Computational Modeling of Nanosystems

TD6 – NEA & Surface Hopping

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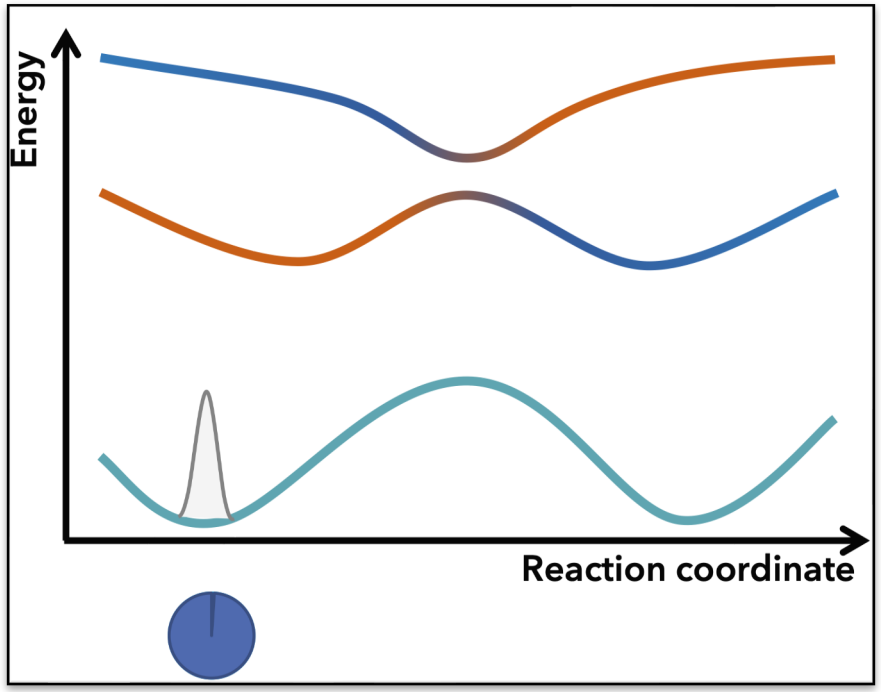
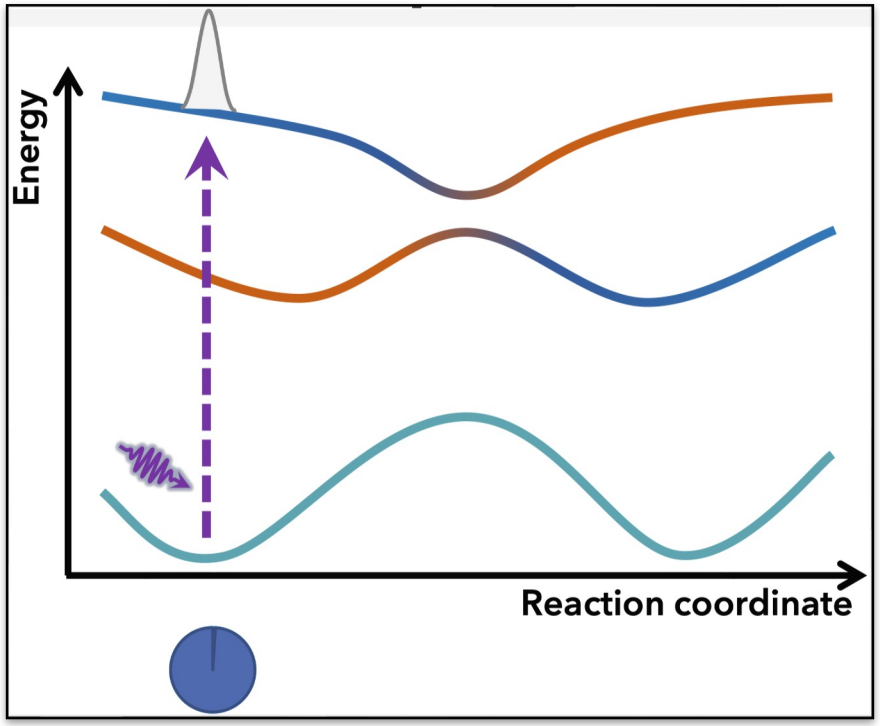
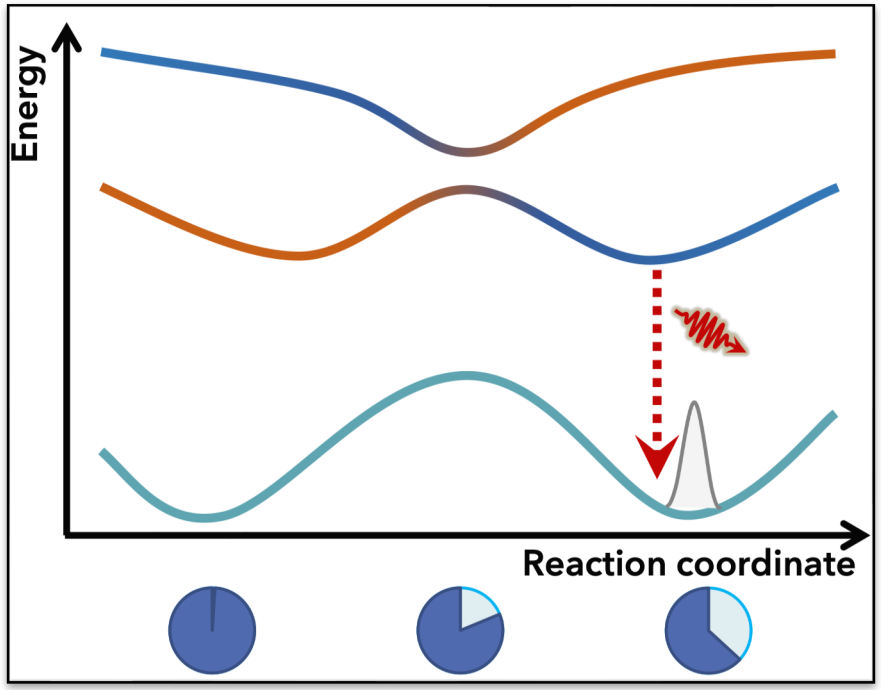


