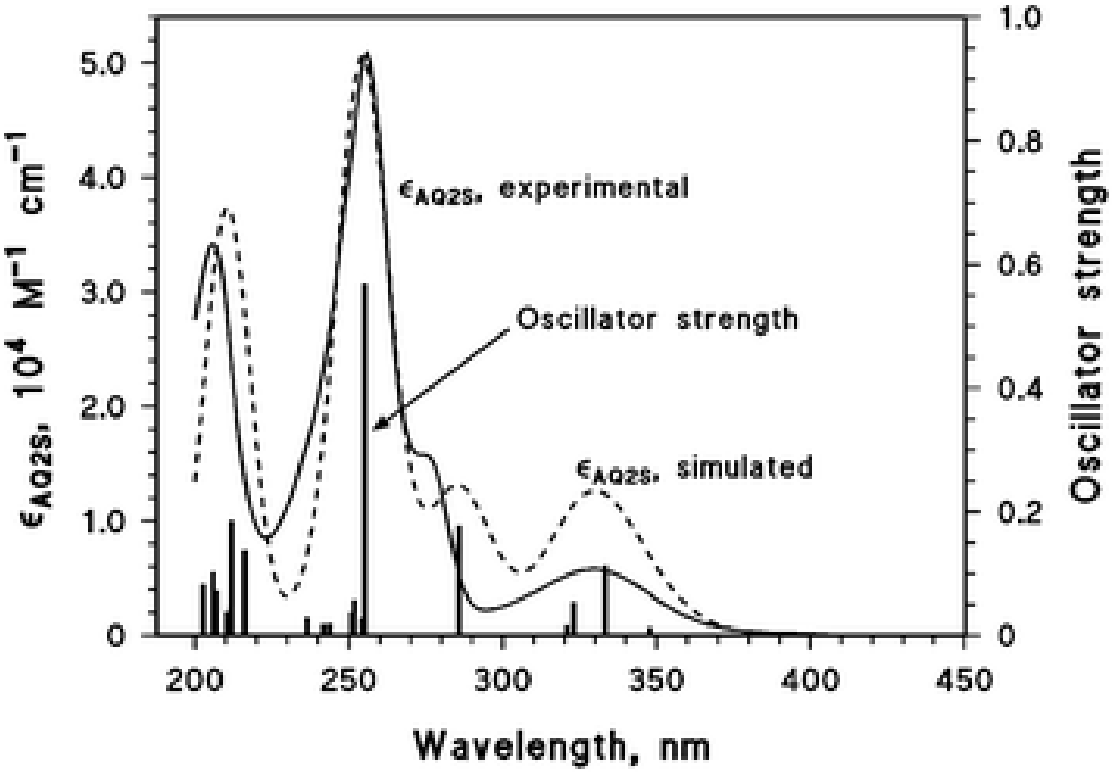
$$\boldsymbol{\mu}_\alpha = Tr(\boldsymbol{\mu}\xi_\alpha)$$

Oscillator strength:

$$f_\alpha \sim \frac{2}{3}\Omega_\alpha((\mu_x)^2_\alpha + (\mu_y)^2_\alpha + (\mu_z)^2_\alpha)$$

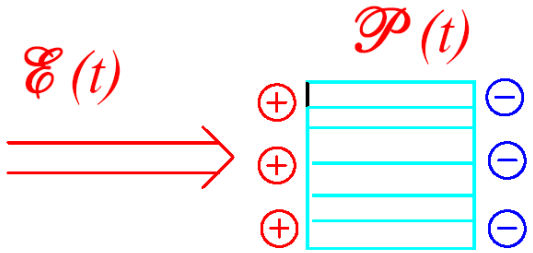
Approximation for calculated absorption profile using empirical broadening:

$$\alpha(\omega) = \sum_\nu \frac{2\Omega_\nu \mu_{g\nu}\mu^*_{g\nu}}{\Omega^2_\nu - (\omega + i\Gamma)^2}$$



A. Bedini et al., Photochem. Photobiol. Sci., 2012,**11**, 1445-1453

Linear and nonlinear optical responses



Optical polarizability

$$\mathcal{P} = \alpha\mathcal{E} + \beta\mathcal{E}^2 + \gamma\mathcal{E}^3 + \cdots$$

$$\mathcal{P}_i(\omega) = \mu_i^{(0)} + \alpha_{ij}(\omega)\cdot\mathcal{E}_j(\omega) + \frac{1}{2!}\beta_{ijk}(\omega=\omega_1+\omega_2)\cdot\mathcal{E}_j(\omega_1)\cdot\mathcal{E}_k(\omega_2) + \frac{1}{3!}\gamma_{ijkl}(\omega=\omega_1+\omega_2+\omega_3)\cdot\mathcal{E}_j(\omega_1)\cdot\mathcal{E}_k(\omega_2)\cdot\mathcal{E}_l(\omega_3)$$

Examples:

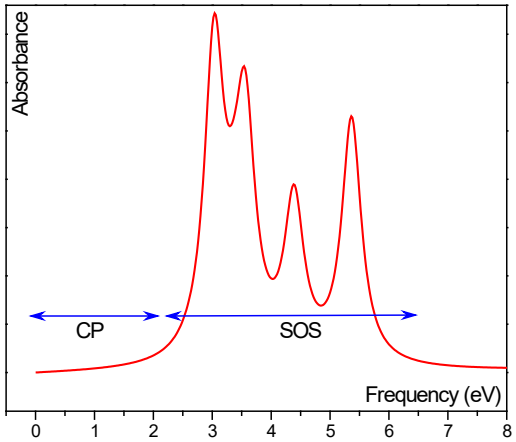
- **Re [α(ω)]** - *linear refraction*
- **Im [α(ω)]** - *linear absorption*
- **Re [β(ω,ω)]** - *second harmonic generation*
- **Re [γ(ω,ω,ω)]** - *third harmonic generation*
- **Im [γ(ω,0,0)]** - *electro-absorption (Stark effect)*
- **Im [γ(ω,ω,–ω)]** - *two-photon absorption*
- **Re [γ(ω,ω,0)]** - *EFISHG*
- *etc.*

How to calculate optical responses

Derivative (coupled-perturbed, CP) approaches:

$$\alpha_{ij} = -\frac{\partial^2 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \qquad \beta_{ijk} = -\frac{\partial^3 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k}$$

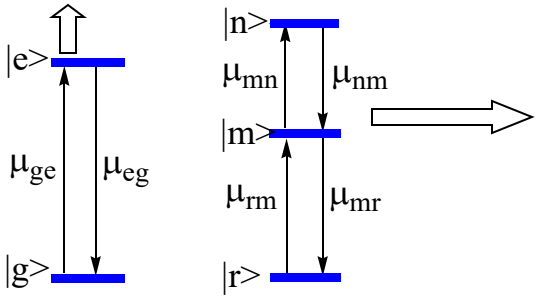
$$\gamma_{ijkl} = -\frac{\partial^4 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k \partial \mathcal{E}_l}$$



H. Sekino, R.J. Bartlett, J. Chem. Phys., 98, 3022 (1993)

Time-dependent (sum-over-state, SOS) approaches:

$$\alpha(\omega) = \sum_{e} \frac{2E_{ge}\mu_{ge}^2}{E_{ge}^2 - (\omega + i\Gamma_{ge})^2}$$

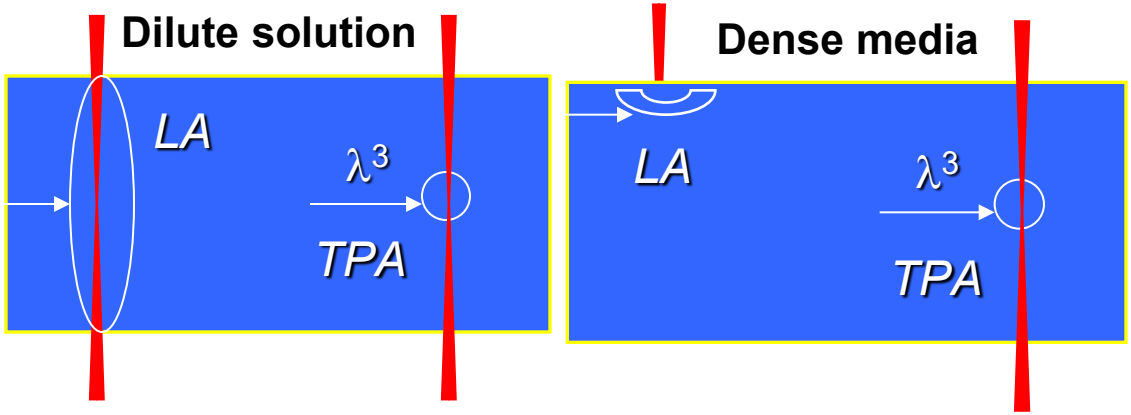


$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{6}\left(\frac{h}{2\pi}\right)^{-3}\sum_{\text{perm}}\Bigg[\sum_{m,n,p(\neq r)} \frac{\langle r|\mu_i|m\rangle\langle m|\bar{\mu}_j|n\rangle\langle n|\bar{\mu}_k|p\rangle\langle p|\mu_l|r\rangle}{(\omega_{mr}-\omega_\sigma-i\Gamma_{mr})(\omega_{nr}-\omega_2-\omega_3-i\Gamma_{nr})(\omega_{pr}-\omega_3-i\Gamma_{pr})} -$$

$$\sum_{m,n(\neq r)} \frac{\langle r|\mu_i|m\rangle\langle m|\mu_j|r\rangle\langle r|\mu_k|n\rangle\langle n|\mu_l|r\rangle}{(\omega_{mr}-\omega_\sigma-i\Gamma_{mr})(\omega_{nr}-\omega_3-i\Gamma_{nr})(\omega_{nr}+\omega_2-i\Gamma_{nr})}\Bigg]$$

B.J. Orr, J.F. Ward, Mol. Phys. 20, 513 (1971) J.L. Bredas, et al. Chem. Rev., 94, 243 (1994)

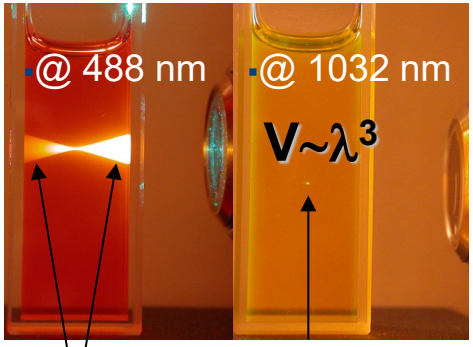
Non-linear spectroscopy, two-photon absorption

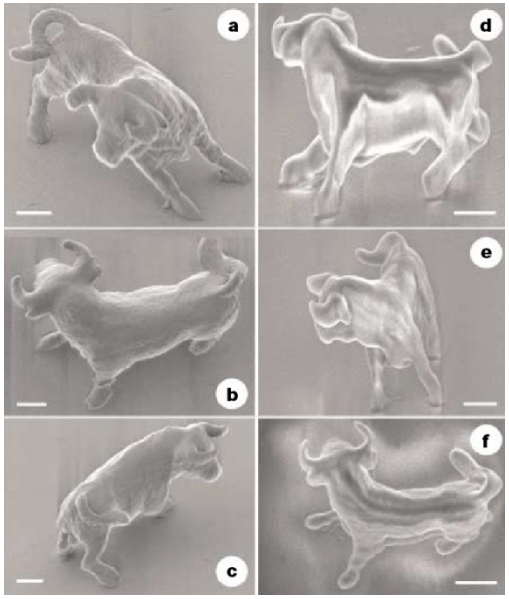


Linear vs. two photon absorption

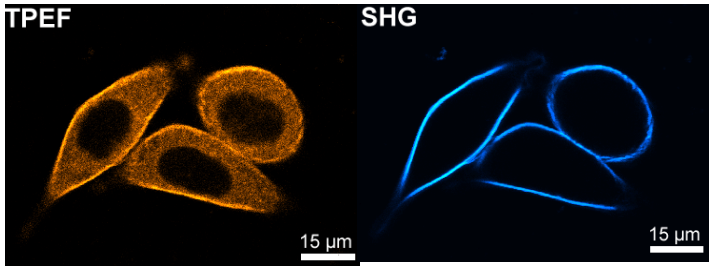
Linear Absorption (LA) $\sigma_{LA} \sim \mathrm{Im}\langle\alpha(\omega)\rangle \sim I$

Two-Photon Absorption (TPA) $\sigma_{TPA} \sim \mathrm{Im}\langle\gamma(\omega,\omega,-\omega)\rangle \sim I^2$





Microfabrication by TPA induced polymerization at subdiffraction-limit resolution: 7x10 μm (size of a blood cell) Kawata S, Sun HB, Tanaka T, Takada K: Nature, 412, 697 (2001)



Scanning fluorescence microscopy, in vivo imaging: J. Neuroscience, 24, 999 (2004)

Derivative technique (Jensen):

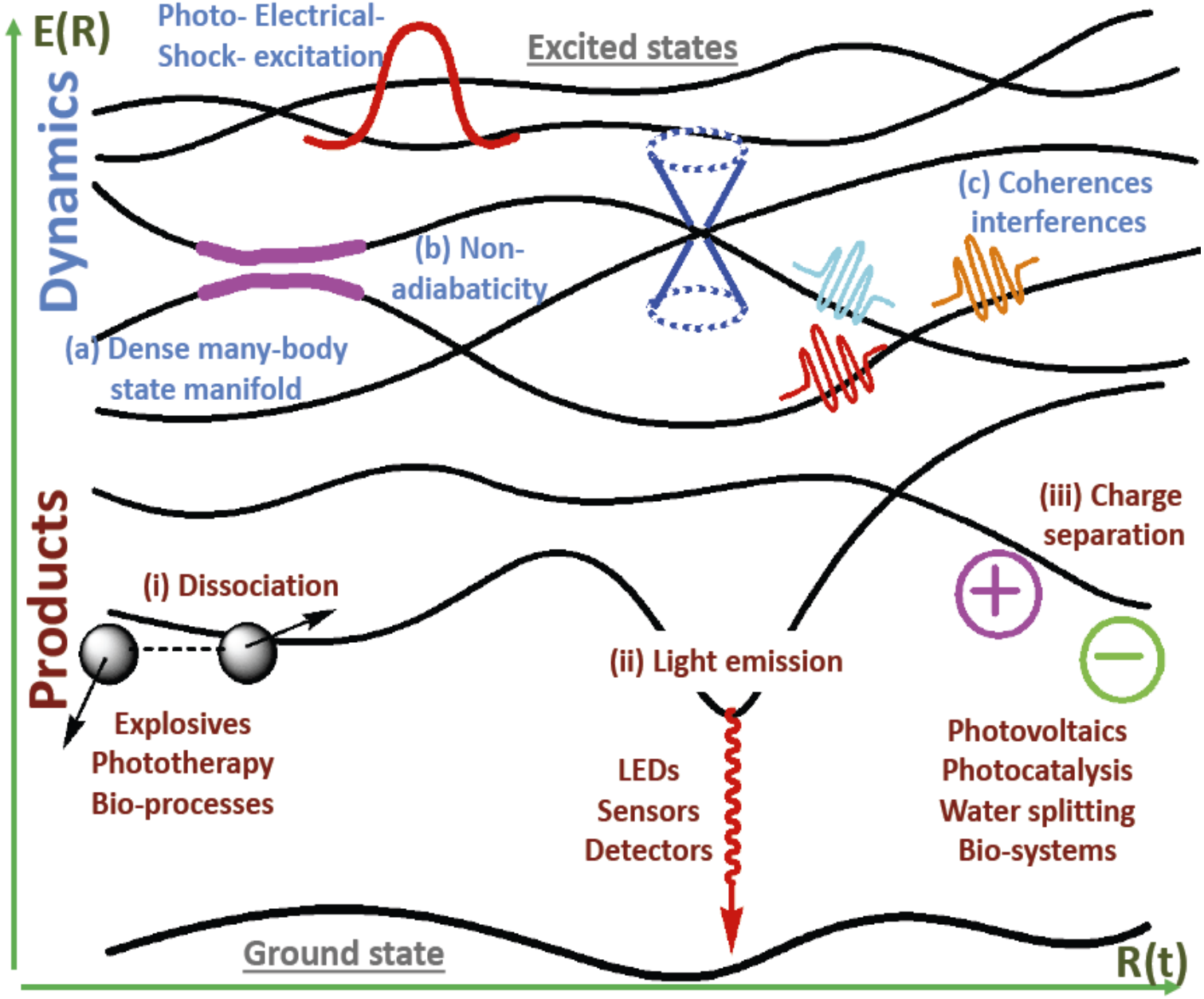
Table 10.1 Examples of properties that may be calculated as derivatives of the energy

n_F	n_B	n_I	n_R	Property
0	0	0	0	Energy
1	0	0	0	Electric dipole moment
0	1	0	0	Magnetic dipole moment
0	0	1	0	Hyperfine coupling constant
0	0	0	1	Molecular (nuclear) gradient
2	0	0	0	Electric polarizability
0	2	0	0	Magnetizability
0	0	2	0	Nuclear spin–spin coupling
0	0	0	2	Harmonic vibrational frequencies
1	0	0	1	Infrared absorption intensities
1	1	0	0	Optical rotation, circular dichroism
0	1	1	0	Nuclear magnetic shielding
3	0	0	0	(first) Electric hyperpolarizability
0	3	0	0	(first) Hypermagnetizability
0	0	0	3	(cubic) Anharmonic corrections to vibrational frequencies
2	0	0	1	Raman intensities
3	0	0	1	Hyper-Raman effects
2	1	0	0	Magnetic circular dichroism (Faraday effect)
1	0	0	2	Infrared intensities for overtone and combination bands
4	0	0	0	(second) Electric hyperpolarizability
0	4	0	0	(second) Hypermagnetizability
0	0	0	4	(quartic) Anharmonic corrections to vibrational frequencies
2	0	0	2	Raman intensities for overtone and combination bands
2	2	0	0	Cotton–Mutton effect

$$\text{Property} \propto \frac{\partial^{n_F+n_B+n_I+n_R} E}{\partial \mathbf{F}^{n_F} \partial \mathbf{B}^{n_B} \partial \mathbf{I}^{n_I} \partial \mathbf{R}^{n_R}}$$

The effect of small perturbations to the ground state can be calculated via appropriate derivatives

Photoexcited dynamics



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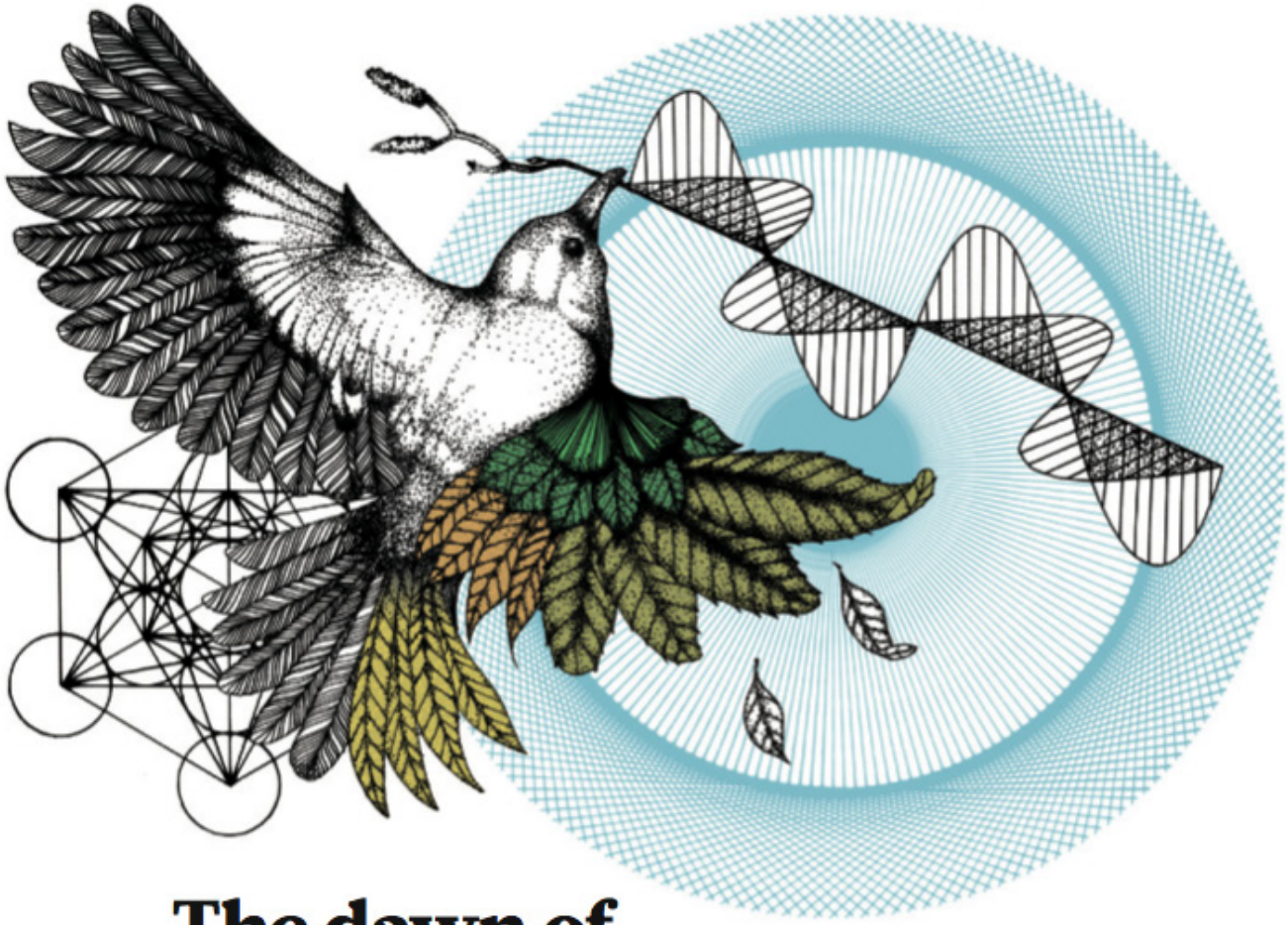


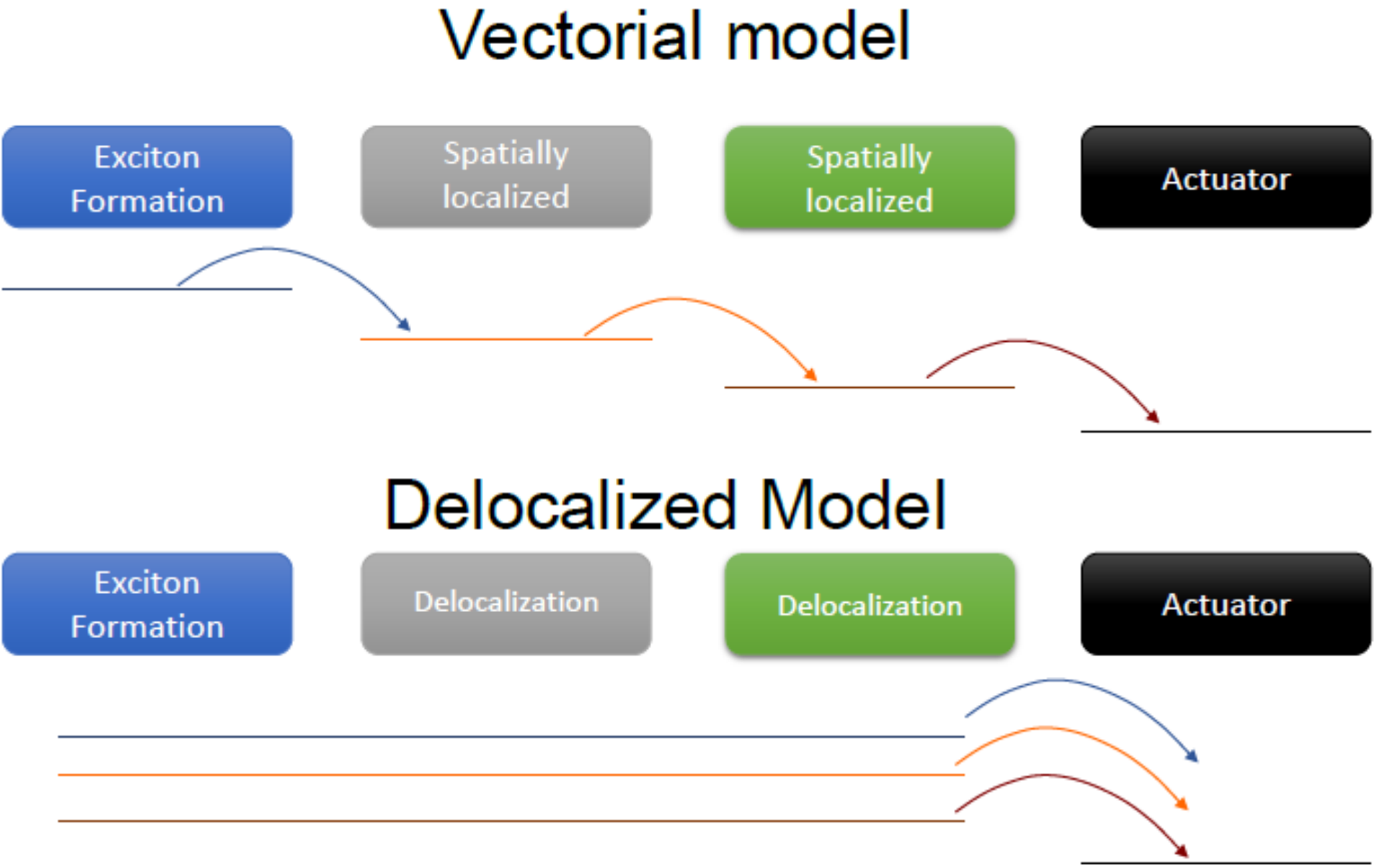
The dawn of quantum biology

The key to practical quantum computing and high-efficiency solar cells may lie in the messy green world outside the physics lab.

BY PHILIP BALL

Nature 474:272–274 (2011)

Light harvesting -> sensitization pathways



Modeling excited state dynamics: Non-adiabatic drivers, coherences, convergence

T. Nelson, A. White, J. Bjorgaard, A. Sifain, Y. Zhang, B. Nebgen, S. Fernandez-Alberti, D. Mozyrsky, A. Roitberg and S. Tretiak, Chem. Rev. 120, 2215 (2020)

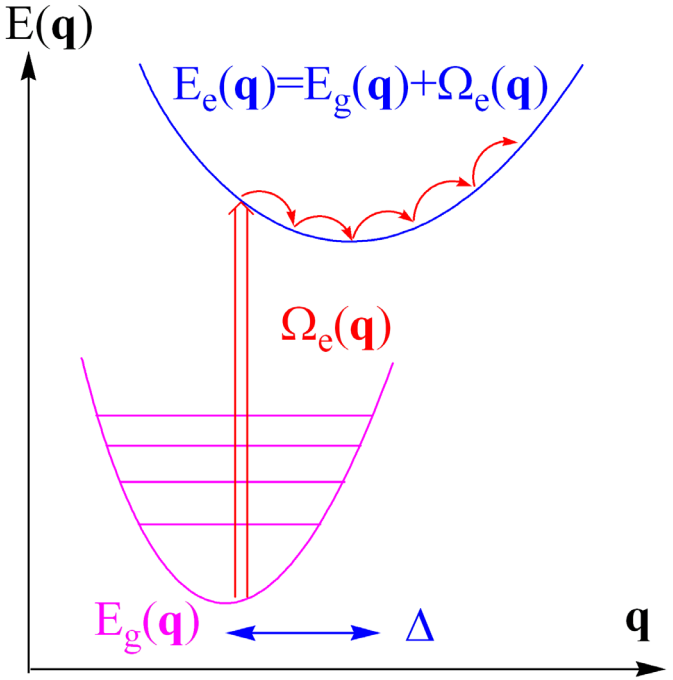
NEXMD 1.0:
J. Chem. Theory Comput. 16, 5771 (2020)

NEXMD 2.0:
J. Chem. Theory Comput. 19, 5356 (2023)

NWChem:
J. Chem. Theory Comput., 19, 7077 (2023)

Excited state molecular dynamics

➢ ***Born-Oppenheimer* (mixed Quantum-Classical) Dynamics:**



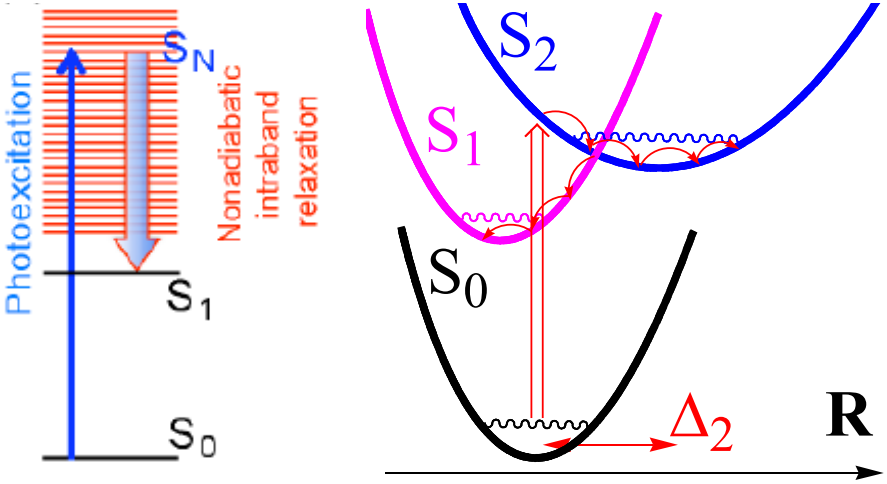
Langevin equation of motion for nuclei

$$M_i\ddot{\mathbf{R}}_i(t) = -\nabla E_\alpha(\mathbf{R}(t)) - \zeta M_i\dot{\mathbf{R}}_i(t) + \mathbf{A}(t)$$

Mass, acceleration ***Force*** ***Viscosity*** ***Stochastic force***

S. Tretiak, A. Saxena, R.L. Martin and A. R. Bishop, Phys. Rev. Lett. 89, 97402 (2002)

➢ ***Non-adiabatic dynamics with Quantum Transitions:***

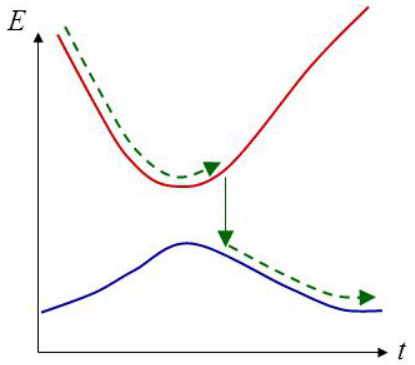


$$\mathbf{d}_{\alpha\beta} = \langle\phi_\alpha(R)|\nabla_R\phi_\beta(R)\rangle$$

- **Non-adiabatic couplings define transition probability between states**
- **Run ensembles of trajectories (wavepacket) to statistically determine the relaxation rate**

T. Nelson, A. White, J. Bjorgaard, A. Sifain, Y. Zhang, B. Nebgen, S. Fernandez-Alberti, D. Mozyrsky, A. Roitberg and S. Tretiak, Chem. Rev. 120, 2215 (2020)

Trajectory surface hopping

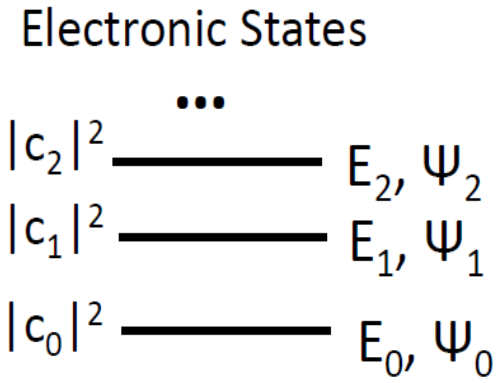


Main Idea: Monte-Carlo

1) Set electrons in ***one*** of the states (n) and evaluate force according to $F=-\partial E_n/\partial x$ and propagate ions for time Δt

2) Propagate occupation probabilities for electrons according to Schrodinger equation

$$i\hbar\partial_t c_n + \sum_m d_{mn}\dot{x}c_m = E_n c_n$$

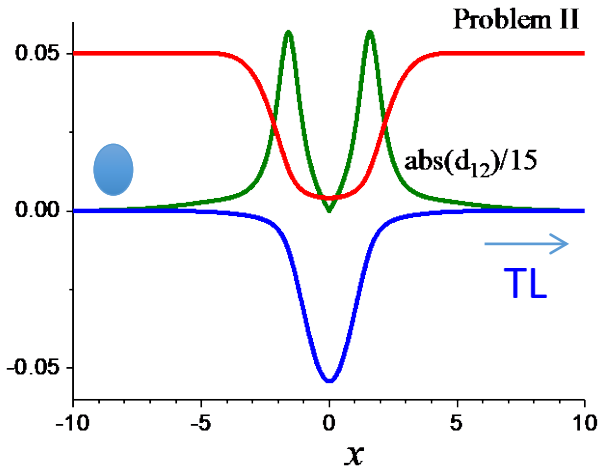


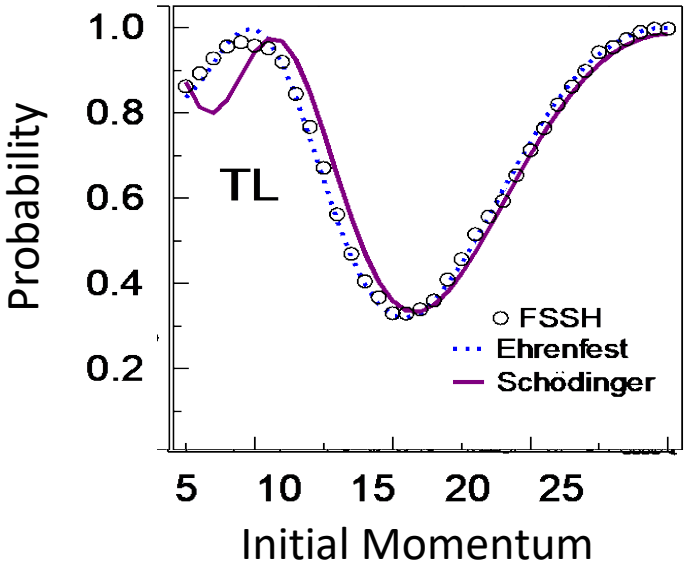
3) "Toss a coin" according to probabilities determined in Step 2. If no switch occurs, go to step 1.

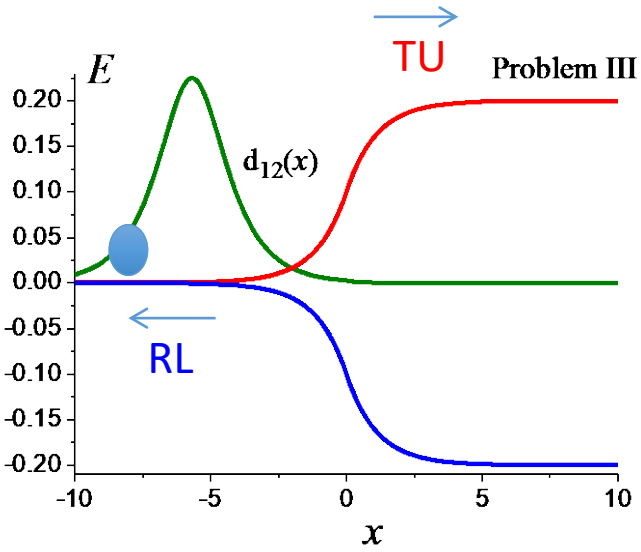
4) If switch occurs, make sure energy is satisfied. If not, discard the switch. If yes, set electrons in the new state and proceed with Step 1.