Excitation ⇨

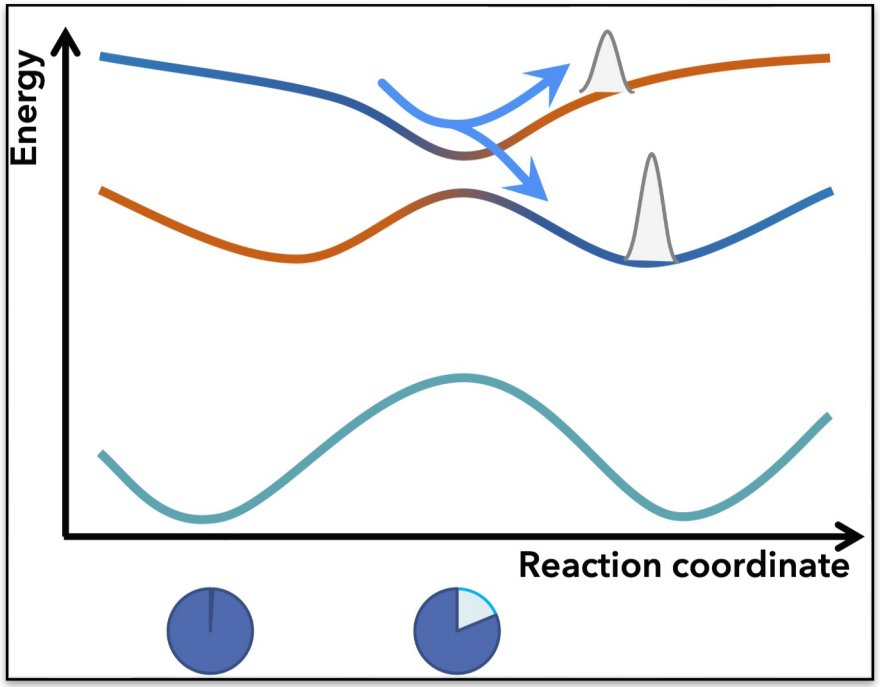
Nonadiabatic Dynamics



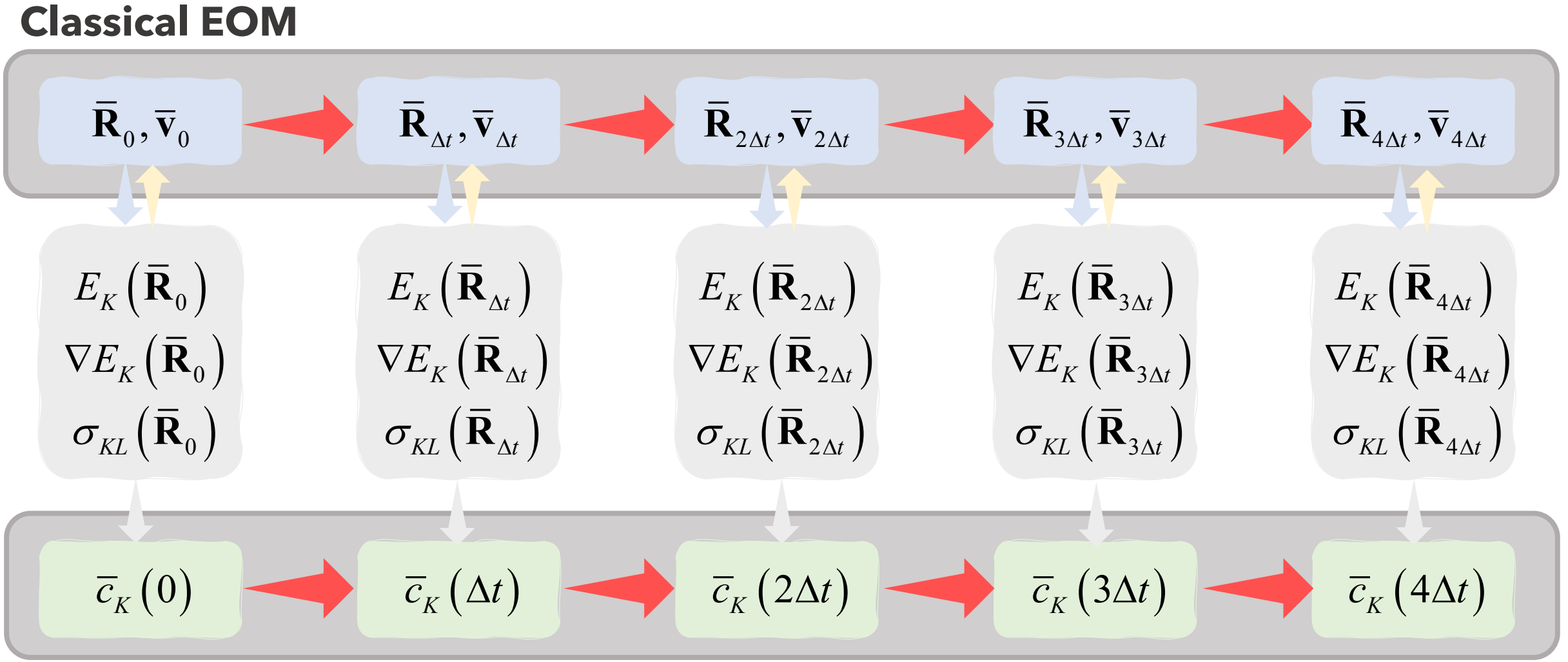


⇦ Relaxation

Branching ⇨



Mixed Quantum-Classical Dynamics



Fewest-Switch Surface Hopping

$$\frac{d^2\mathbf{R}_\alpha}{dt^2} = \frac{1}{M_\alpha}\mathbf{F}(\mathbf{R}) \qquad \mathbf{F}(\bar{\mathbf{R}}) = -\nabla_\alpha E_L$$

Nuclei are propagated Classically

$$\frac{dc_J}{dt} = \sum_K -c_K\left(\frac{i}{\hbar}E_K + \sigma_{JK}\right) \qquad \sigma_{JK}(\mathbf{R}) \equiv \left\langle \psi_J \left| \frac{\partial \psi_K}{\partial t} \right\rangle \right.$$

Electrons are treated Quantum Mechanically

$$P_{L\to J}^{FSSH} = \max\left[0, \frac{-2\Delta t}{|c_L|^2}\mathrm{Re}\left(\sigma_{LJ}c_J c_L^*\right)\right]$$

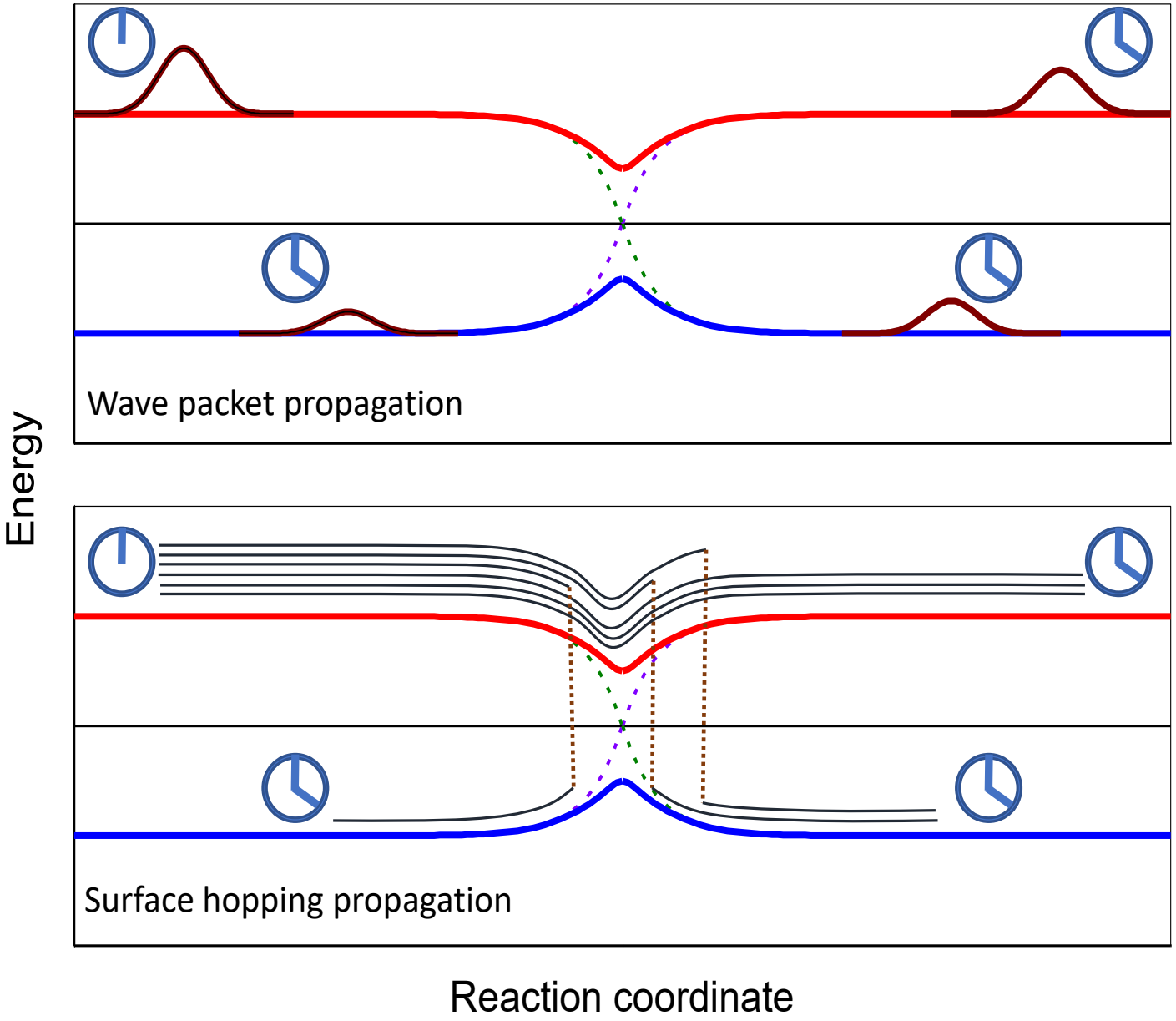
$$\sum_{K=1}^{J-1} P_{L\to K}^{FSSH} < r_t \le \sum_{K=1}^{J} P_{L\to J}^{FSSH}$$

Hopping Probabilities

Nonadiabatic Algorithm for surface hopping

Fewest-Switch Surface Hopping

- Wavepacket is mimicked by a swarm of independent classical trajectories propagated on a single PES.
- FSSH dictates the nonadiabatic events.
- The wavepacket branching/bifurcation will be captured on average over all the trajectories.

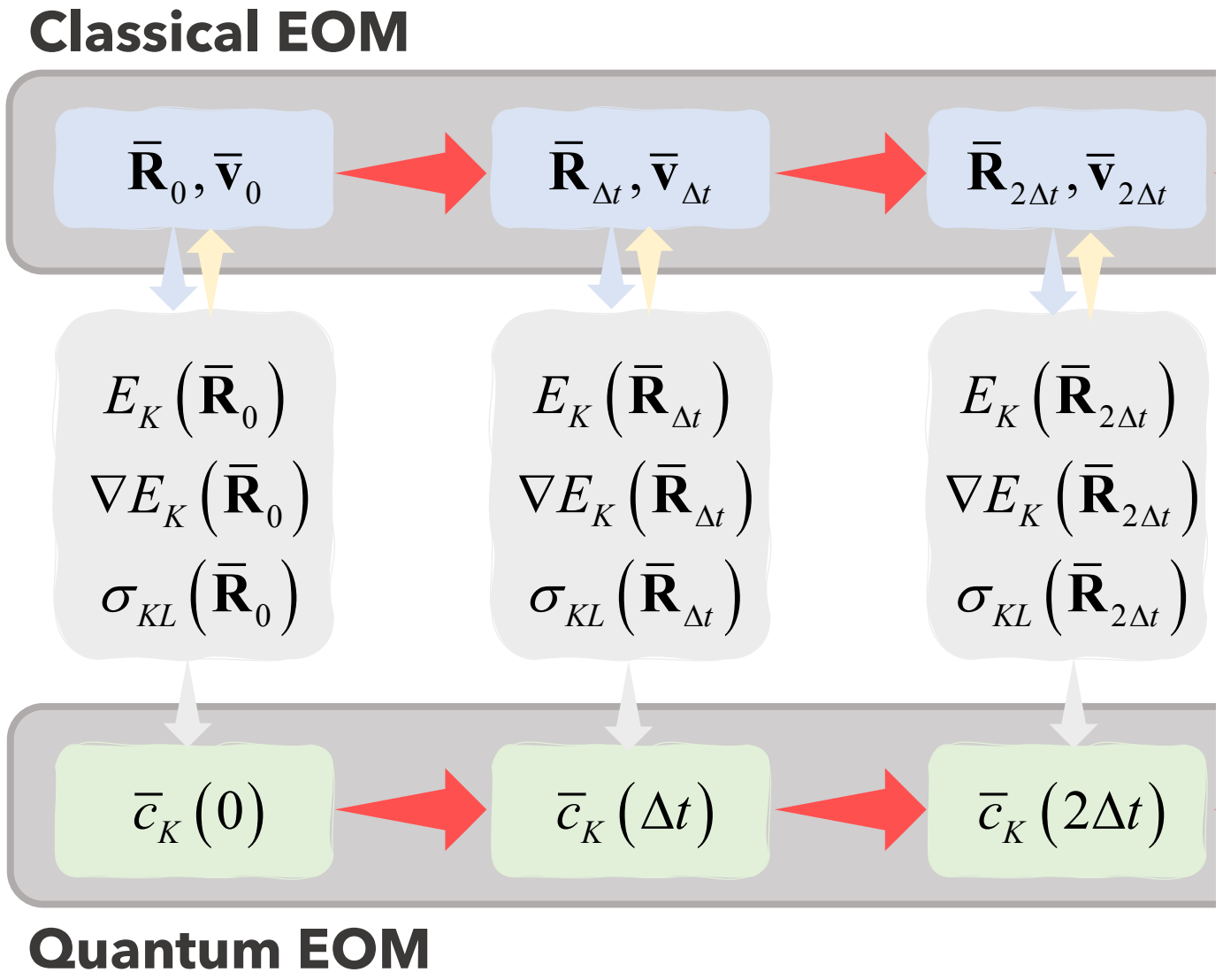


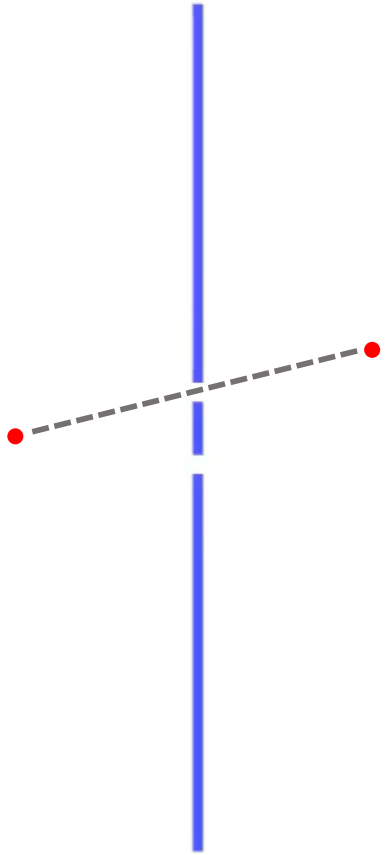
Initial Conditions

build an ensemble of nuclear points $\{\mathbf{R}, \mathbf{P}\}$

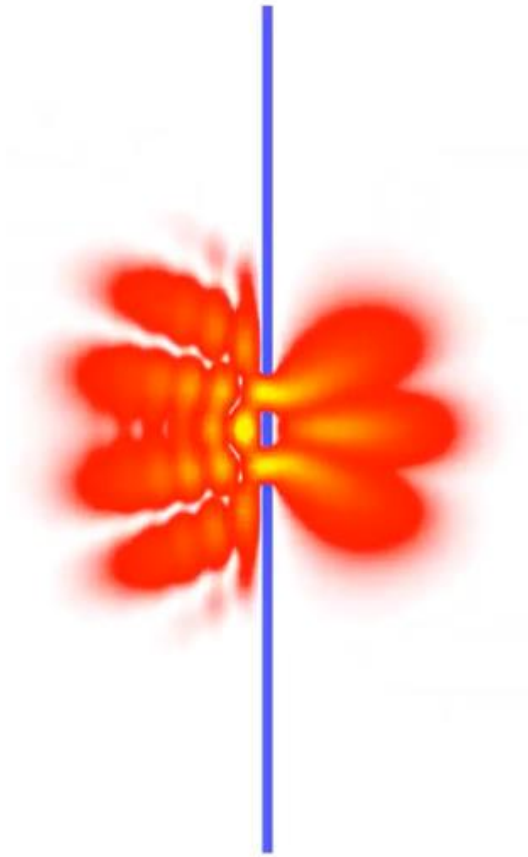
- **Initial geometry**
- **Initial velocity**
- **Initial electronic state**
- **Initial TDSE coefficients**

BUT WHY ENSEMBLE

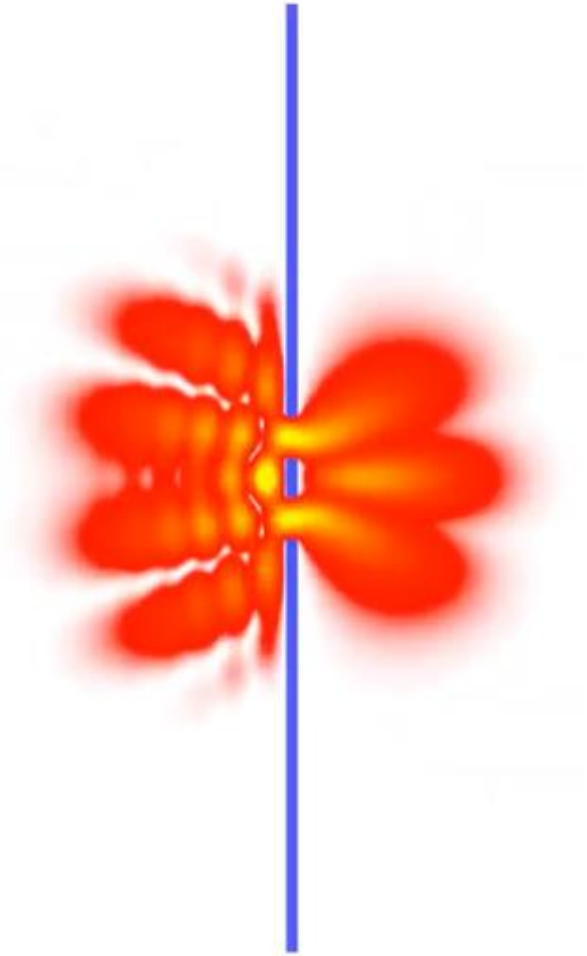




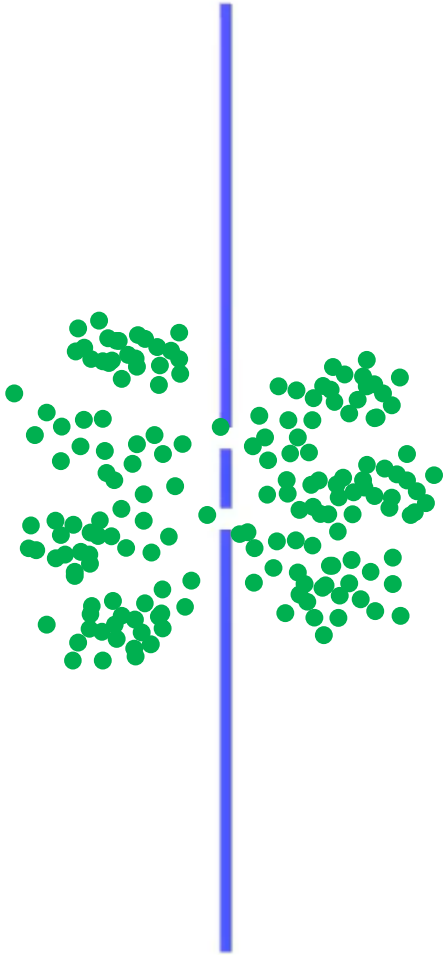
A **classical particle**
is a particle (!)



A **quantum particle**
delocalizes over space



QM Wavefunction



Swarm of Classical trajectories

Nuclear Ensemble Approach

- **Classical Harmonic oscillator**
- **Uncorrelated Quantum Harmonic Oscillator (Wigner Distribution)**
- **Correlated quantum Harmonic Oscillator**
- **Pick points from previous dynamics**
- **Random Velocities**

Wigner Distribution: linking wavefunction to a probability distribution in phase space (position, momenta)

$$W(x,p) = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \psi^{\star}(x+y)\psi(x-y)e^{2ipy/\hbar}dy$$

E. P. Wigner, On the quantum correction for thermodynamic equilibrium, *Phys. Rev.* **40**, 749 (1932).
M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner, Distribution functions in physics: Fundamentals, *Phys. Rep.* **106**, 121 (1984).
Y. S. Kim and E. P. Wigner, Canonical transformations in quantum mechanics, *Am. J. Phys.* **58**, 439 (1990).

Nuclear Ensemble Approach

- Sampling ground-state density at the initial time considering the harmonic approximation and employing the Wigner distribution

$$P_W(\boldsymbol{q},\boldsymbol{p}) = \prod_{i=1}^{3N-6} \frac{\alpha_i}{\pi\hbar} exp\left(-\frac{2\alpha_i}{\hbar\omega_i}\left[\frac{\mu_i\omega_i^2 q_i^2}{2} + \frac{p_i^2}{2\mu_i}\right]\right); \qquad \alpha_i = tanh\left(\frac{\hbar\omega_i}{2k_BT}\right)$$

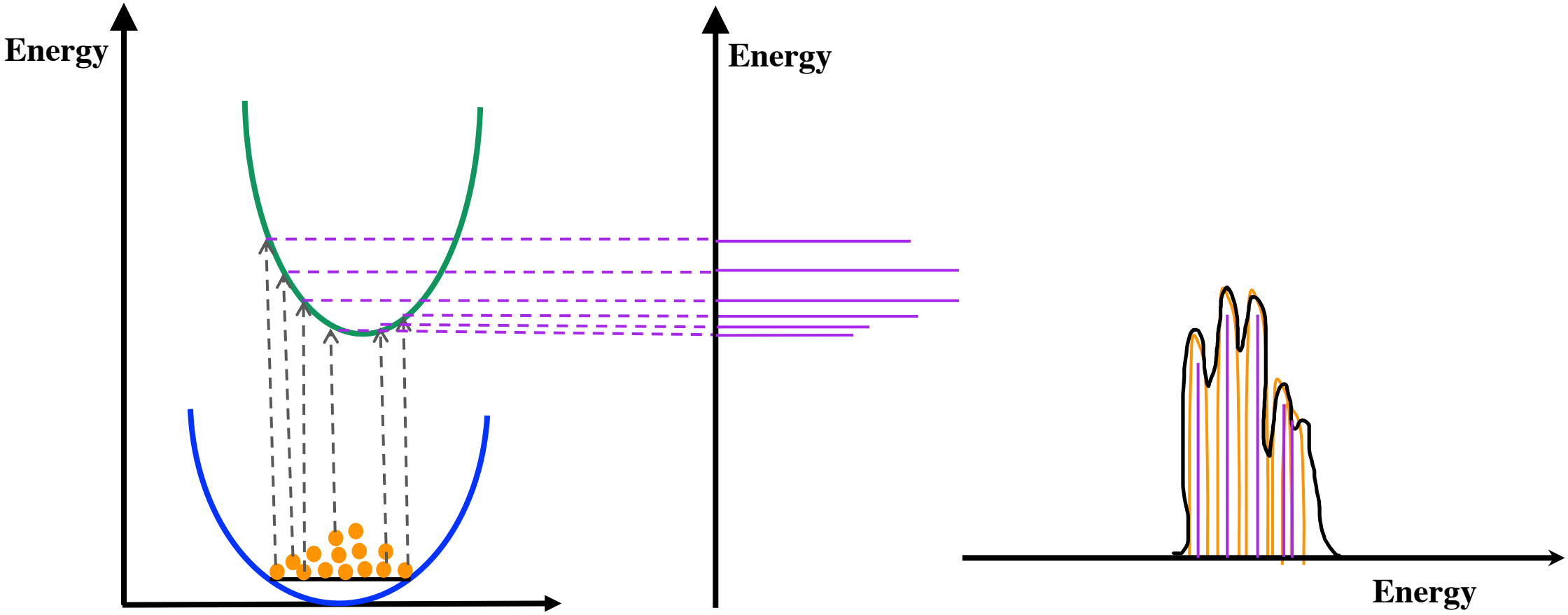
- A stochastic algorithm generates an ensemble of N_c normal coordinates from the Wigner distribution and then they are converted to Cartesian geometries. → $\{\mathbf{R}, \mathbf{P}\}$