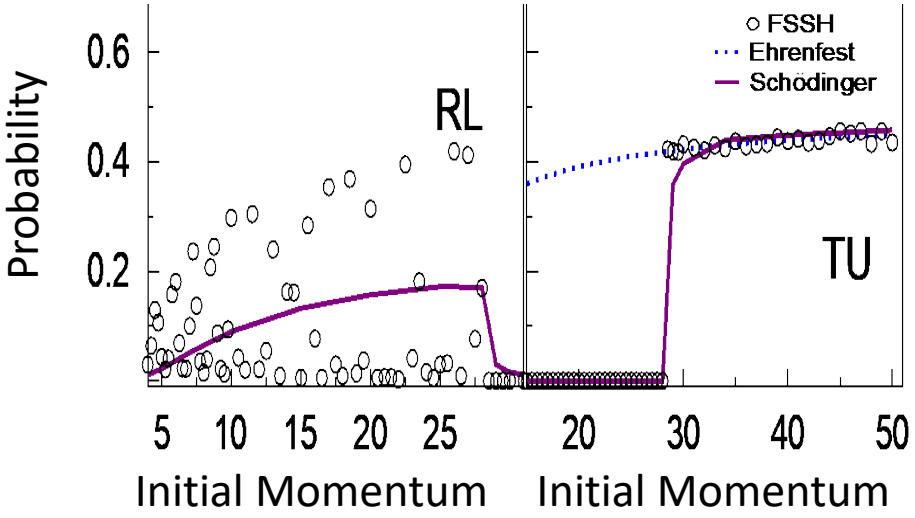
J. Tully, J. Chem. Phys. 93, 1061 (1990)

Failure of FSSH and Ehrenfest to describe coherences and interferences









Multiconfigurational Ehrenfest approach (MCE)

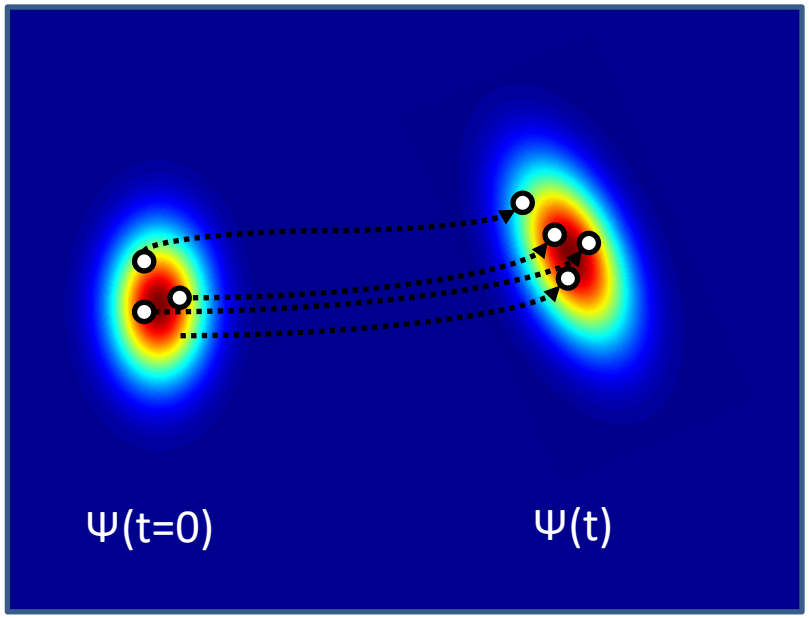
- ***Trajectory guided basis allows to run on the fly dynamics***

The wavefunction in a trajectory-guided basis

$$|\Psi(t)\rangle = \sum_n c_n(t)|\psi_n(t)\rangle .$$

with

$$|\psi_n(t)\rangle = |\chi_n(t)\rangle \left(\sum_I a_I^{(n)}(t) \left| \phi_I^{(n)} \right\rangle \right)$$



Trajectory guided grid

nuclear part: *Gaussian wave-packet moving along an Ehrenfest trajectory*

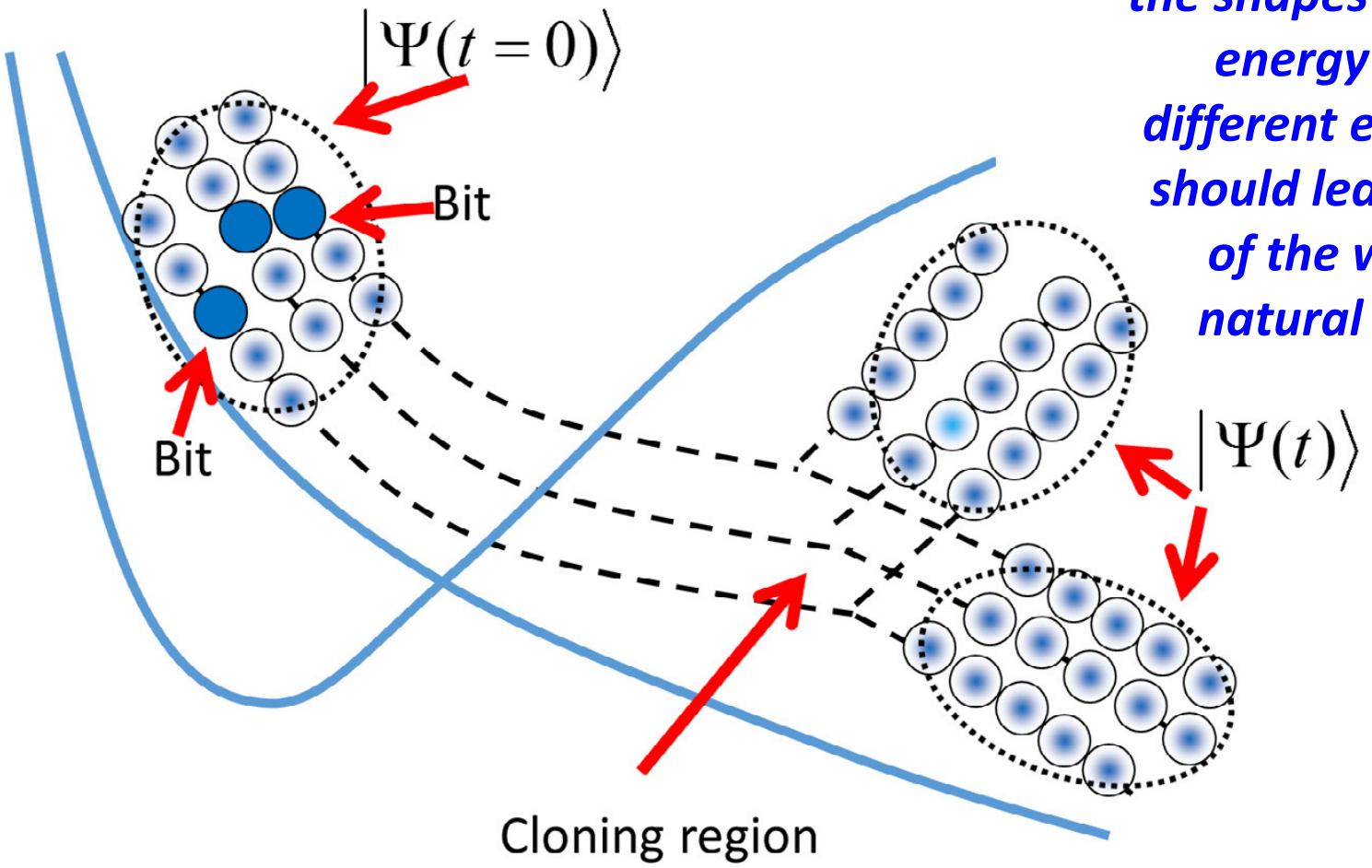
electronic part: *superposition of several electronic eigenstates*

$$\chi_n(\mathbf{R},t) = \left(\frac{2\alpha}{\pi}\right)^{N_{\mathrm{dof}}/4} \exp\left(-\alpha(\mathbf{R}-\bar{\mathbf{R}}_n(t))^2 + \frac{i}{\hbar}\bar{\mathbf{P}}_n(t)(\mathbf{R}-\bar{\mathbf{R}}_n(t)) + \frac{i}{\hbar}\gamma_n(t) \right)$$

D. Shalashilin, Faraday Disc. 153, 105 (2011)

AIMC-MCE: Ab initio multiple cloning

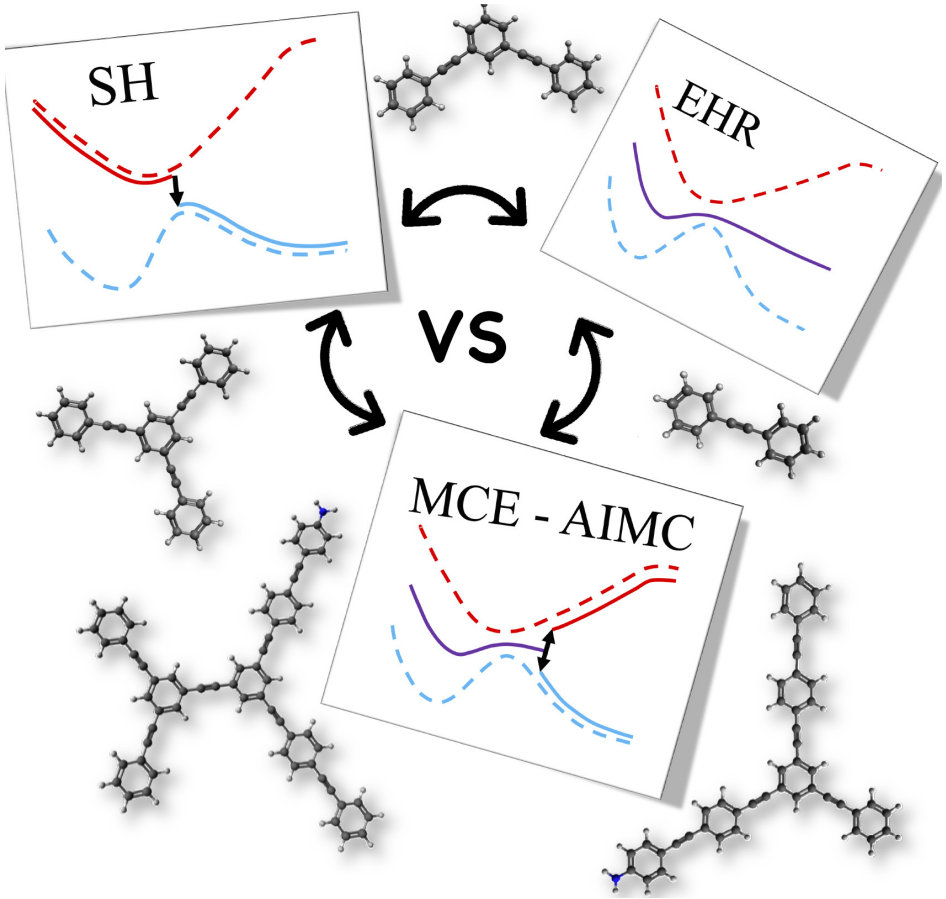
The difference between the shapes of the potential energy surfaces for different electronic states should lead to branching of the wave packet: natural decoherence

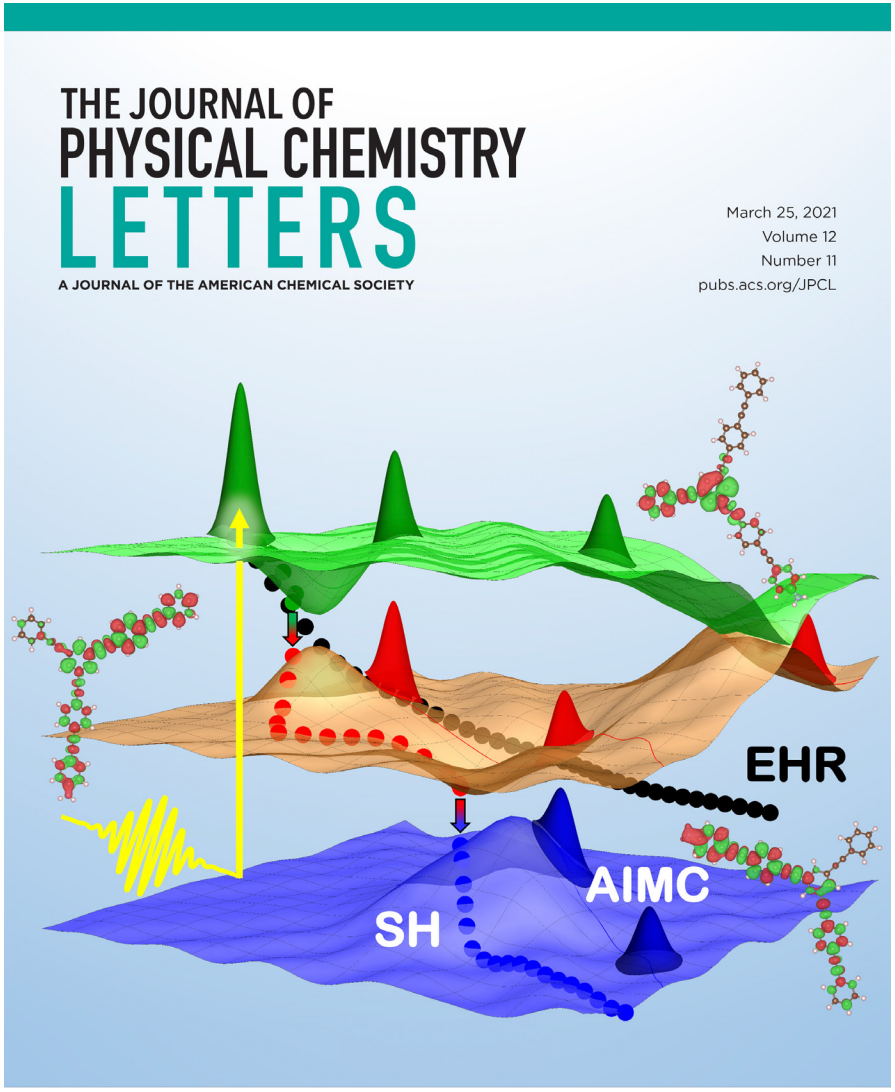


D. V. Makhov, W. J. Glover, T. J. Martinez and D. V. Shalashilin, J. Chem. Phys., 141, 054110 (2014)

V. M. Freixas S. Fernandez-Alberti, S. Tretiak, D. Shalashilin, Phys. Chem. Chem. Phys. 20, 17762 (2018)

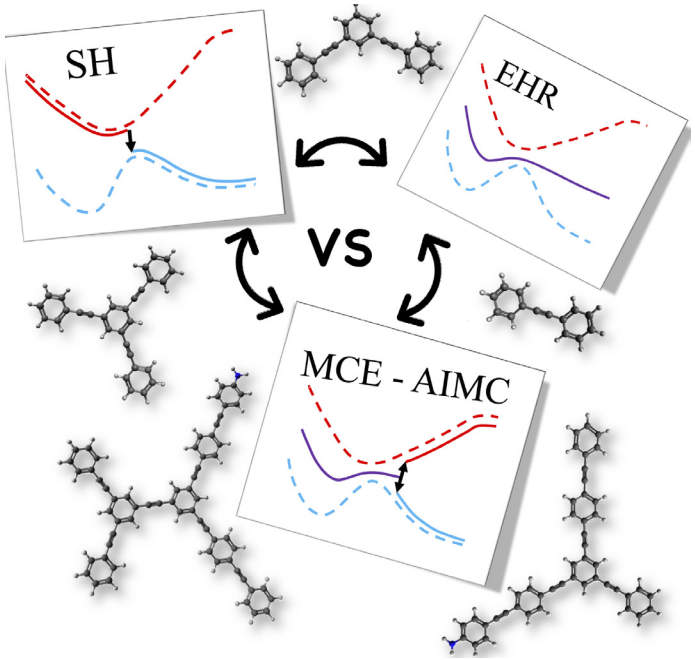
SH vs Ehr vs AIMC-MCE





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

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!)

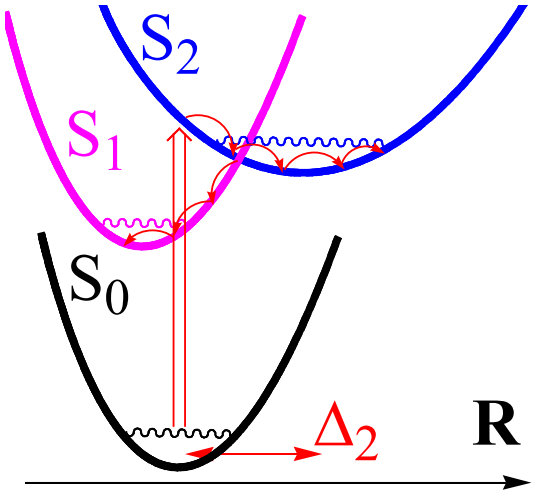
AIMC desirable – in between SH and Ehr

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)

Our current solution: NEXMD code

- *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/DFTB 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: calculations ~1000 atoms molecules and ~10ps timescales

T. Nelson, A. White, J. Bjorgaard, A. Sifain, Y. Zhang, B. Nebgen, S. Fernandez-Alberti, D. Mozyrsky, A. Roitberg and S. Tretiak, Chem. Rev. 120, 2215 (2020)

NEXMD 1.0:
J. Chem. Theory Comput. 16, 5771 (2020)

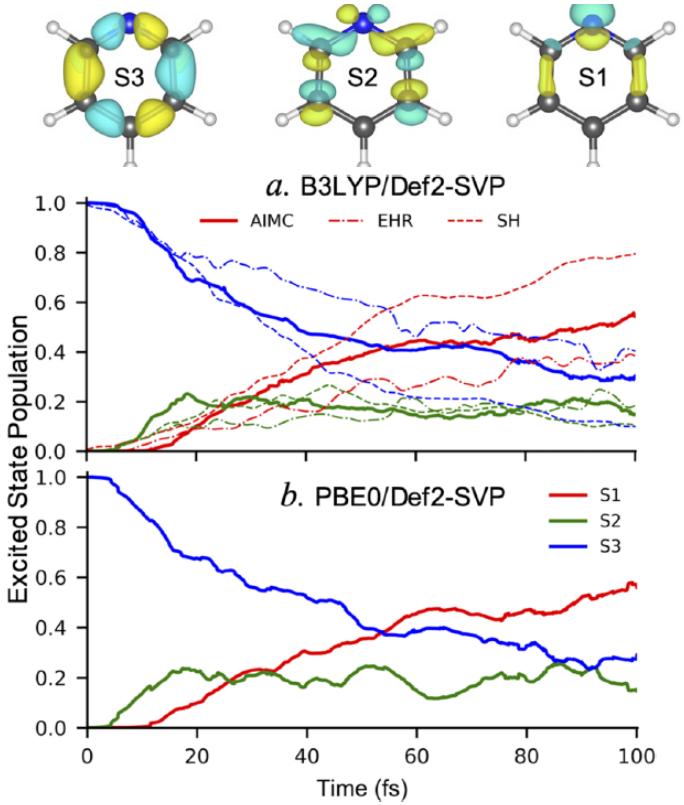
NEXMD 2.0:
J. Chem. Theory Comput. 19, 5356 (2023)

An expensive solution: NAMD in NWChem code

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

Software package

https://www.nwchem-sw.org



- ***Surface hopping (FSSH), Ehrenfest or ab initio multiple cloning with multiconfigurational Ehrenfest (AIMC-MCE);***
- **Efficient TDDFT calculations of the excited states at RPA or TDA level (Krylov space algorithms);**
- **Analytic AND numerical 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, solvation models (PCE or QM/MM).***

NAMD in NWChem: calculations ~50 atoms molecules and ~1ps timescales

H. Song, S. A. Fischer, Y. Zhang, C. J. Cramer, S. Mukamel, N. Govind, S. Tretiak, J. Chem. Theory Comput. 16, 6418 (2020)

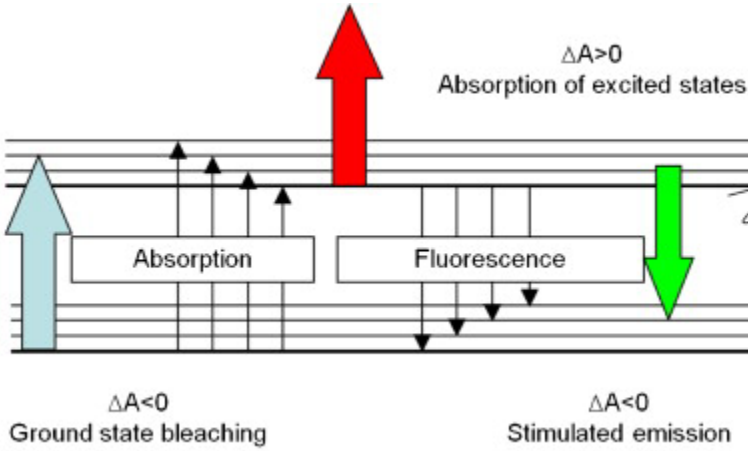
H. Song, V. M. Freixas, S. Fernandez-Alberti, A. J. White, Y. Zhang, S. Mukamel, N. Govind and S. Tretiak, J. Chem. Theory Comput., 17, 3629 (2021)

NWChem: J. Chem. Theory Comput., 19, 7077 (2023) https://doi.org/10.1021/acs.jctc.3c00421

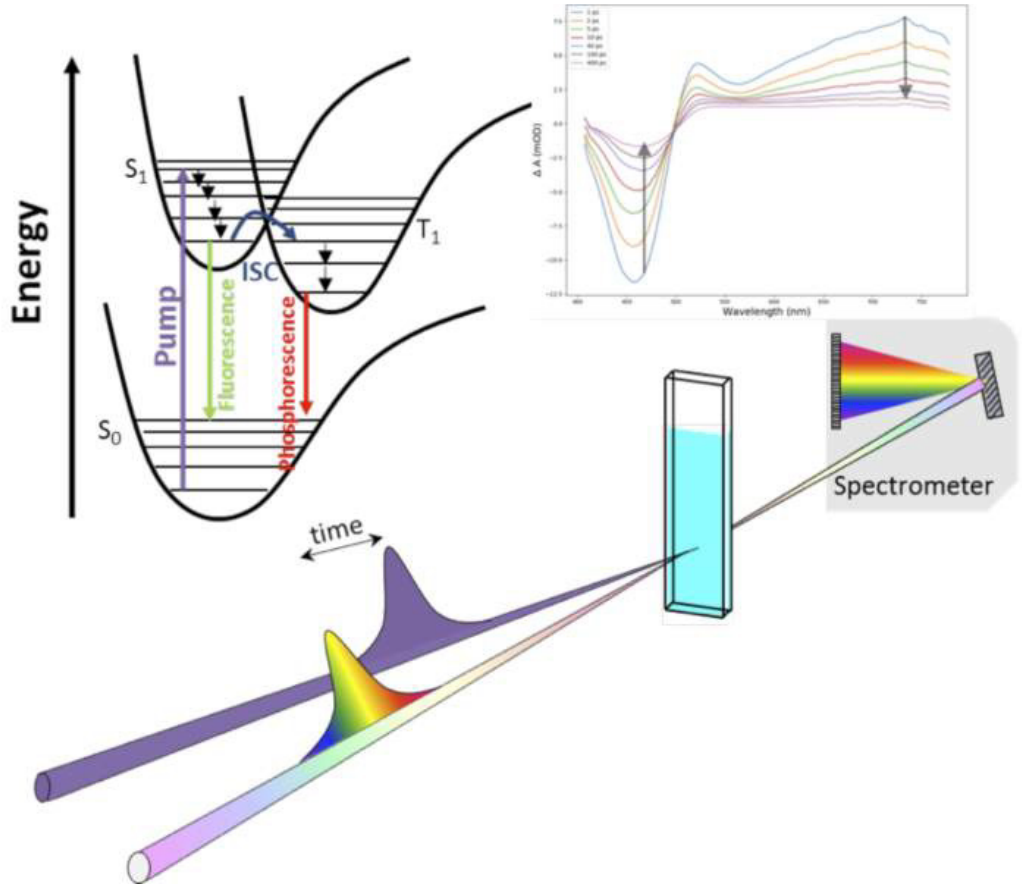
Modeling of time-resolved spectroscopy: Transient-Absorption Spectroscopy of Dendrimers

R. Perez-Castillo, V. M. Freixas, S. Mukamel, A. Martinez-Mesa, L. Uranga-Piña, S. Tretiak, M. F. Gelin, and S. Fernandez-Alberti, Chem. Sci., 15, 13250 (2024)

Transient absorption spectroscopy signals



Nonlinear signal probing population dynamics by taking a difference of signals in the presence/absence of pump pulse.



Distinct components of the signal can be separated:

- **Ground state bleaching (GSB)**
- **Stimulated emission (SE)**
- **Excited state absorption (ESA)**
- **Polarization dependence variances**

https://en.wikipedia.org/wiki/Time-resolved_spectroscopy

Doorway-window formalism

Evaluation of transient absorption pump-probe (TA-PP) through semiclassical trajectories (for NOW trajectory surface hopping only): includes sampling of initial nuclear coordinates/momenta and polarization-sensitive detection

Positively-defined doorway (window is defined in a similar way) function for each trajectory:

$$D_{in}(\boldsymbol{R}_0, \boldsymbol{P}_0, E_{pu}) = \mathcal{E}_{pu}^2\left(E_{pu} - E_{0\alpha}(\boldsymbol{R}_0)\right)|\boldsymbol{\mu}_{0\alpha}(\boldsymbol{R}_0)|^2$$

$$\mathcal{E}_{pu}\left(E_{pu} - E_{0\alpha}(\boldsymbol{R}_0)\right) = \exp\left[-2\pi^2\sigma^2\left(E_{pu} - E_{0\alpha}(\boldsymbol{R}_0)\right)^2\right]$$

$\mathcal{E}_{pu}(\omega)$ and E_{pu} are the spectrum and the carrier frequency of the pump pulse
$\boldsymbol{\mu}_{0\alpha}(\boldsymbol{R}_0)$ are transition dipole vectors between the ground state and excited states

Examples of 'typical parameters' for molecular example shown later:

$E_{pu} = 426\ nm$ (absorption max) with a Gaussian envelope $\mathcal{E}_{pu}(t) = \exp(-t^2/2\sigma^2)$ in the time domain with $\sigma = 42.5$ fs which corresponds to the FWHM (Full Width at Half Maximum) of 100 fs. Up to 300 excited state are needed for simulations.

M. F. Gelin, X. Huang, W. Xie, L. Chen, N. Došlić, W. Domcke, J. Chem. Theory Comput. 17, 2394 (2021)

Doorway-window formalism of TA-PP

Signal = GSB + SE + ESA

$$S_{int}^{(abcd)}(t, E_{pr}) \sim \langle \mathrm{D}^{(ab)}(\boldsymbol{R}_0) \left(W_0^{int(cd)}\left(\boldsymbol{R}_0(t), \boldsymbol{P}_0(t), E_{pr}\right) + W_I^{int(cd)}\left(\boldsymbol{R}_\alpha(t), \boldsymbol{P}_\alpha(t), E_{pr}\right) - W_{II}^{int(cd)}\left(\boldsymbol{R}_\alpha(t), \boldsymbol{P}_\alpha(t), E_{pr}\right)\right)\rangle ,$$

$$\mathrm{D}^{(ab)}(\boldsymbol{R}_0) = \frac{\mu_{0\alpha}^{(a)}(\boldsymbol{R}_0)\mu_{0\alpha}^{(b)}(\boldsymbol{R}_0)}{|\boldsymbol{\mu}_{0\alpha}(\boldsymbol{R}_0)|^2}$$

$$W_0^{int(cd)}\left(\boldsymbol{R}_0(t), \boldsymbol{P}_0(t), E_{pr}\right) = \mathcal{E}_{pr}^2 \left(E_{pr} - E_{0\alpha}(\boldsymbol{R}_0(t))\right) \mu_{0\alpha}^{(c)}(\boldsymbol{R}_0(t))\mu_{0\alpha}^{(d)}(\boldsymbol{R}_0(t))$$

$$W_I^{int(cd)}\left(\boldsymbol{R}_\alpha(t), \boldsymbol{P}_\alpha(t), E_{pr}\right) = \mathcal{E}_{pr}^2 \left(E_{pr} - E_{0\alpha}(\boldsymbol{R}_\alpha(t))\right) \mu_{0\alpha}^{(c)}(\boldsymbol{R}_\alpha(t))\mu_{0\alpha}^{(d)}(\boldsymbol{R}_\alpha(t))$$

$$W_{II}^{int(cd)}\left(\boldsymbol{R}_\alpha(t), \boldsymbol{P}_\alpha(t), E_{pr}\right) = \mathcal{E}_{pr}^2 \left(E_{pr} - E_{\alpha\beta}(\boldsymbol{R}_\alpha(t))\right) \mu_{\alpha\beta}^{(c)}(\boldsymbol{R}_\alpha(t))\mu_{\alpha\beta}^{(d)}(\boldsymbol{R}_\alpha(t))$$

$a, b, c, d = x, y, z$ correspond to orientation of the transition dipole moments

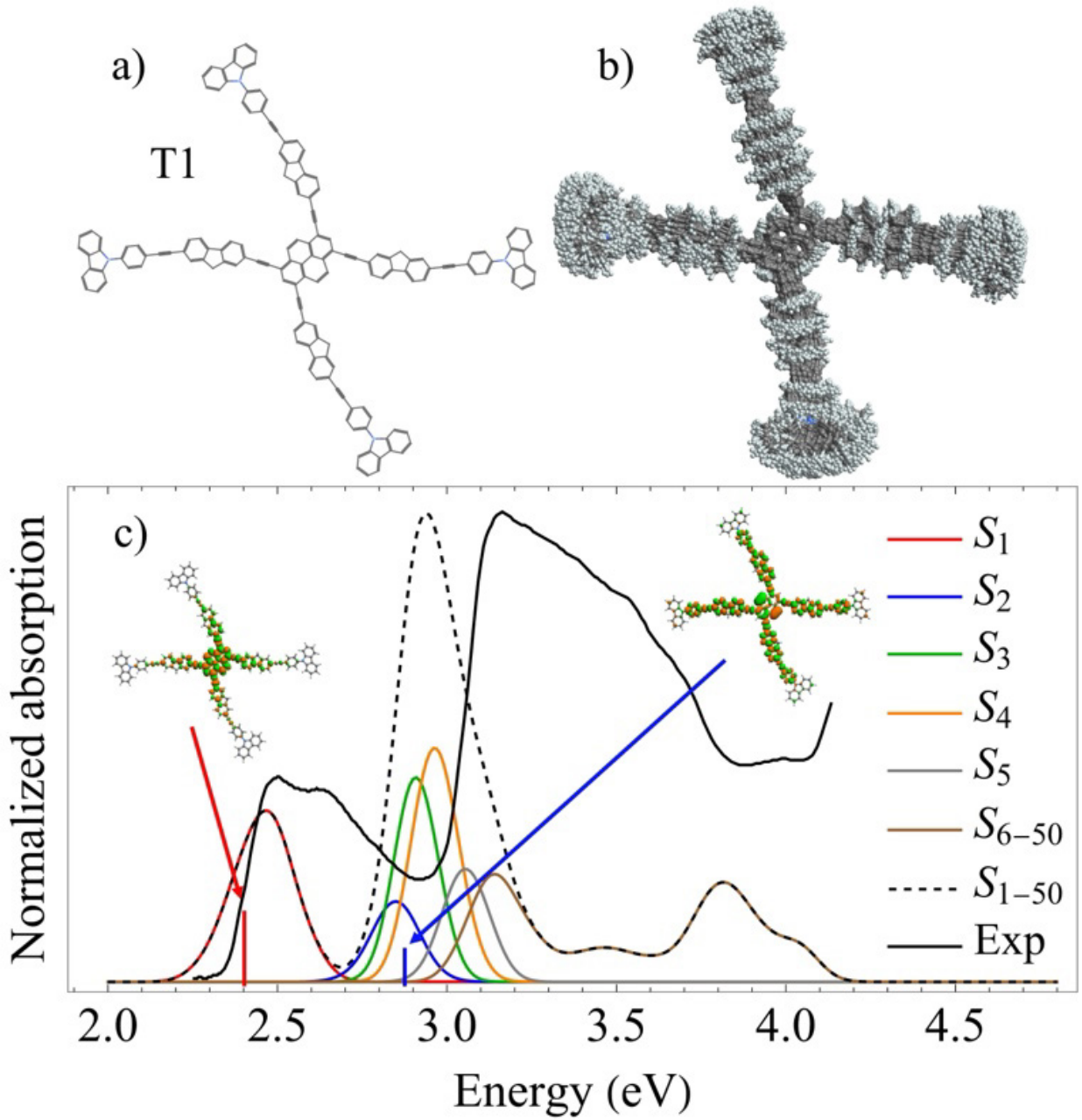
0 and α, β are ground and excited electronic states,

$\boldsymbol{R}_0, \boldsymbol{P}_0,$ and $\boldsymbol{R}_\alpha(t), \boldsymbol{P}_\alpha(t)$ are nuclear positions and momenta in these states

$E_{0\alpha}(\boldsymbol{R}_0(t))$ and $E_{\alpha\beta}(\boldsymbol{R}_\alpha(t))$ are the gaps between the electronic energies along trajectories

M. F. Gelin, X. Huang, W. Xie, L. Chen, N. Došlić, W. Domcke, J. Chem. Theory Comput. 17, 2394 (2021)

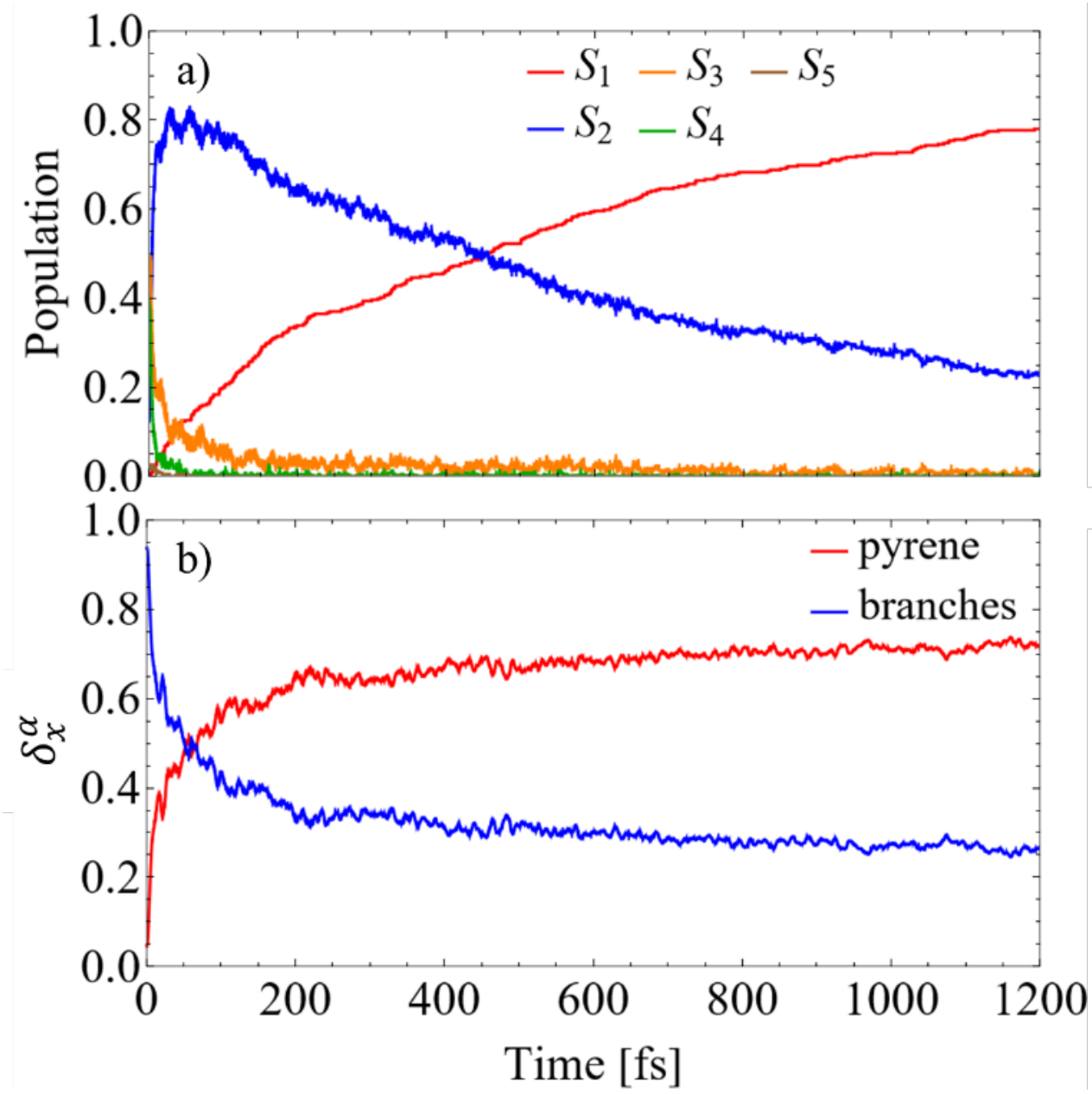
Molecule and absorption spectra



T-1 dendrimer: conformational structure at ambient conditions, absorption spectra and transition density orbital picture.

R. Perez-Castillo, V. M. Freixas, S. Mukamel, A. Martinez-Mesa, L. Uranga-Piña, S. Tretiak, M. F. Gelin, and S. Fernandez-Alberti, Chem. Sci., 15, 13250 (2024)