Rachel Crespo-Otero and Mario Barbatti, *Theor Chem Acc* **131**, 1237 (2012).

Absorption Spectra

The absorption cross-section

$$\sigma(E) = \frac{\pi e^2 \hbar}{2mc\epsilon_0 n_r E} \sum_{n}^{nstate} \frac{1}{N_c} \sum_{i}^{N_c} \Delta E_{0n}(R_i) f_{0n}(R_i) \times g(E - \Delta E(R_i), \delta_n)$$



❖ **Electronic Structure:**

ORCA – Prof. Frank Neese, MPI Mulheim

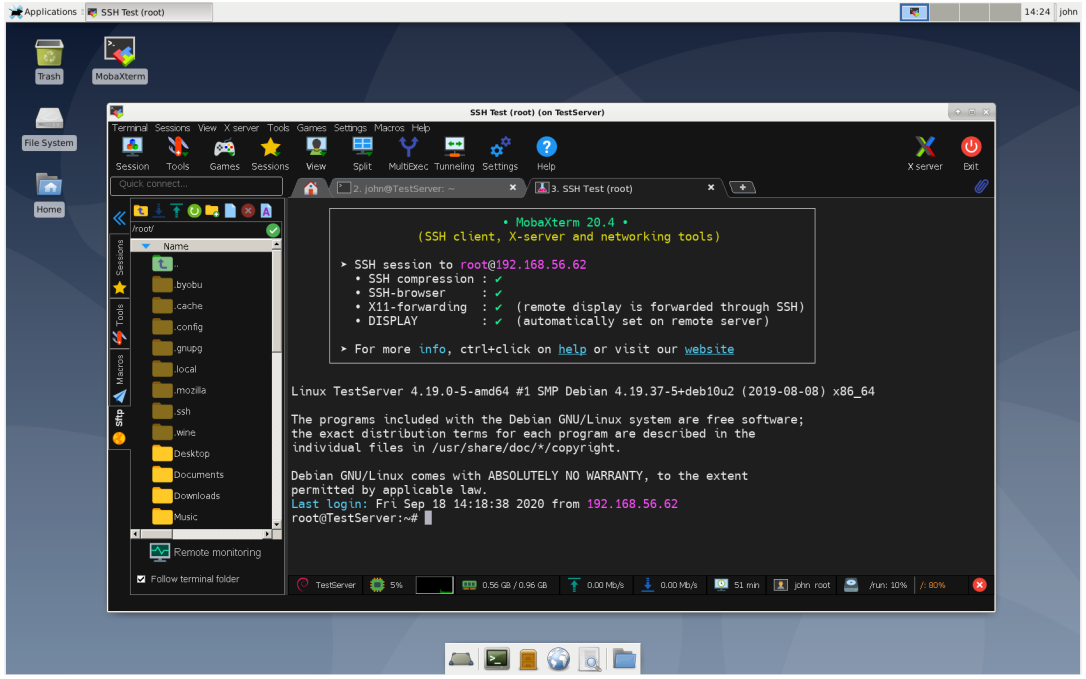
https://www.faccts.de/orca/

❖ **Surface Hopping Dynamics:**

Newton-X – Prof. Mario Barbatti, Aix-Marseille University

https://newtonx.org/

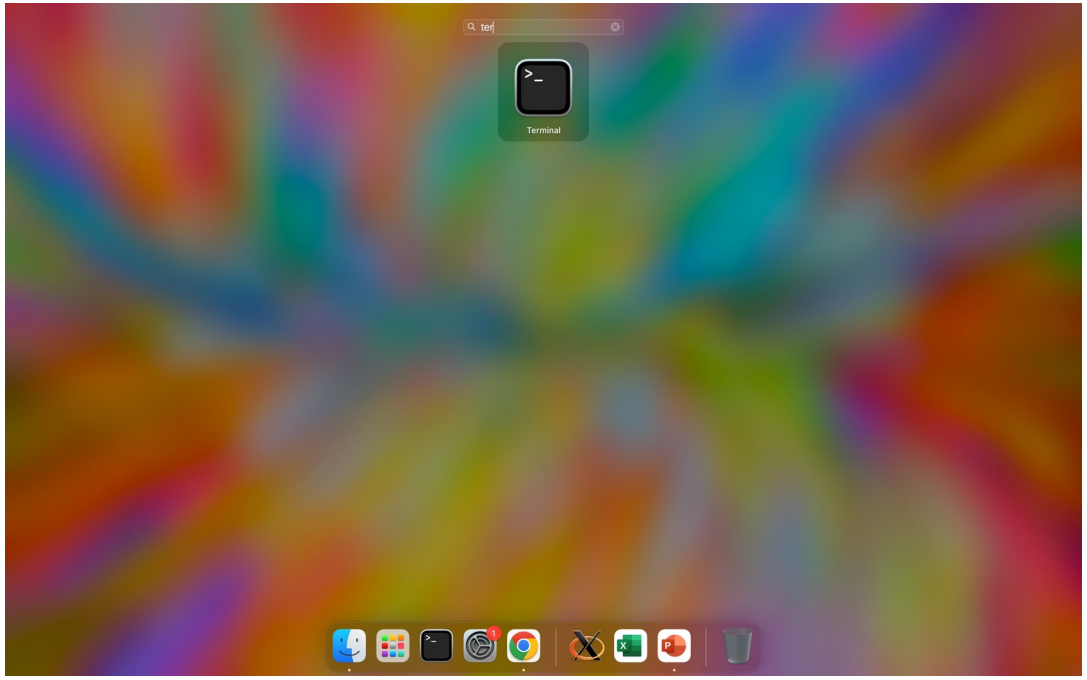
Windows User: MobaXterm

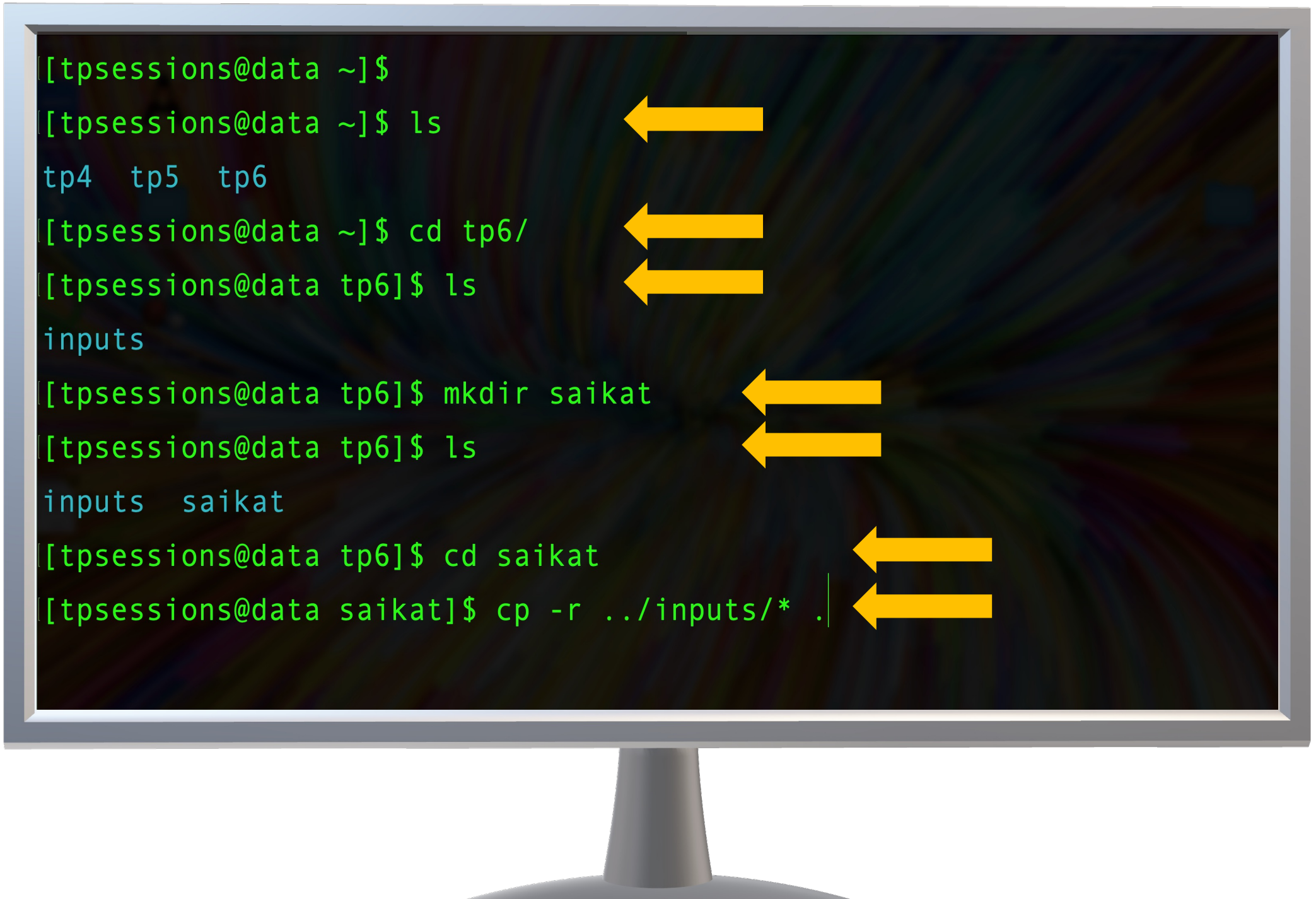


Mac User: Terminal

Go to “Launchpad”