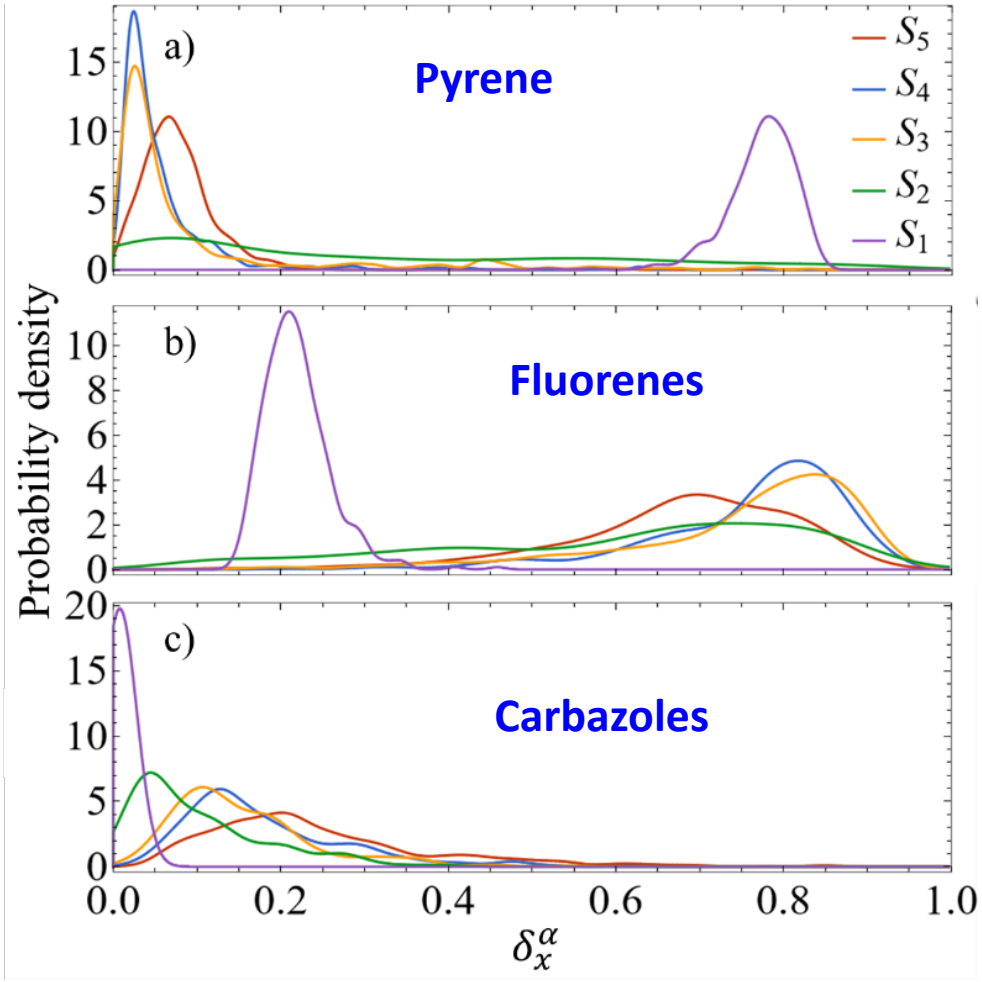
Non-adiabatic dynamics

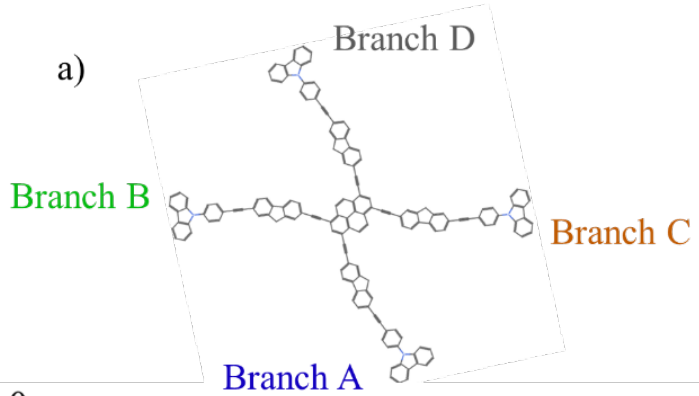


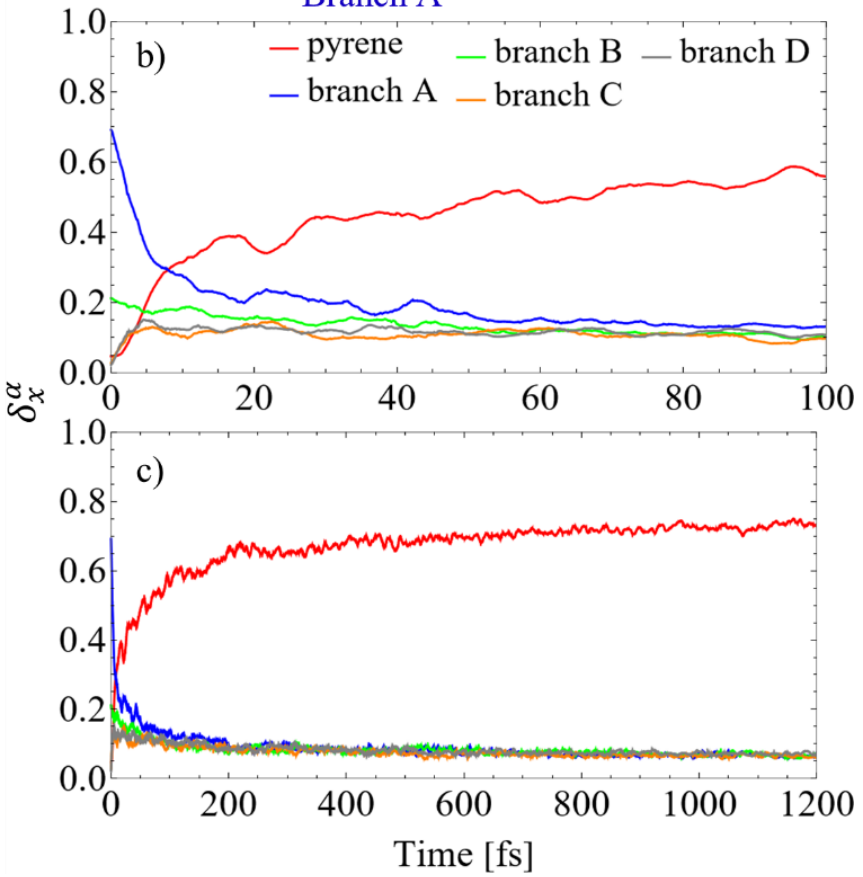
Non-adiabatic population relaxation dynamics reflects energy transfer from periphery to the center

R. Perez-Castillo, V. M. Freixas, S. Mukamel, A. Martinez-Mesa, L. Uranga-Piña, S. Tretiak, M. F. Gelin, and S. Fernandez-Alberti, Chem. Sci., 15, 13250 (2024)

Spatial localization of electronic excitation

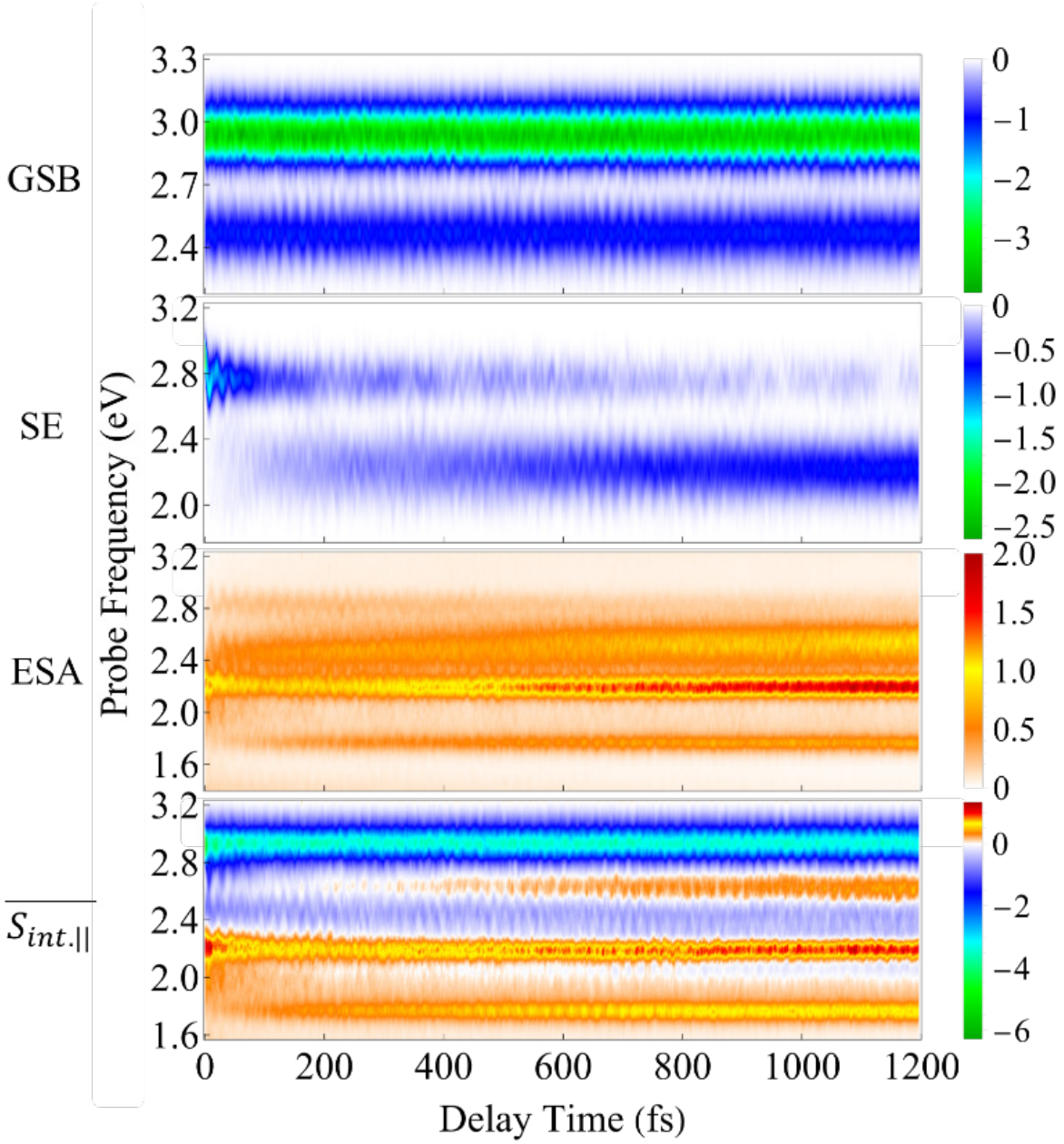






R. Perez-Castillo, V. M. Freixas, S. Mukamel, A. Martinez-Mesa, L. Uranga-Piña, S. Tretiak, M. F. Gelin, and S. Fernandez-Alberti, Chem. Sci., 15, 13250 (2024)

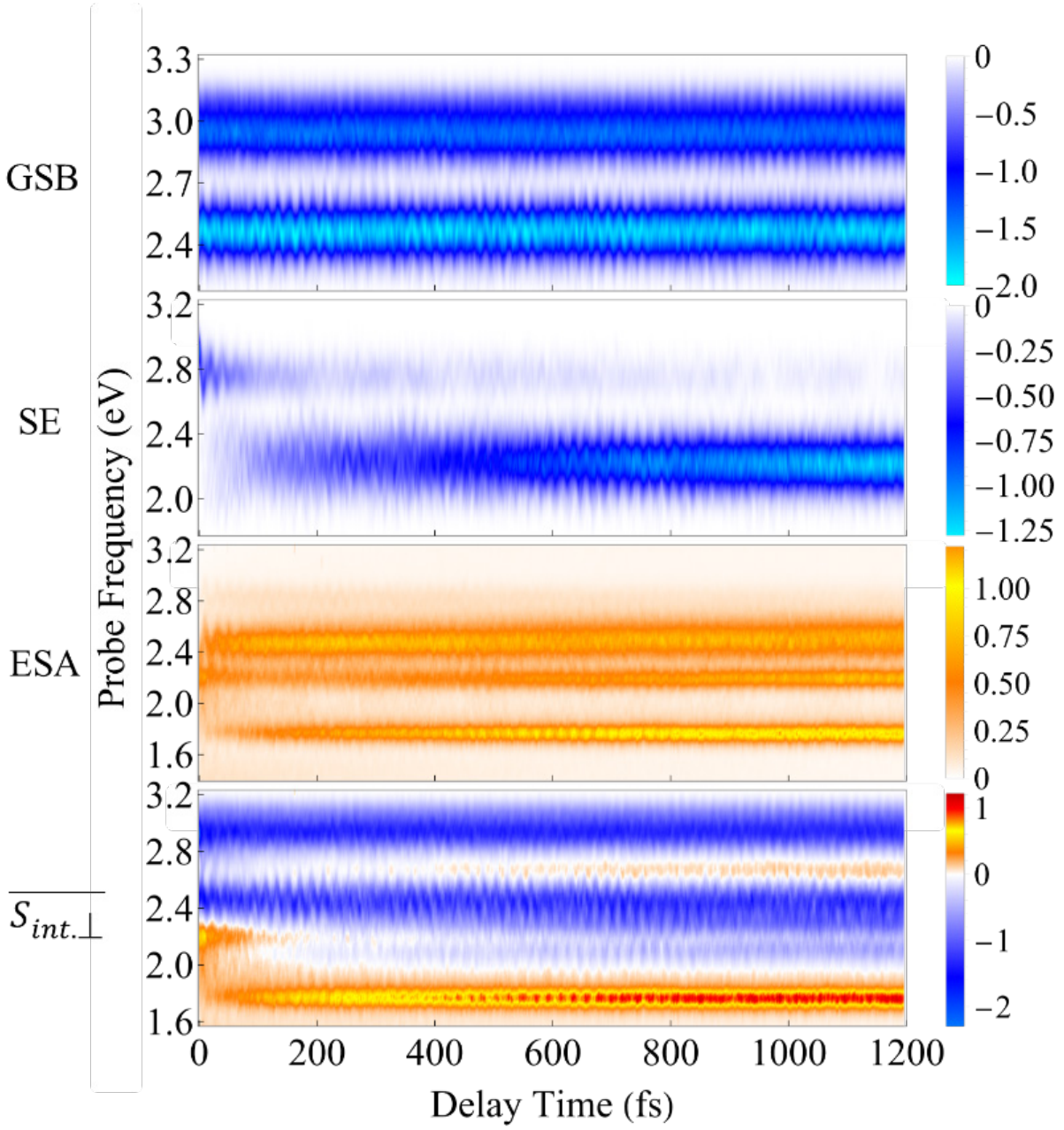
Modeling of transient absorption $\overline{S_{int,\|}}$ signal



- GSB: $E_{pr} \approx 2.9$ eV, electronic transitions between the states S_0 and S_3, S_4.
- SE: Ultrafast $S_n \rightarrow S_2$ internal conversion as a redshift of the signal
- ESA: Initially centered at $E_{pr} \approx 2.3$ eV. Shifts towards $E_{pr} \approx 2.4$ eV and $E_{pr} \approx 1.8$ eV with different relative intensities

R. Perez-Castillo, V. M. Freixas, S. Mukamel, A. Martinez-Mesa, L. Uranga-Piña, S. Tretiak, M. F. Gelin, and S. Fernandez-Alberti, Chem. Sci., 15, 13250 (2024)

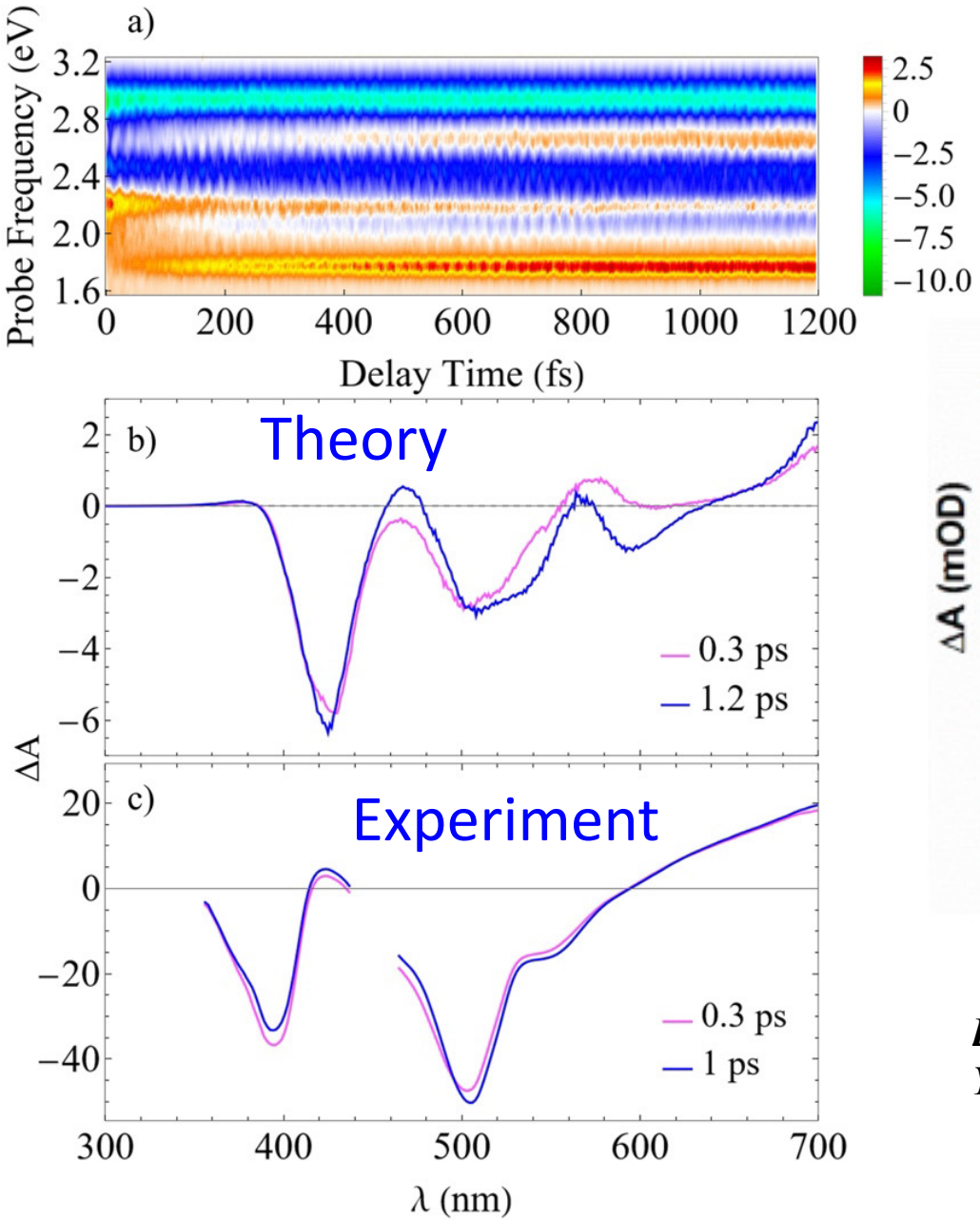
Modeling of transient absorption $S_{int,\perp}$ signal



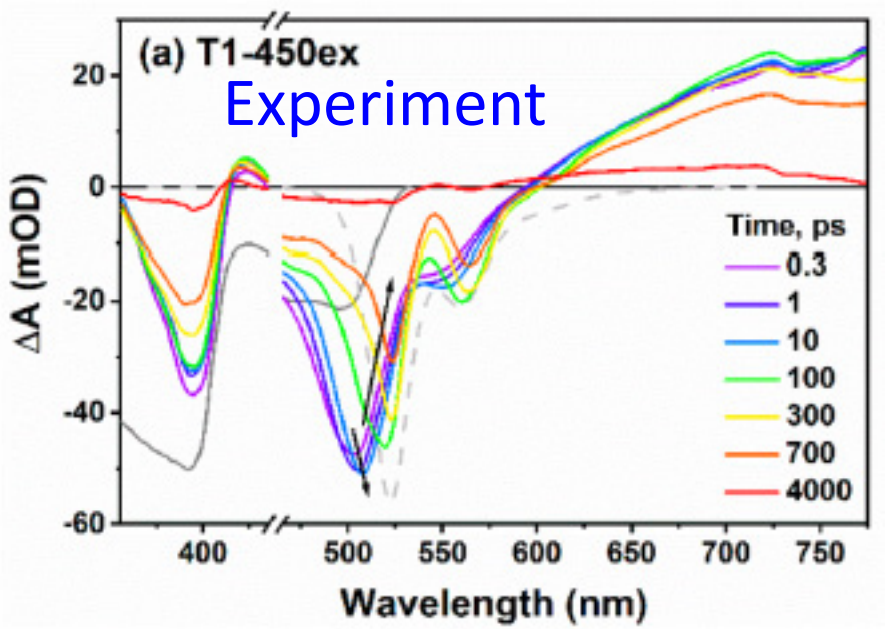
- GSB: $E_{pr} \approx 2.5$ eV, electronic transitions between the states S_0 and S_1 due to transition dipole orientation.
- SE: Ultrafast $S_n \rightarrow S_2$ internal conversion as a redshift of the signal. Lower for $\boldsymbol{S_{int,\perp}}$
- ESA: Initially centered at $E_{pr} \approx 2.3$ eV. Shifts towards $E_{pr} \approx 2.4$ eV and $E_{pr} \approx 1.8$ eV (higher for $\boldsymbol{S_{int,\perp}}$).