→ look for “Terminal”

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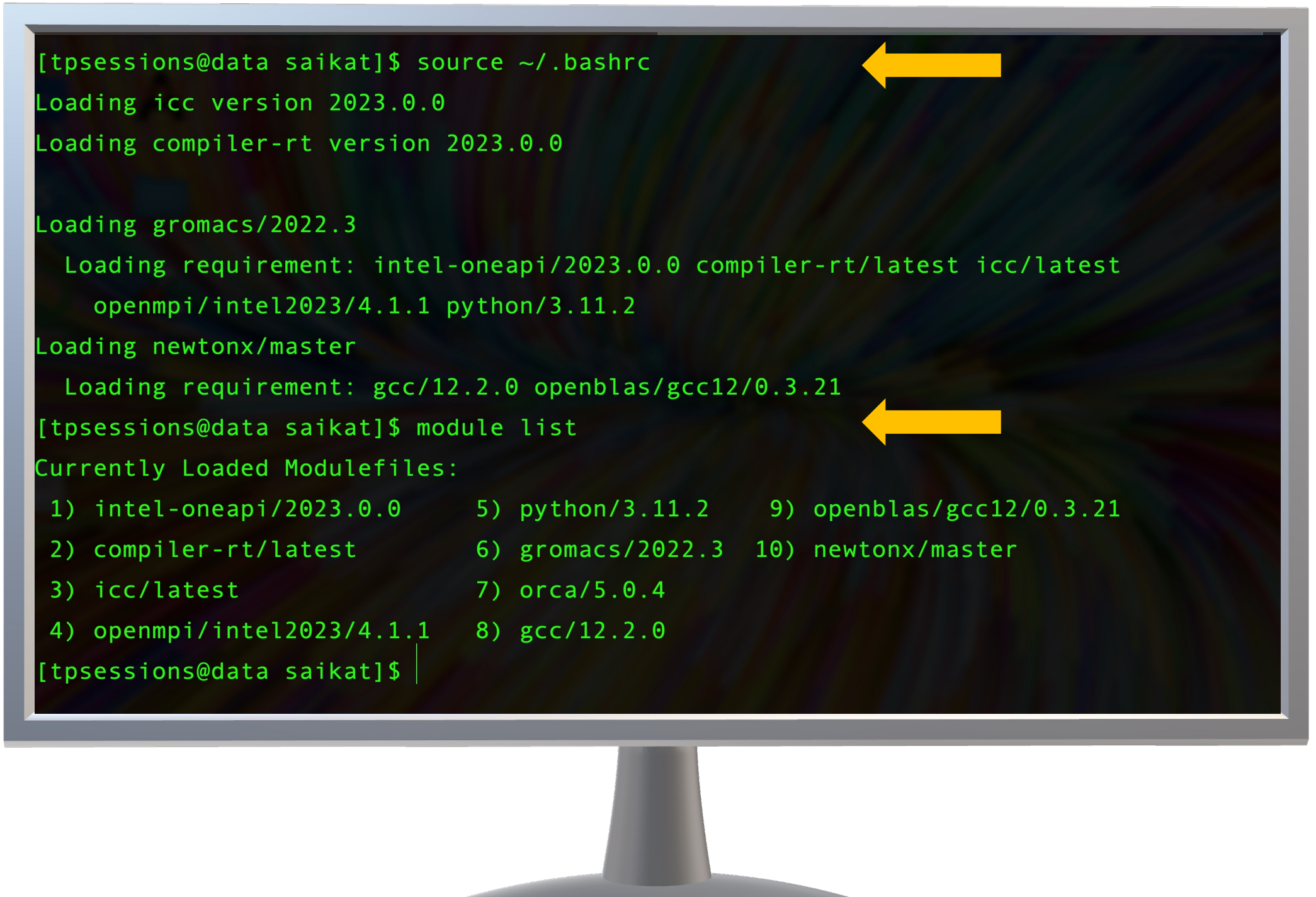
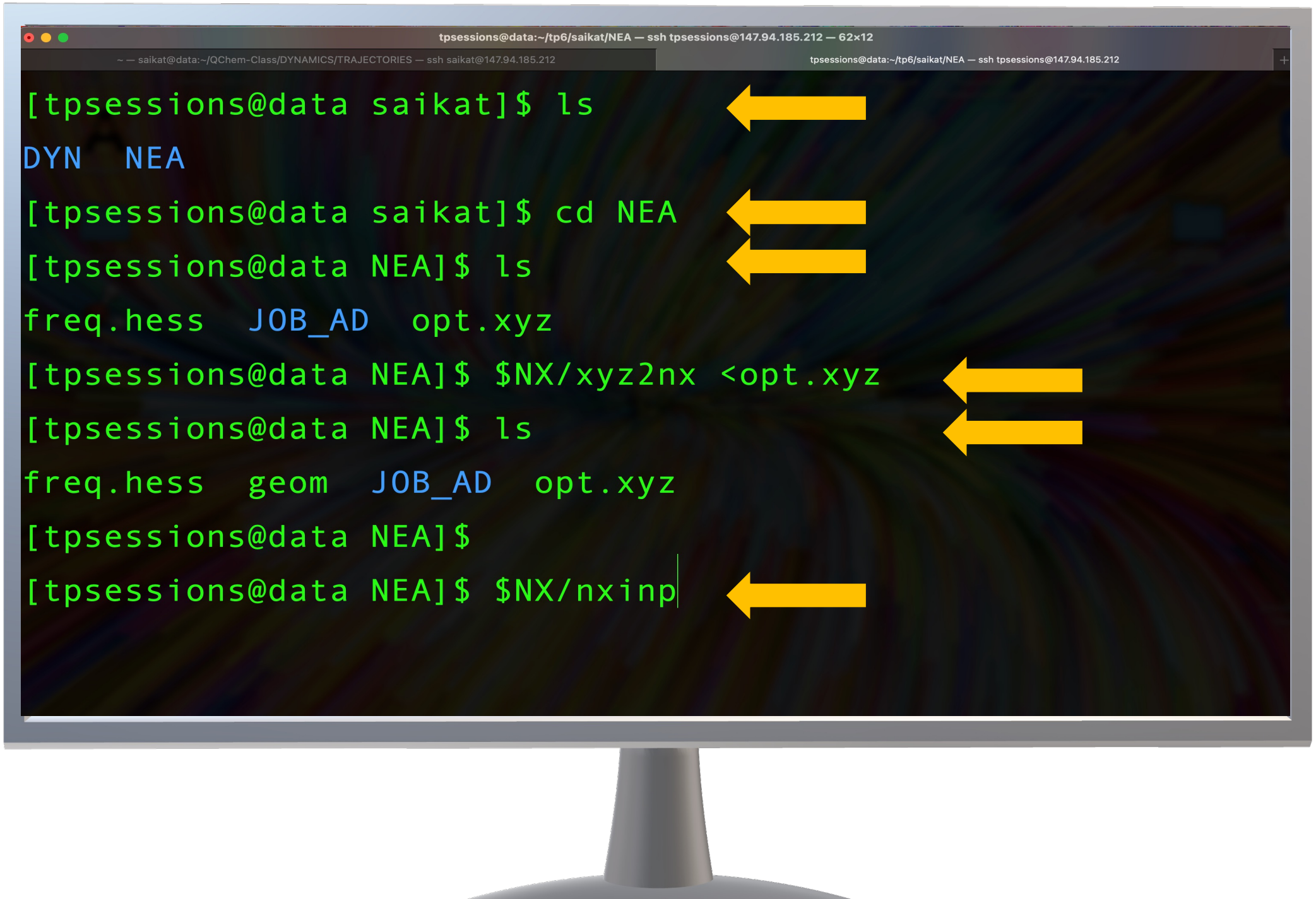
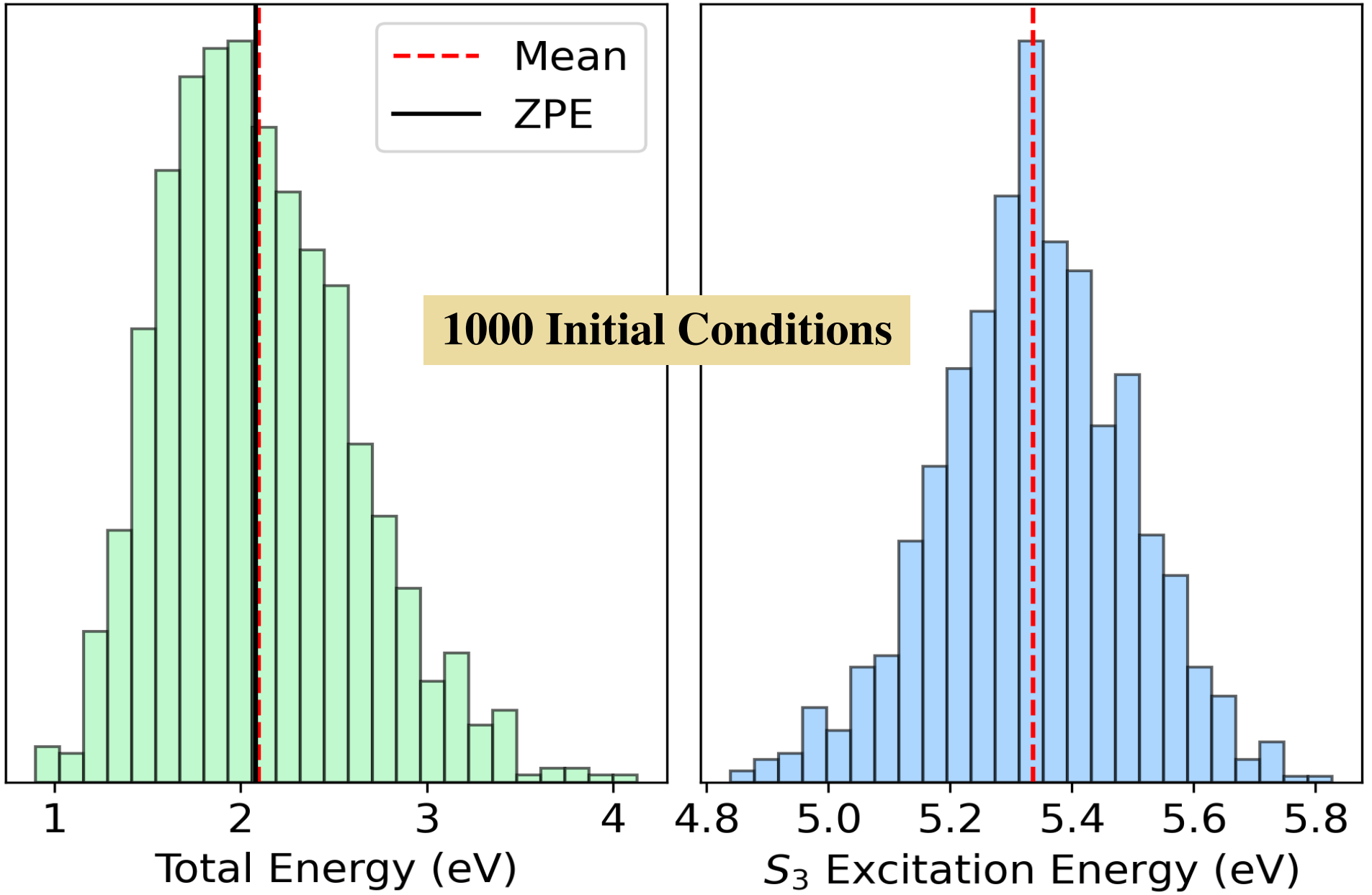
[tpsessions@data ~]$ ls
tp4 tp5 tp6
[tpsessions@data ~]$ cd tp6/
[tpsessions@data tp6]$ ls
inputs
[tpsessions@data tp6]$ mkdir saikat
[tpsessions@data tp6]$ ls
inputs saikat
[tpsessions@data tp6]$ cd saikat
[tpsessions@data saikat]$ cp -r ../inputs/* .