R. Perez-Castillo, V. M. Freixas, S. Mukamel, A. Martinez-Mesa, L. Uranga-Piña, S. Tretiak, M. F. Gelin, and S. Fernandez-Alberti, Chem. Sci., 15, 13250 (2024)

Total transient pump-probe average



An average computed TA-PP spectra show a good quantitative agreement with experimental measurements



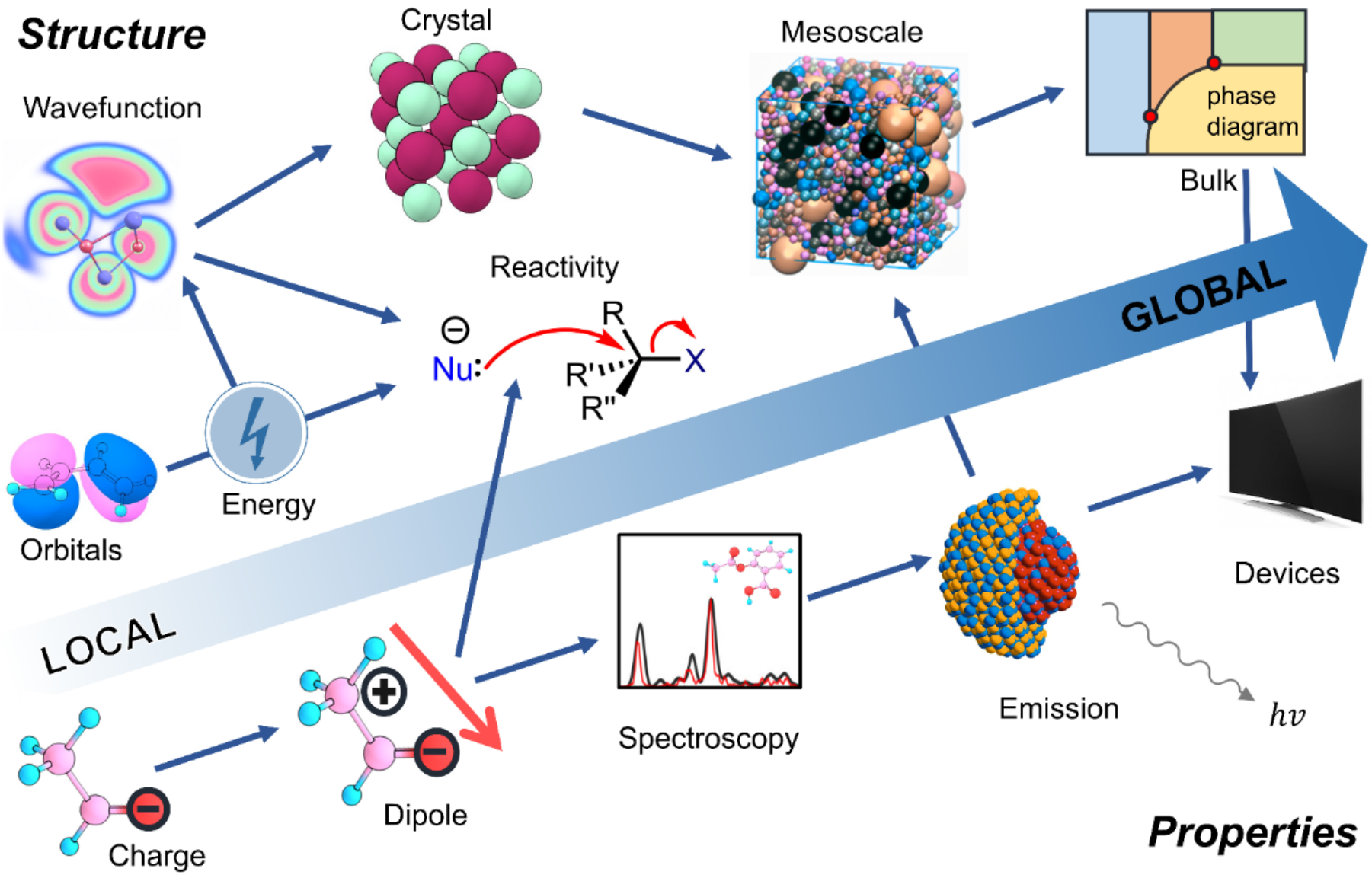
D. Huo, M. Li, Z. Zhao, X. Wang, A. Xia, P. Lu, Y. Wan, J. Phys. Chem. Lett., 12, 7717 (2021)

The emergence of machine learning for excited state modeling. Triplet excitations example.

N. Fedik, R. Zubatyuk, N. Lubbers, J. S. Smith, B. Nebgen, R. Messerly, Y. W. Li, M. Kulichenko, A. I. Boldyrev, K. Barros, O. Isayev, and S. Tretiak, Nature Rev. Chem. 6, 653 (2022)

A. E. Sifain, L. Lystrom, R. Messerly, J. S. Smith, B. Nebgen, K. Barros, S. Tretiak, N. Lubbers, and B. J. Gifford, Chem. Sci., 12, 10207 (2021)

Structure vs. Properties

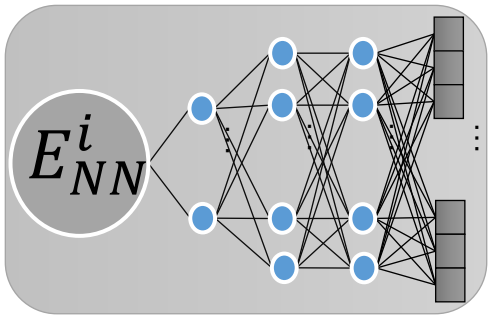


N. Fedik, R. Zubatyuk, N. Lubbers, J. S. Smith, B. Nebgen, R. Messerly, Y. W. Li, M. Kulichenko, A. I. Boldyrev, K. Barros, O. Isayev, and S. Tretiak, Nature Rev. Chem. 6, 653 (2022)

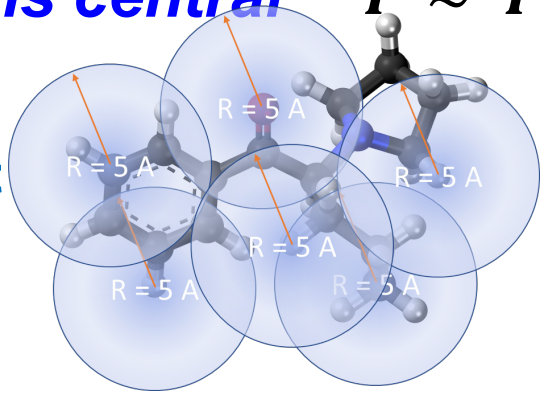
Big challenges for Machine Learning in chemistry and materials science:

Typically, the idea of locality is central

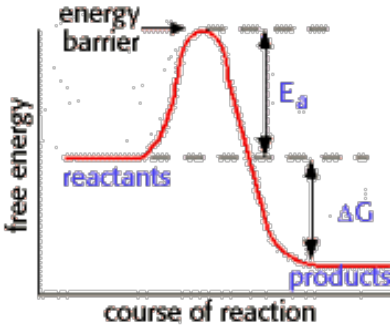
$$P \approx \hat{P} = \sum_{i=1}^{Natoms} \hat{P}_i$$



Atomic environment vector

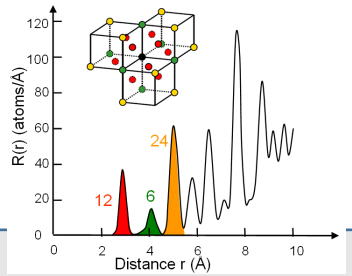


Concept of effective atoms in a specific environment

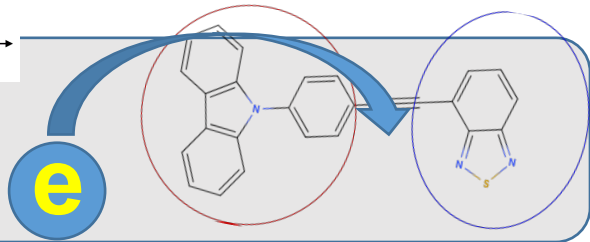


Challenge 1: How to construct a proper training set in chemical and conformational space?

Challenge 2: How to learn from experiment?

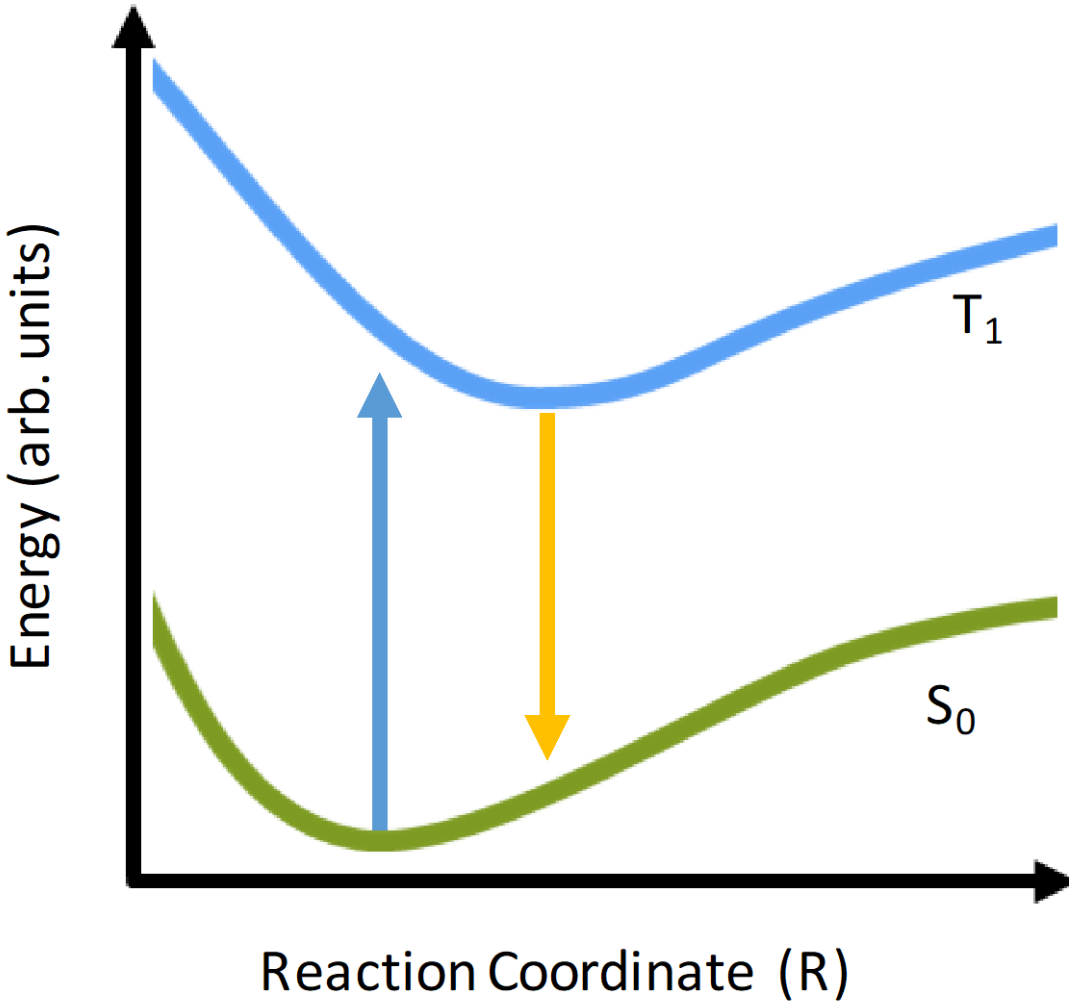


Challenge 3: How to overcome the locality approximation?



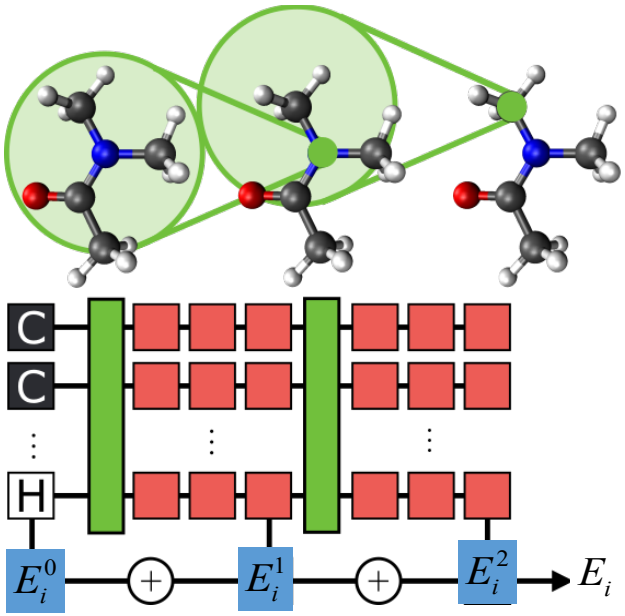
PES for ground (S_0) and excited (T_1) states

- The goal is to rapidly predict the energy difference (ΔE) between S_0 and T_1 using a ML model;
- Potentially, this rapidly screens phosphorescence emissive wavelength (applications such as TADF – thermally activated delayed fluorescence)



A. E. Sifain, L. Lystrom, R. Messerly, J. S. Smith, B. Nebgen, K. Barros, S. Tretiak, N. Lubbers, and B. J. Gifford, Chem. Sci., 12, 10207 (2021)

HIP-NN model



Interaction layers (aka many-body perturbation theory)

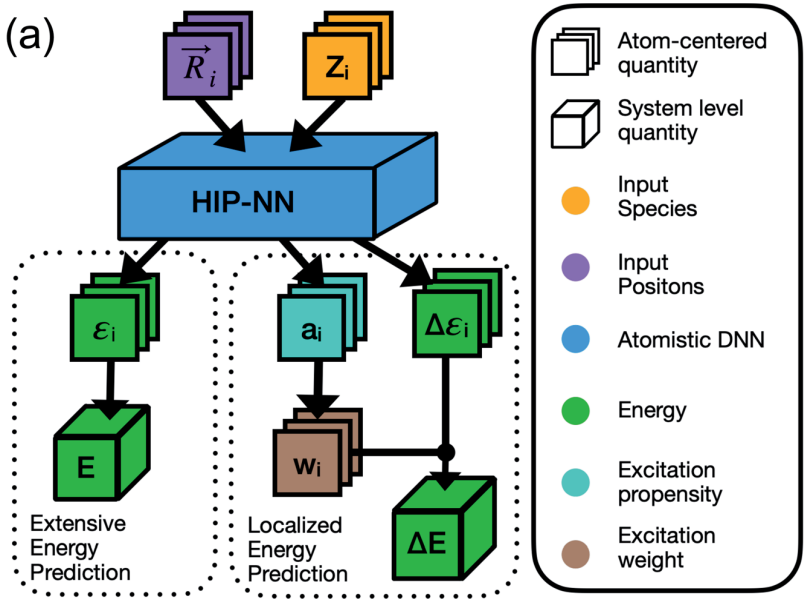
$$P \approx \hat{P} = \sum_{i=1}^{Natoms} \hat{P}_i$$

$$\hat{P}_i = \sum_{n=0}^{Ninteraction} \hat{P}_i^n \qquad \hat{P}_i^n > \hat{P}_i^{n+1}$$

HIP-loc (localized) enhancement via learnable atomic weights

$$\Delta E = w_i \Delta \varepsilon_i$$

What are these?



A. E. Sifain, L. Lystrom, R. Messerly, J. S. Smith, B. Nebgen, K. Barros, S. Tretiak, N. Lubbers, and B. J. Gifford, Chem. Sci., 12, 10207 (2021)

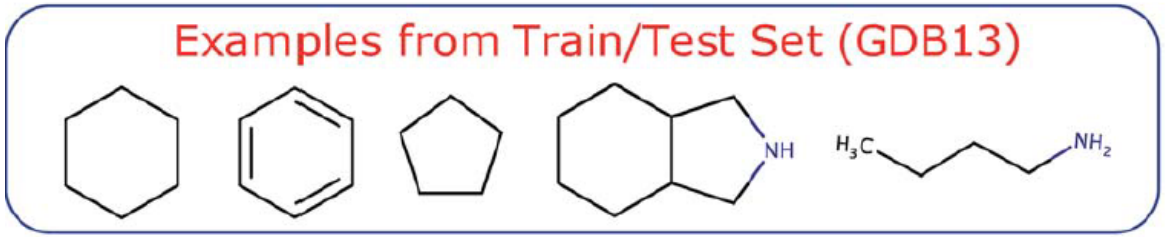
Sampling compounds with C, N, O, S atoms

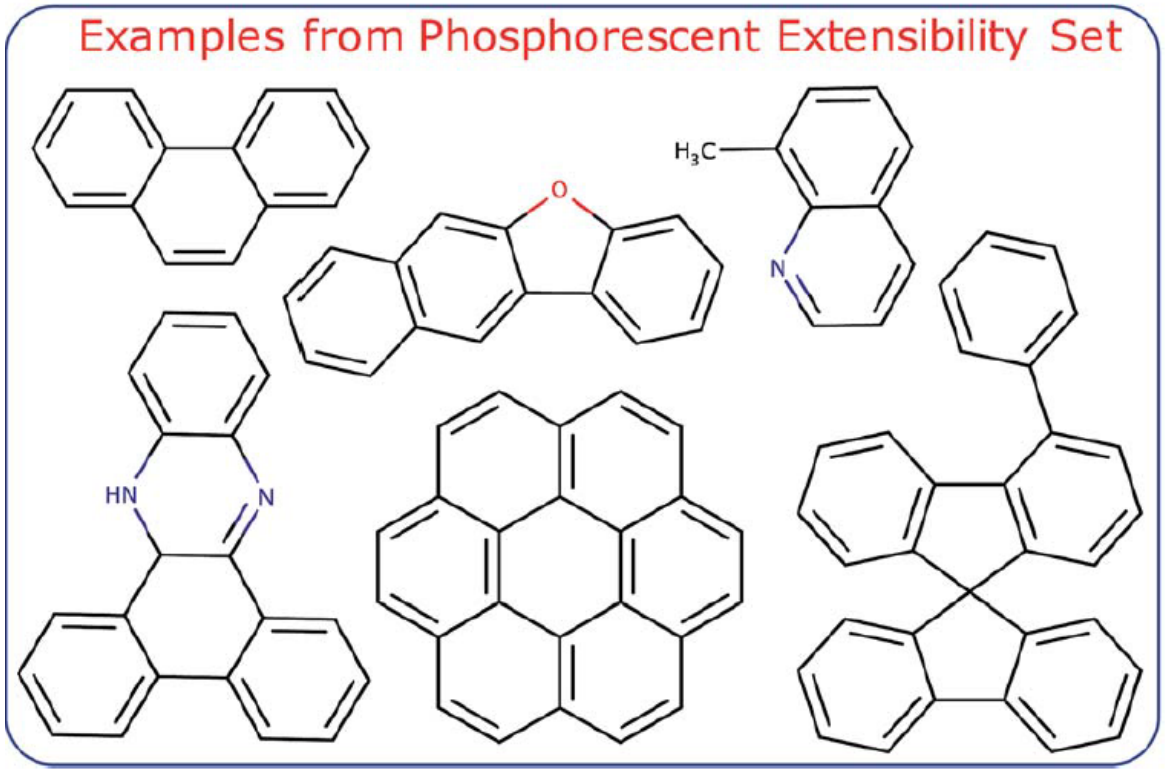
- Aromatic Ring Dataset (ARD) generation
  - Approximately 1.8 million functionalized aromatic rings
- Active Learning (AL) was used to sample the ARD
  - Reduce the number of total calculations
- Train was preformed on ~1.5 million data points
  - The cost function has both energy and forces, with the weight on forces 1/50th of energy.

DFT: ωB97X/6-31g*

$\Delta E = \Delta SCF$

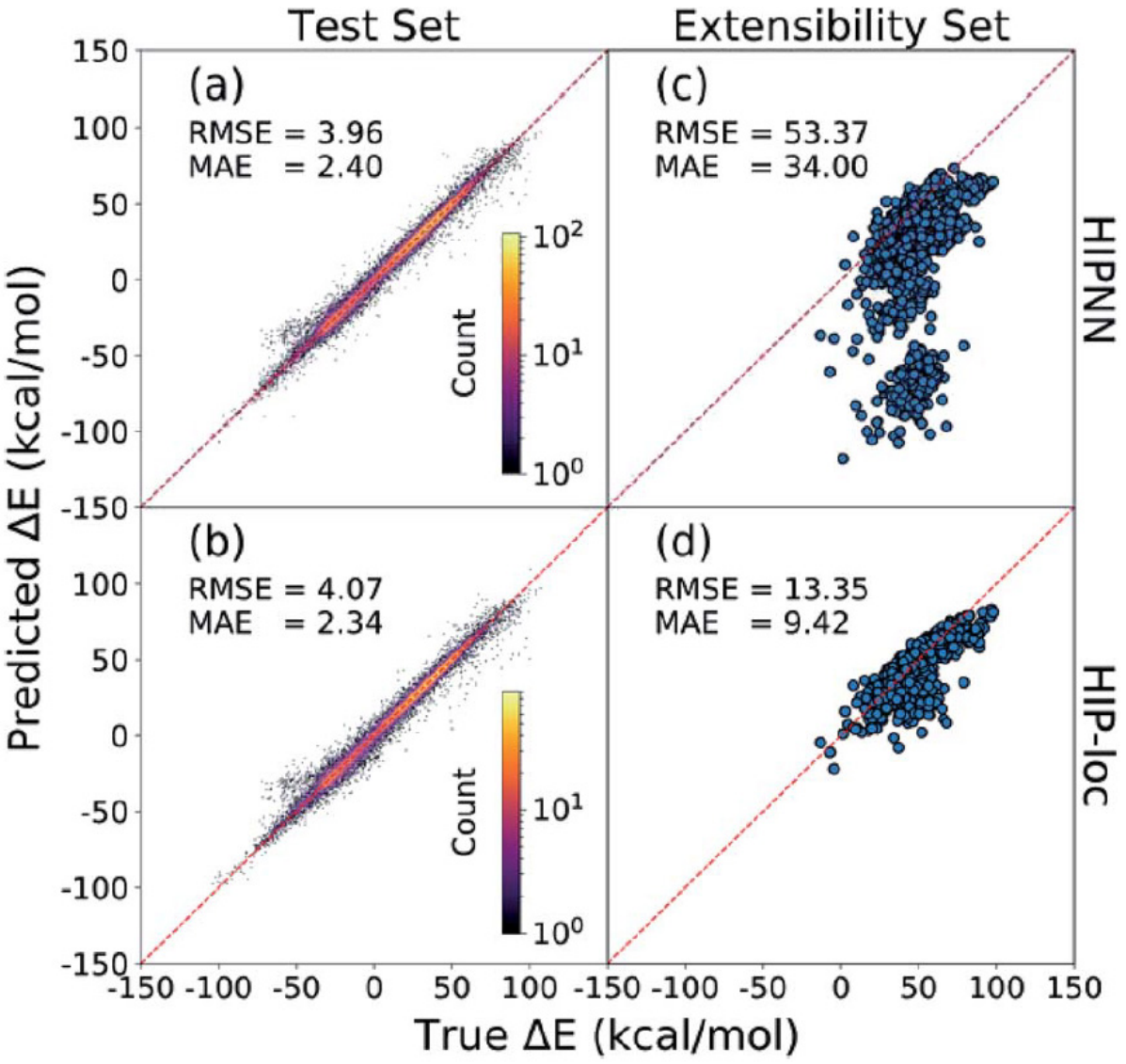
Hip-NN framework





A. E. Sifain, L. Lystrom, R. Messerly, J. S. Smith, B. Nebgen, K. Barros, S. Tretiak, N. Lubbers, and B. J. Gifford, Chem. Sci., 12, 10207 (2021)

Results for phosphorescence energies

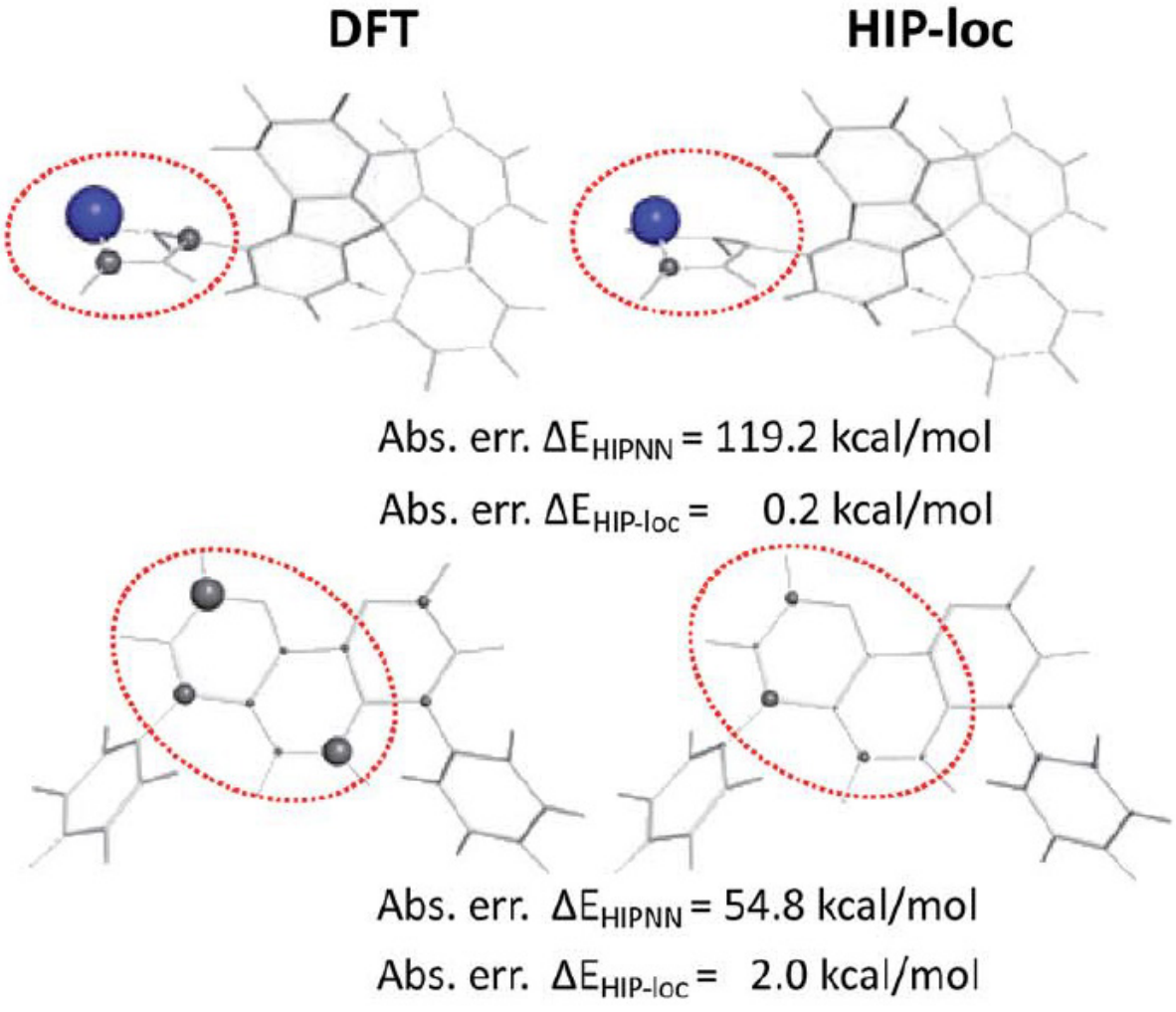


~10 kcal/mol accuracy for ΔE vs. reference DFT

Note DFT accuracy vs. experiment is ~10-20 kcal/mol

A. E. Sifain, L. Lystrom, R. Messerly, J. S. Smith, B. Nebgen, K. Barros, S. Tretiak, N. Lubbers, and B. J. Gifford, Chem. Sci., 12, 10207 (2021)

Comparison of atomic weights and triplet spin density

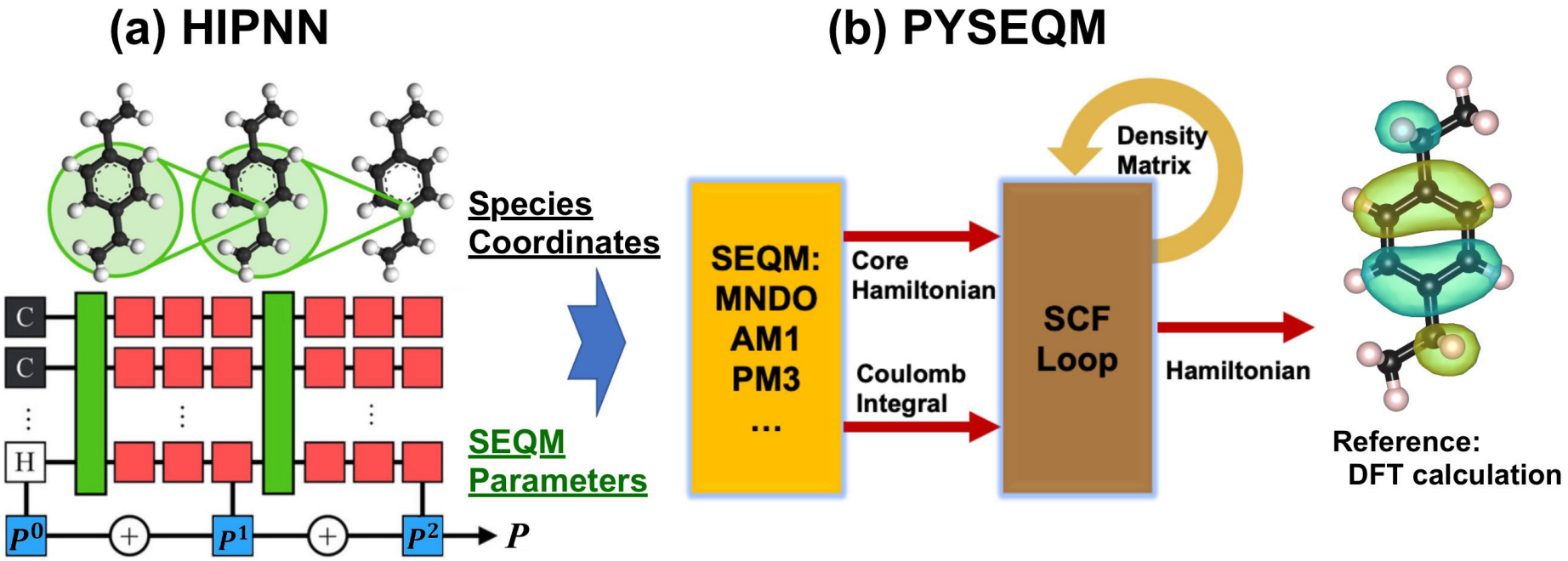


Atomic weights reflect distribution of spin density on atoms.

Obtained from ENERGY only!

A. E. Sifain, L. Lystrom, R. Messerly, J. S. Smith, B. Nebgen, K. Barros, S. Tretiak, N. Lubbers, and B. J. Gifford, Chem. Sci., 12, 10207 (2021)

Training of semiepirical models in PySeQM



- Underlying neural network layer HIPPNN (includes flavors HIPP-vec & HIPP-quad)
- Active Learning Framework (ALF)
- Full backpropagation with PySeQM

Fitting degrees of freedom:

- **Space 1: Hamiltonian parameters**
- **Space 2: Basis set**
- **Space 3 (new): Geometry-dependent parameters – environment aware Hamiltonian**

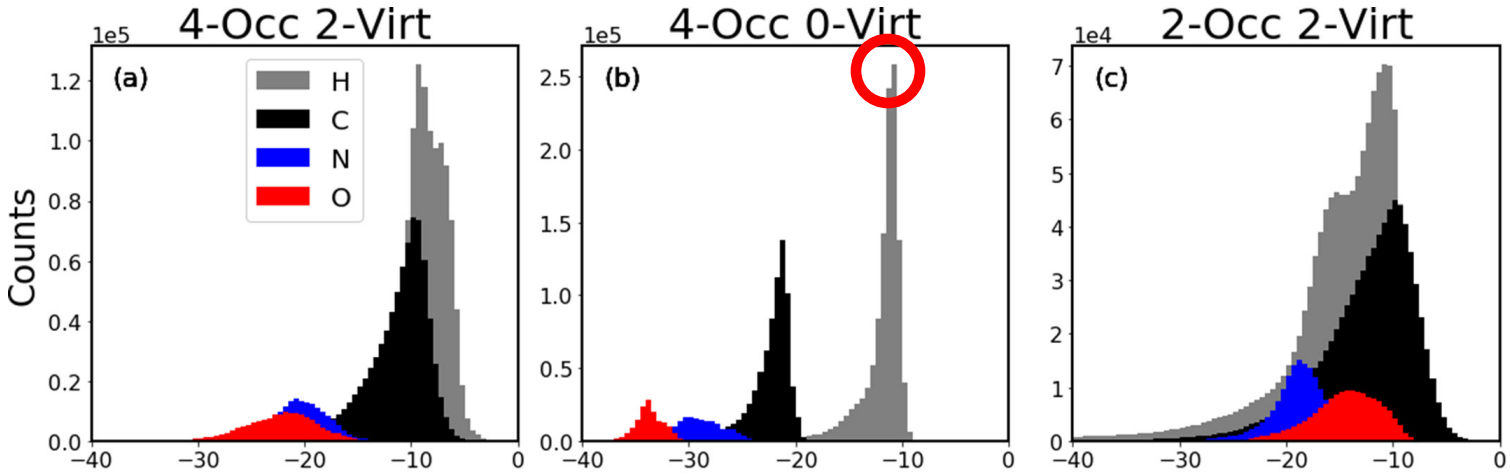
G. Zhou, N. Lubbers, K. Barros, S. Tretiak, B. Nebgen, PNAS, 19, e2120333119 (2022)

The concept of environment-aware Hamiltonians

- ***The standard thinking (e.g. DFTB) is to have 'fixed' Hamiltonian parameters, which can be augmented as necessary to improve accuracy.***
- ***Environment-aware models feature minimal number of parameters but they vary as a function of molecular geometry.***

Learning Huckel Hamiltonian. Is tight-binding model physical?

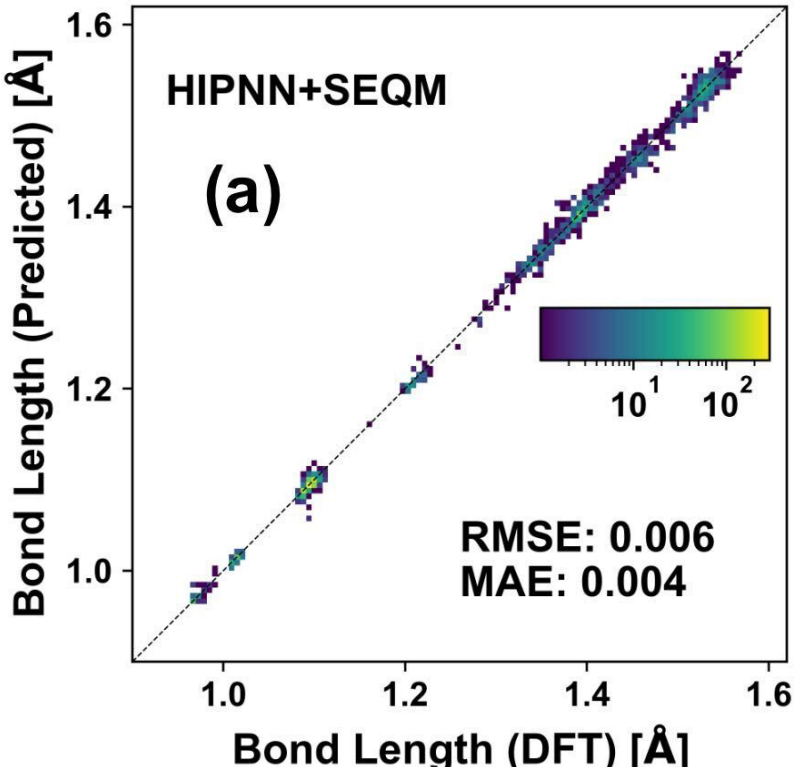
α

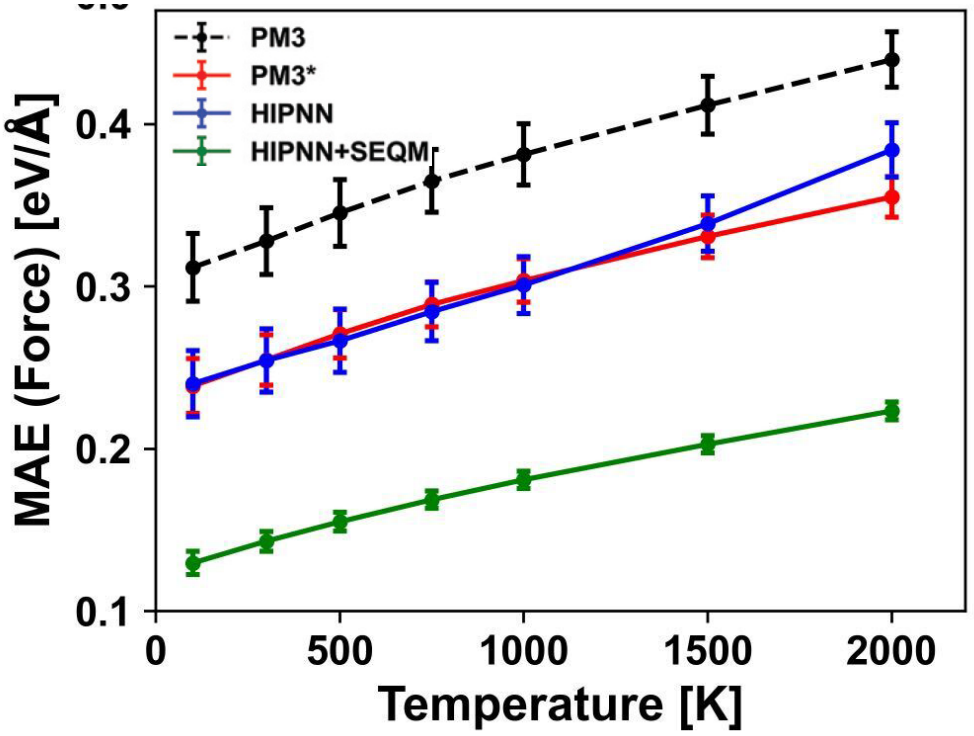


For 4-Occ 0-Virt" mode $\alpha_{H,S}$ orbital energy is -13.6 eV and O<N<C

T. Zubatiuk, B. Nebgen, N. Lubbers, J. S. Smith, R. Zubatiuk, G. Zhou, C. Coh, K. Barros, O. Isayev, S. Tretiak, J. Chem. Phys. 154, 244108 (2021)