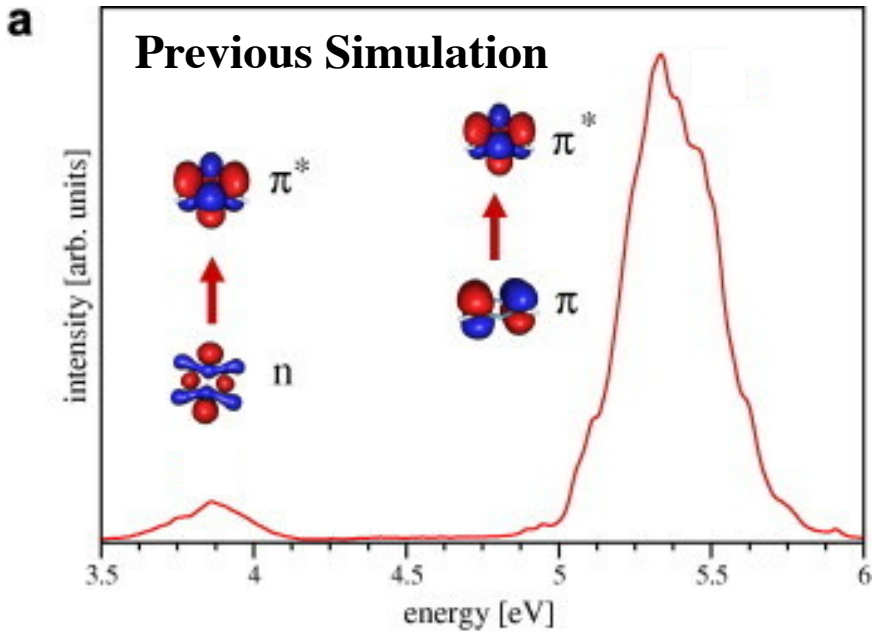

[tpsessions@data saikat]$ source ~/.bashrc
Loading icc version 2023.0.0
Loading compiler-rt version 2023.0.0
Loading gromacs/2022.3
Loading requirement: intel-oneapi/2023.0.0 compiler-rt/latest icc/latest
openmpi/intel2023/4.1.1 python/3.11.2
Loading newtonx/master
Loading requirement: gcc/12.2.0 openblas/gcc12/0.3.21
[tpsessions@data saikat]$ module list
Currently Loaded Modulefiles:
1) intel-oneapi/2023.0.0
2) compiler-rt/latest
3) icc/latest
4) openmpi/intel2023/4.1.1
5) python/3.11.2
6) gromacs/2022.3
7) orca/5.0.4
8) gcc/12.2.0
9) openblas/gcc12/0.3.21
10) newtonx/master
[tpsessions@data saikat]$

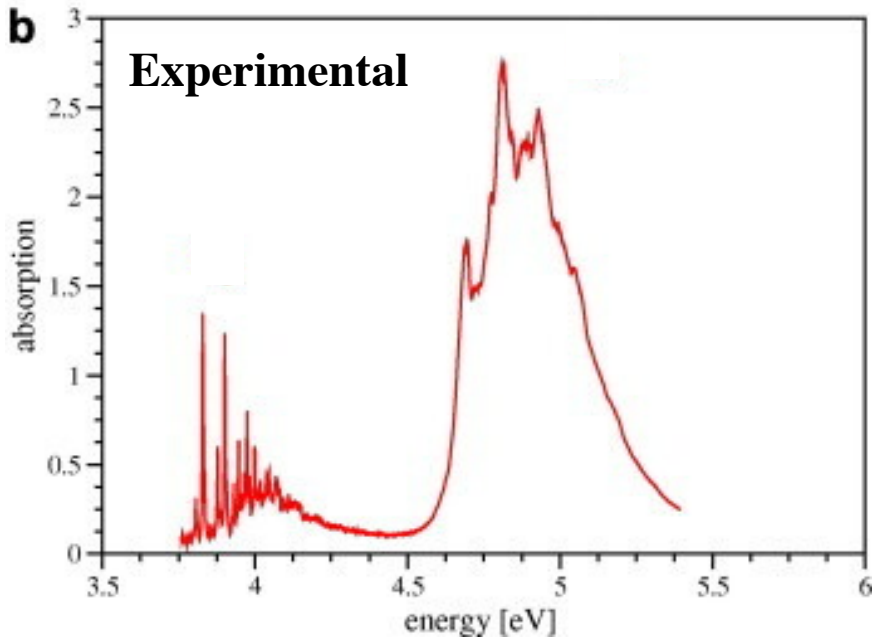

tpsessions@data:~/tp6/saikat/NEA — ssh tpsessions@147.94.185.212 — 62×12
~ — saikat@data:~/QChem-Class/DYNAMICS/TRAJECTORIES — ssh saikat@147.94.185.212
tpsessions@data:~/tp6/saikat/NEA — ssh tpsessions@147.94.185.212
[tpsessions@data saikat]$ ls
DYN NEA
[tpsessions@data saikat]$ cd NEA
[tpsessions@data NEA]$ ls
freq.hess JOB_AD opt.xyz
[tpsessions@data NEA]$ $NX/xyz2nx <opt.xyz
[tpsessions@data NEA]$ ls
freq.hess geom JOB_AD opt.xyz
[tpsessions@data NEA]$
[tpsessions@data NEA]$ $NX/nxinp