Training of semiempirical models: PM3-ML



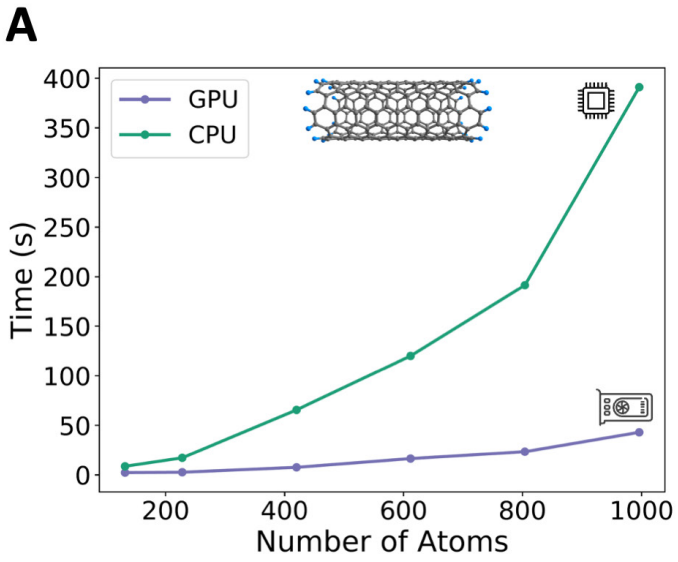


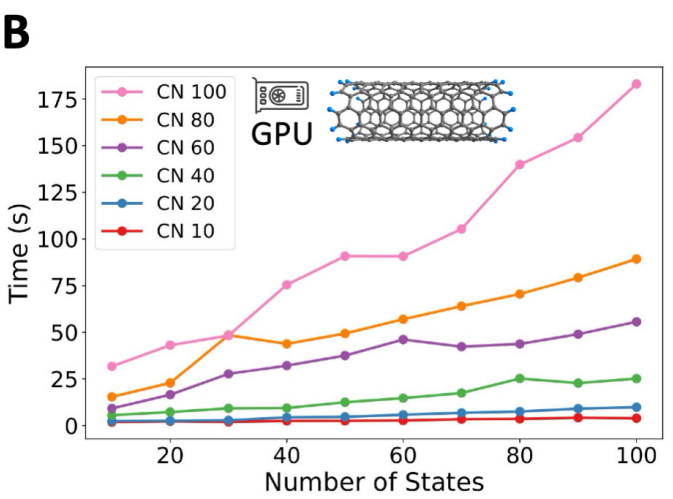
- Prediction of bond lengths in HIPPNN-SEQM
- 658 optimized structures from Drug Bank subset in COMP6

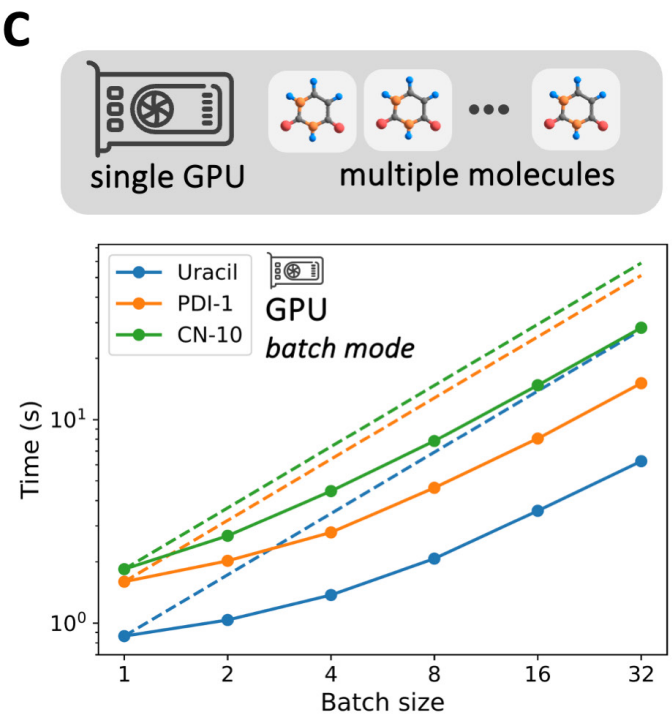
- Prediction of non-equilibrium conditions in HIPPNN-SEQM
- 48 molecules in Drug Bank with ~40 atoms in size

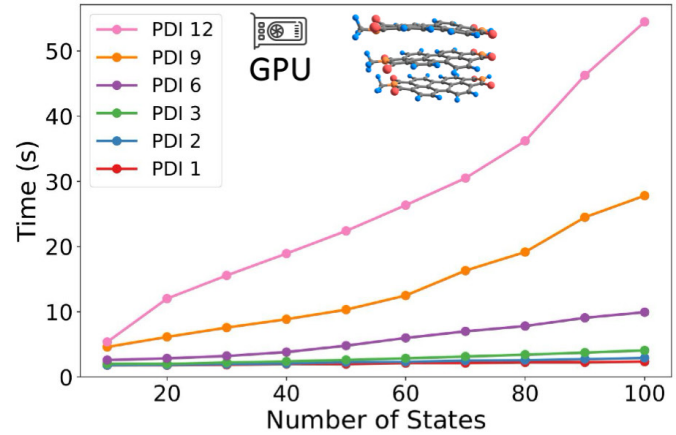
G. Zhou, N. Lubbers, K. Barros, S. Tretiak, B. Nebgen, PNAS, 19, e2120333119 (2022)

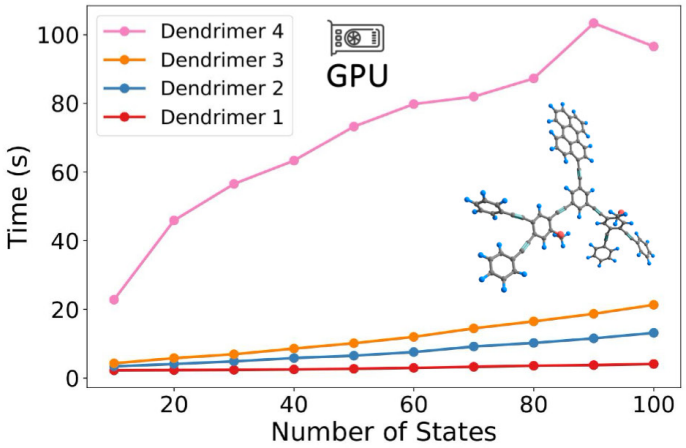
Excited State Calculations on GPU









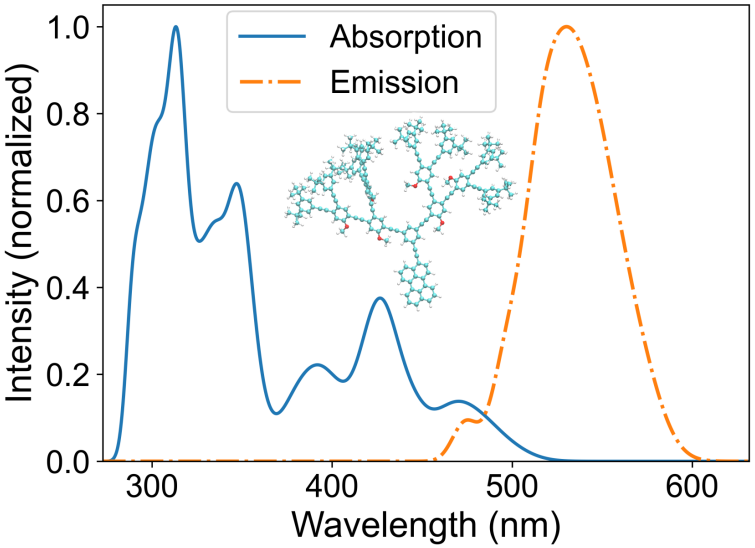


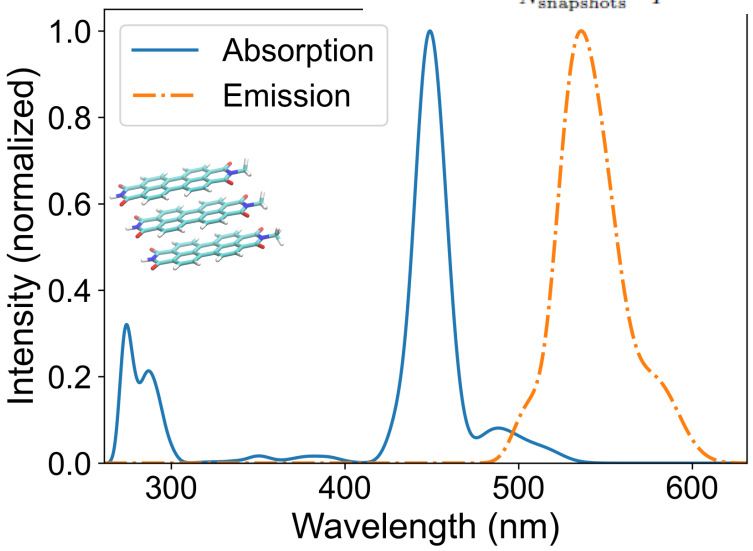
V. Athavale, N. Fedik, W. Colglazier, A.M.N.Niklasson, M. Kulichenko, S. Tretiak J. Chem. Theory Comput, 21, 9498 (2025)

How about absorption/emission and IR spectra?

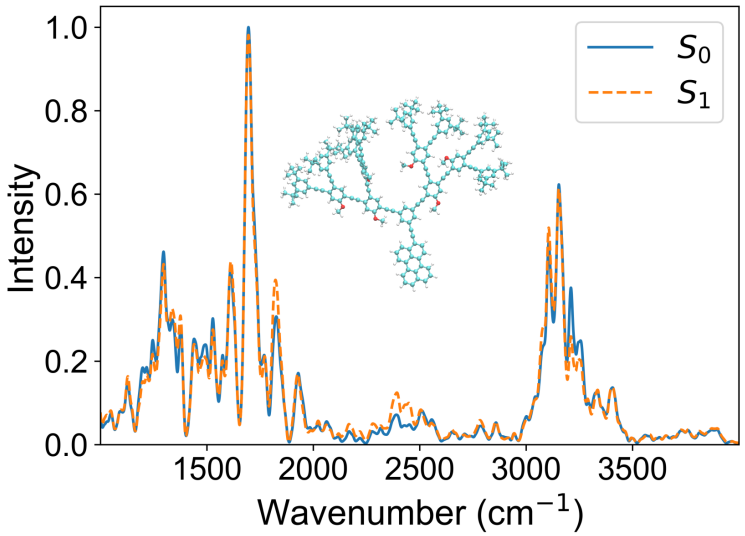
$$\alpha_{\text{abs}}(\Omega) \propto \sum_{N_{\text{snapshots}}} \sum_{I} \frac{f_I}{\sigma} \exp \frac{-(\Omega - \Omega_I)^2}{2\sigma^2}$$

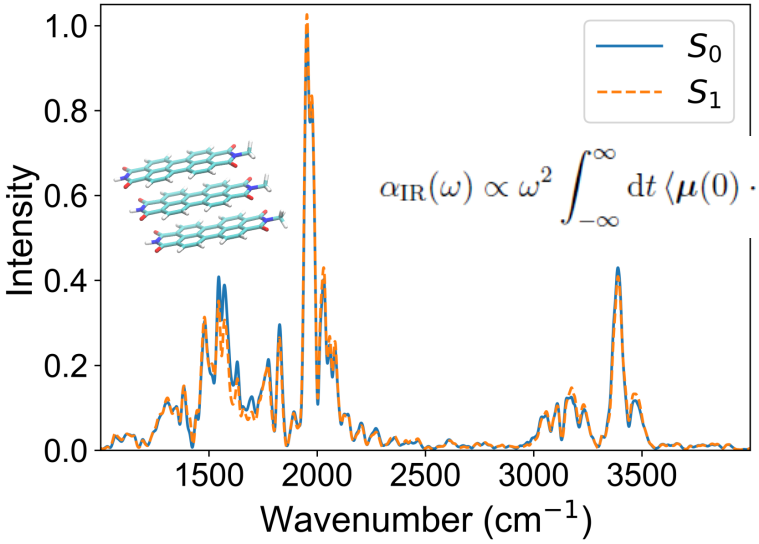
(a)





(b)

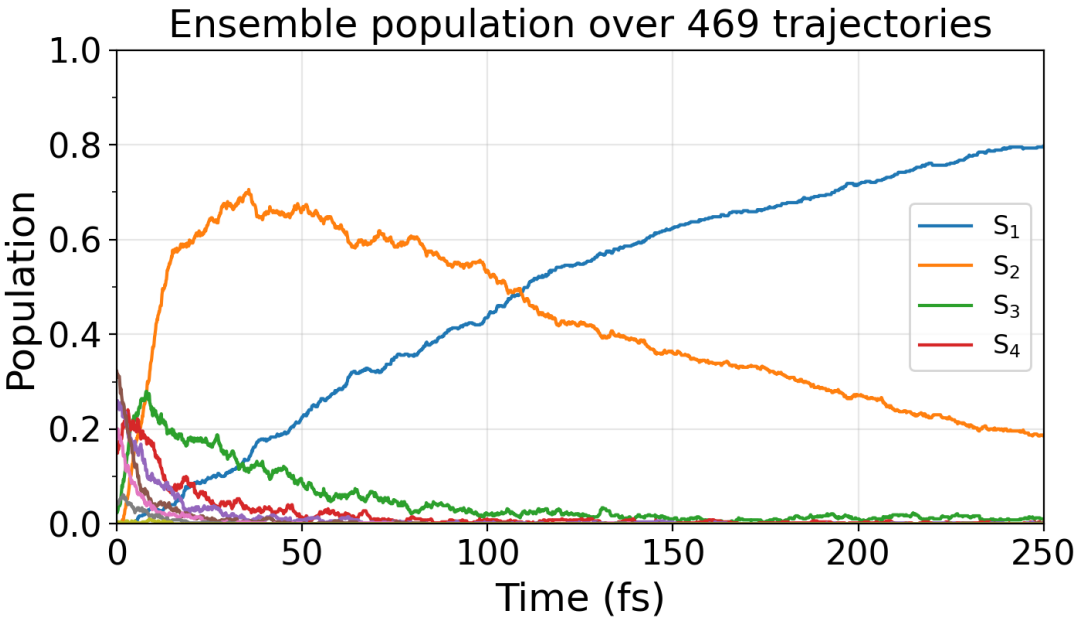


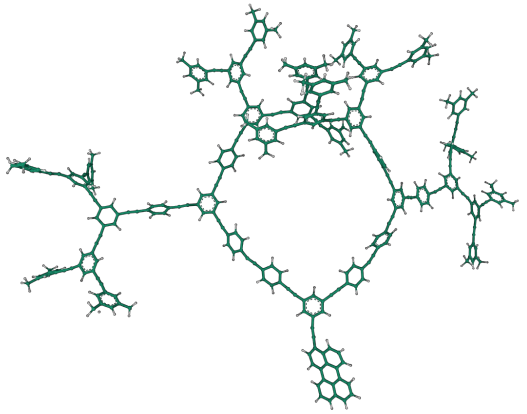


$$\alpha_{\text{IR}}(\omega) \propto \omega^2 \int_{-\infty}^{\infty} \mathrm{d}t \, \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle \exp(i\omega t)$$

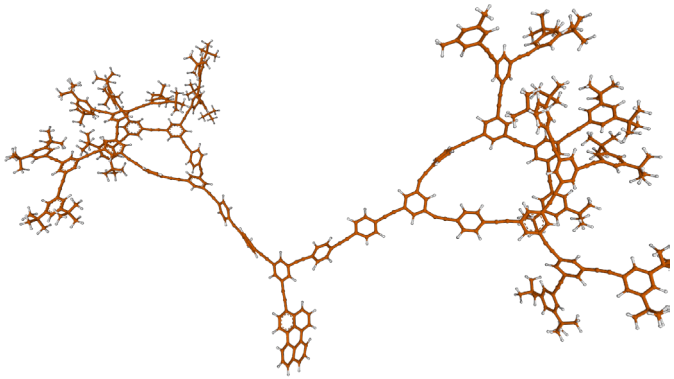
V. Athavale, M. Kulichenko, S. Fernandez-Alberti, A.M.N.Niklasson, S. Tretiak, J. Phys. Chem. Lett. 17, 3757 (2026)

Non-adiabatic dynamics (surface hopping)

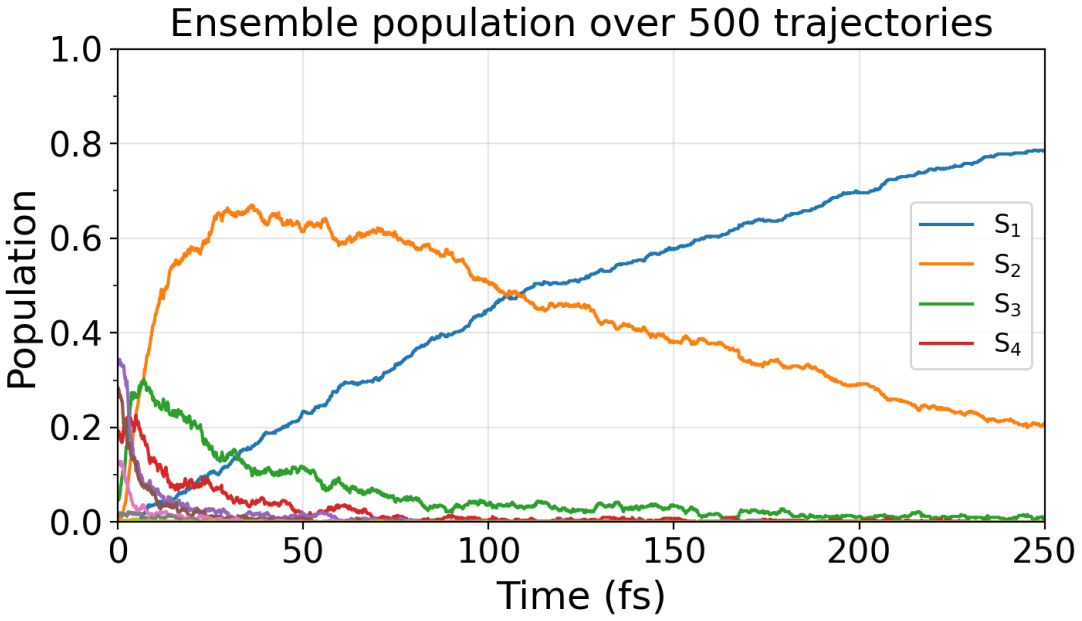




~5hrs/ 500fs trajectory for ~900 atom system (A100 GPU)



~8hrs/ 500fs trajectory for ~1,200 atom system (A100 GPU)



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Code and applications

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Team: Sebastian Fernandez-Alberti (Argentina)

Team: Thomas Frauenheim (Bremen, Germany): Fulu Zheng, Mohamed Madjet

Team: Niri Govind (PNNL)

Team: Marco Garavelli (U. Bologna, Italy)

Team: Sahar Sharifzadeh (BU)

Team: Shaul Mukamel (UCI): Daniel Keefer, Victor Freixas Yeonsig Nam

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Dmitry Makhov (UK, Leeds)

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Justin Smith (Nvidia)

Guoqing Zhou (NVidia)

Pump-Probe Spectroscopy

Maxim Gelin (Hangzhou University)

Polaritonics

Yu Zhang (LANL)

Experiment: many!

Christoph Lienau and Antonietta De Sio (Oldenburg, Germany)

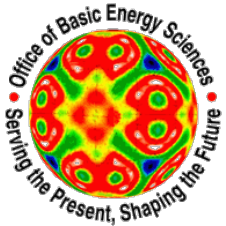
Group homepage: http://cnls.lanl.gov/~serg

tretiak@lanl.gov

Center for Integrated Nanotechnologies (CINT)

Center for Nonlinear Studies (CNLS)

LDRD program at LANL. DOE BES, EFRC



Thank you!