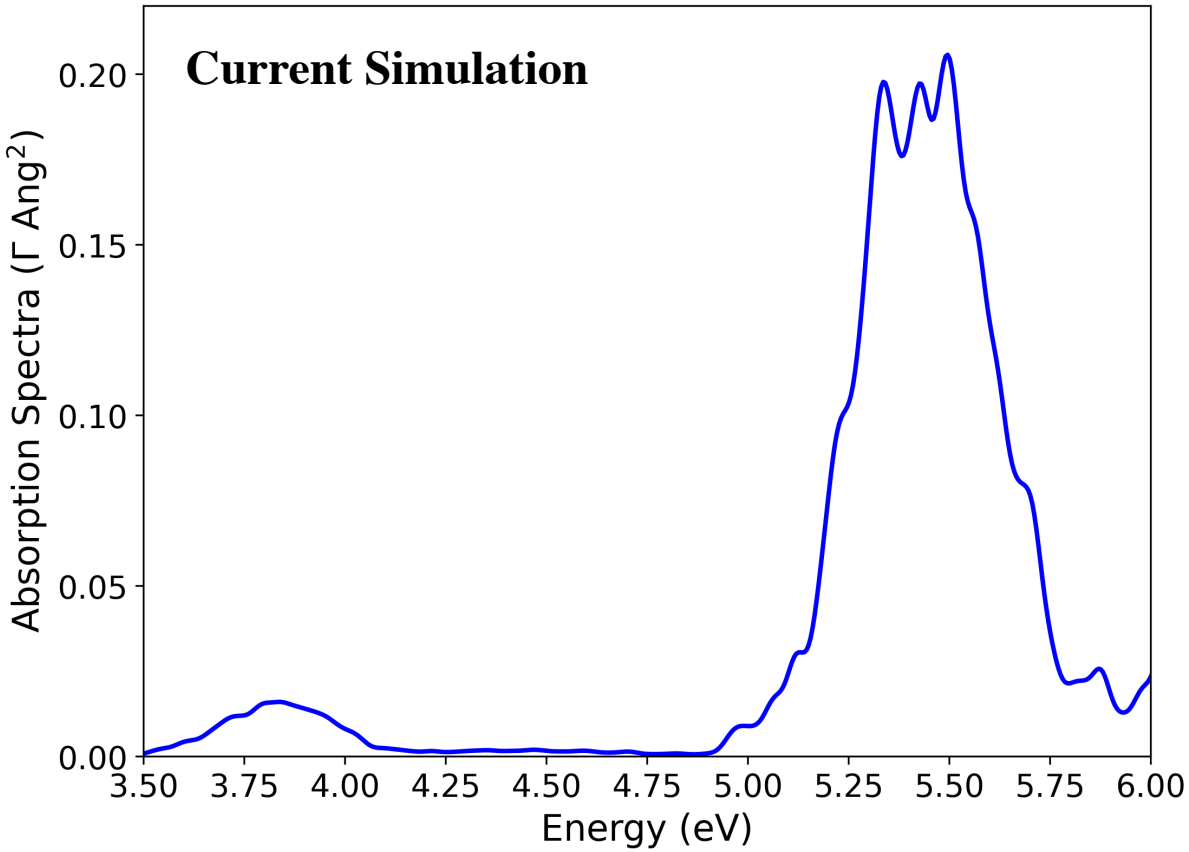
NEA Wigner Sampling: Pyrazine



Absorption Spectra

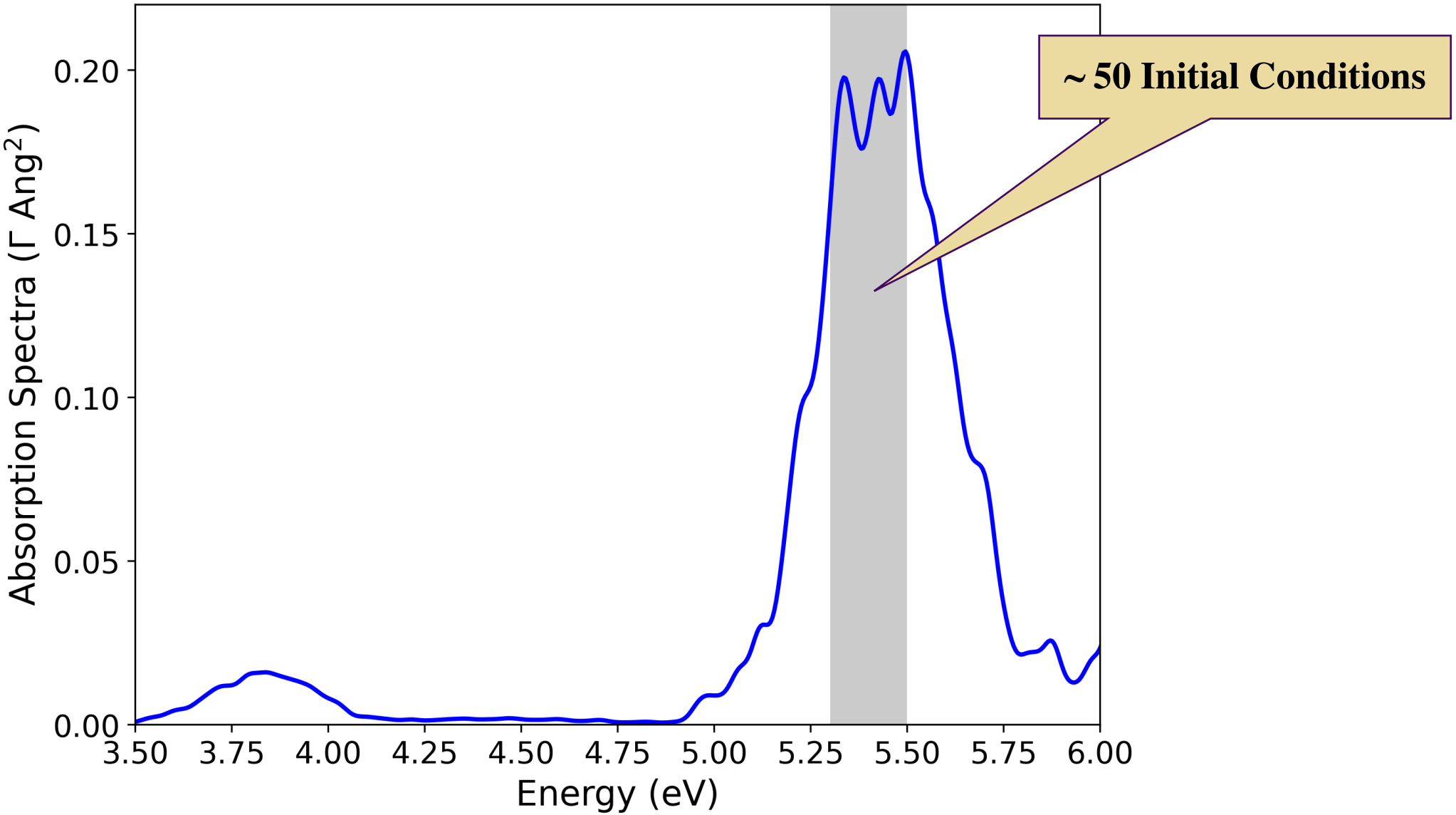




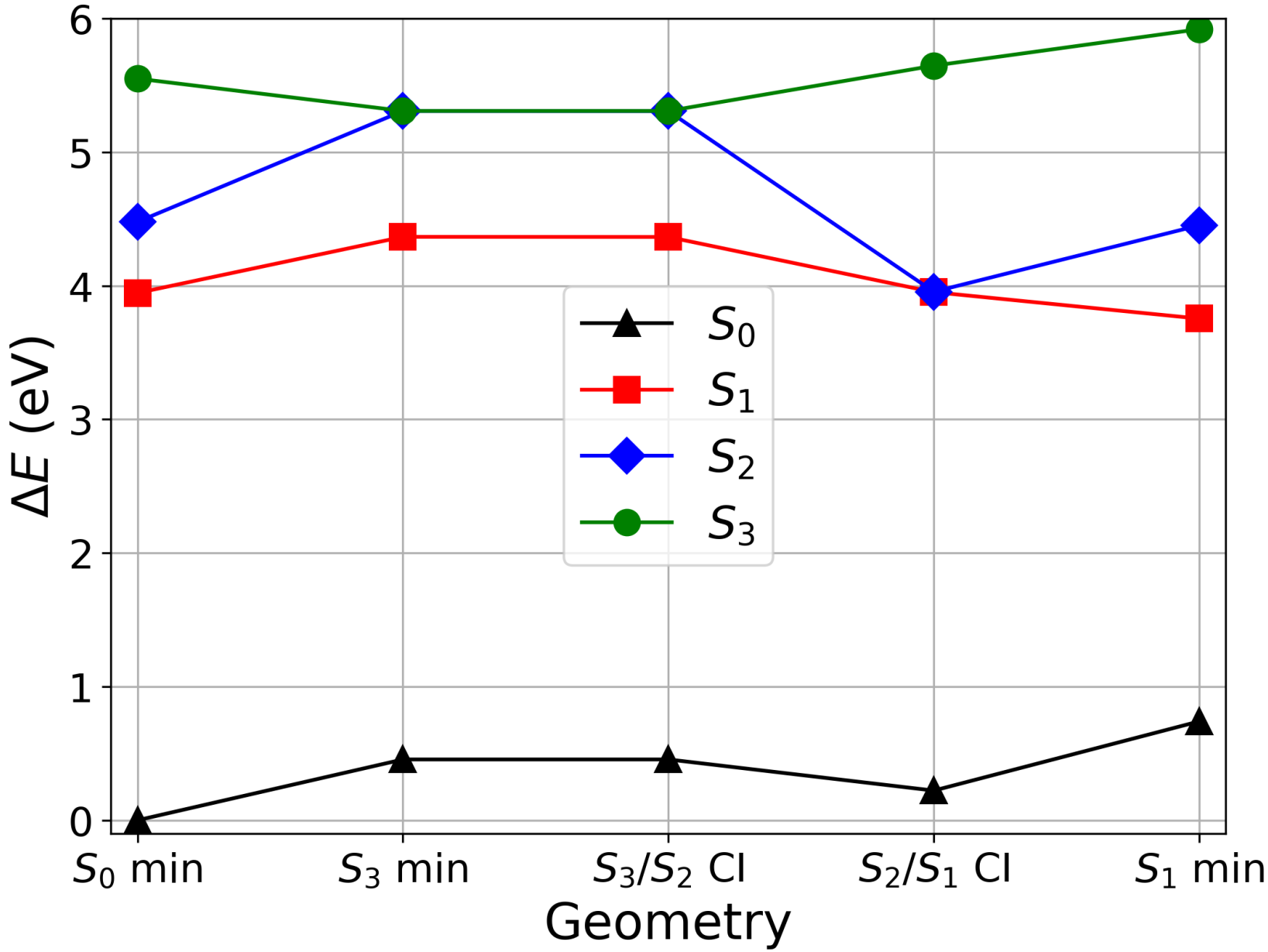


U. Werner, r. Mitric, T. Suzuki, V. Bonacic-Koutecky, *Chem. Phys.* **349**, 319 (2008).

Selected Initial Conditions



Pyrazine: PESs Topology



Fewest-Switch Surface Hopping

$$\frac{d^2\mathbf{R}_\alpha}{dt^2} = \frac{1}{M_\alpha}\mathbf{F}(\mathbf{R}) \qquad \mathbf{F}(\bar{\mathbf{R}}) = -\nabla_\alpha E_L$$

$$\frac{dc_J}{dt} = \sum_K -c_K\left(\frac{i}{\hbar}E_K + \sigma_{JK}\right) \qquad \sigma_{JK}(\mathbf{R}) \equiv \left\langle \psi_J \middle| \frac{\partial \psi_K}{\partial t} \right\rangle$$

$$P_{L\to J}^{FSSH} = \max\left[0, \frac{-2\Delta t}{|c_L|^2}\mathrm{Re}\left(\sigma_{LJ}c_J c_L^*\right)\right]$$

$$\sum_{K=1}^{J-1} P_{L\to K}^{FSSH} < r_t \le \sum_{K=1}^{J} P_{L\to J}^{FSSH}$$

Initial Geometries ✓

Initial Velocities ✓

Initial Electronic State ✓

Initial TDSE coefficients ✓

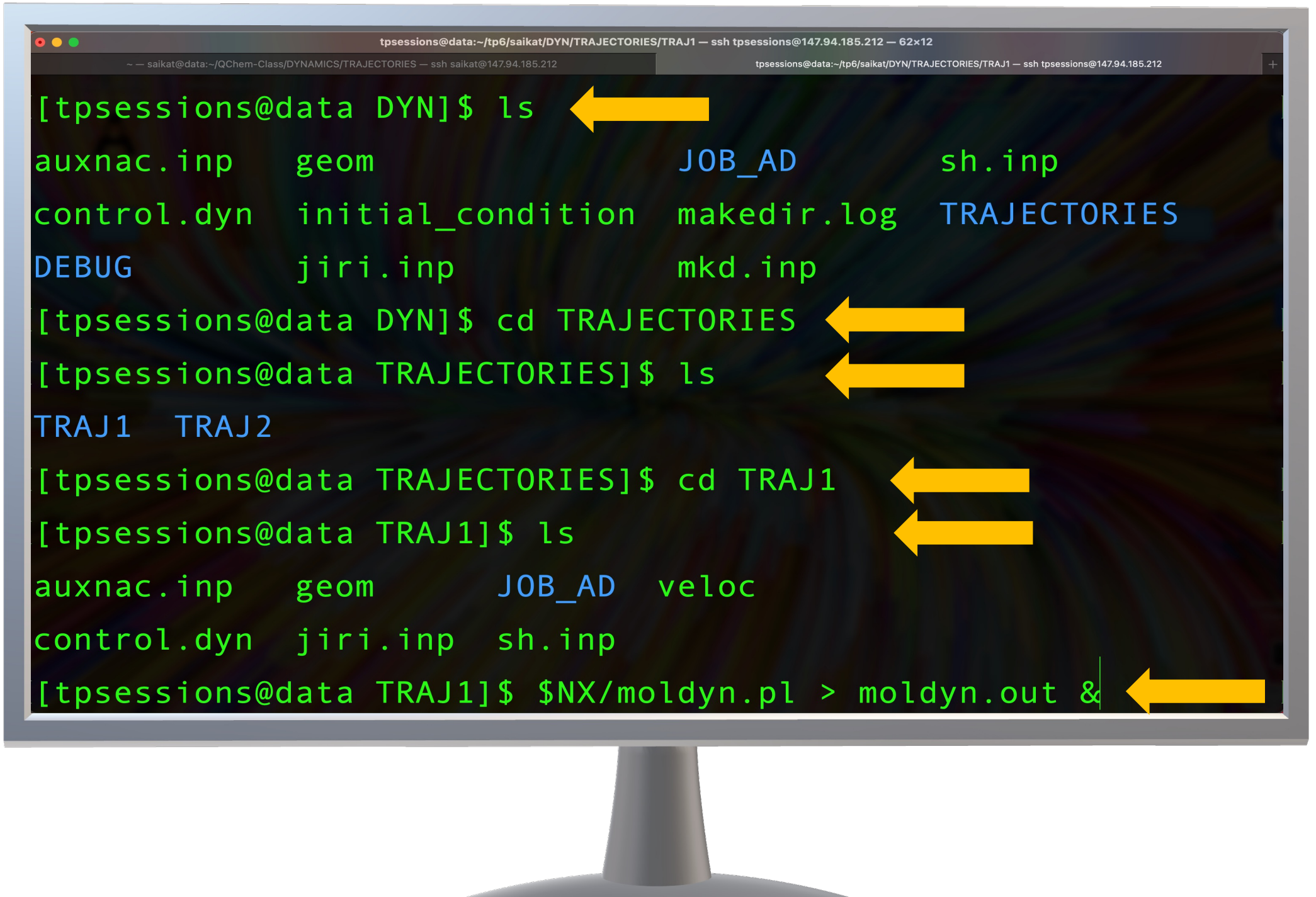
What to do with NAC σ

Time-dependent Baeck-An (TDBA) NAC

$$\sigma_{JL} \equiv \mathbf{v} \cdot \mathbf{h}_{JL} \approx \begin{cases} \dfrac{\mathrm{sgn}\left(\Delta E_{JL}\right)}{2} \sqrt{\dfrac{1}{\Delta E_{JL}} \dfrac{d^2 \Delta E_{JL}}{dt^2}} & \text{if } \dfrac{1}{\Delta E_{JL}} \dfrac{d^2 \Delta E_{JL}}{dt^2} > 0 \\ 0 & \text{if } \dfrac{1}{\Delta E_{JL}} \dfrac{d^2 \Delta E_{JL}}{dt^2} \leq 0 \end{cases}$$

K. K. Baeck, H. An, *J. Chem. Phys.* **146**, 064107 (2017).
M. T. do Casal, J. Toldo, M. Pinheiro Jr., M. Barbatti, *Open Res Europe* **1**, 49 (2022).


tpsessions@data:~/tp6/saikat/DYN — ssh tpsessions@147.94.185.212 — 62×12
~ — saikat@data:~/QChem-Class/DYNAMICS/TRAJECTORIES — ssh saikat@147.94.185.212
tpsessions@data:~/tp6/saikat/DYN — ssh tpsessions@147.94.185.212
[tpsessions@data NEA]$ cd ../
[tpsessions@data saikat]$ ls
DYN NEA
[tpsessions@data saikat]$ cd DYN
[tpsessions@data DYN]$ ls
geom initial_condition JOB_AD
[tpsessions@data DYN]$ $NX/nxinp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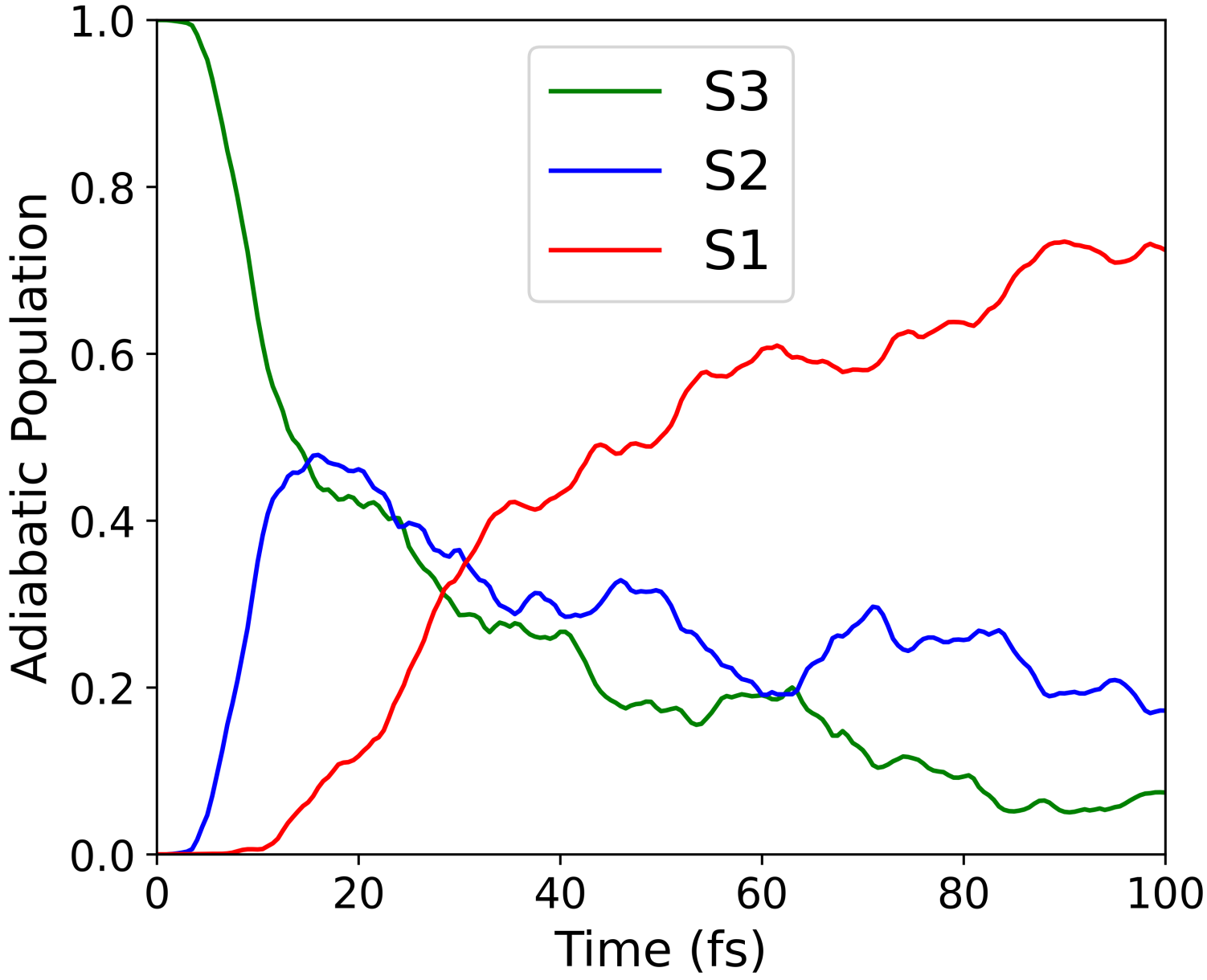
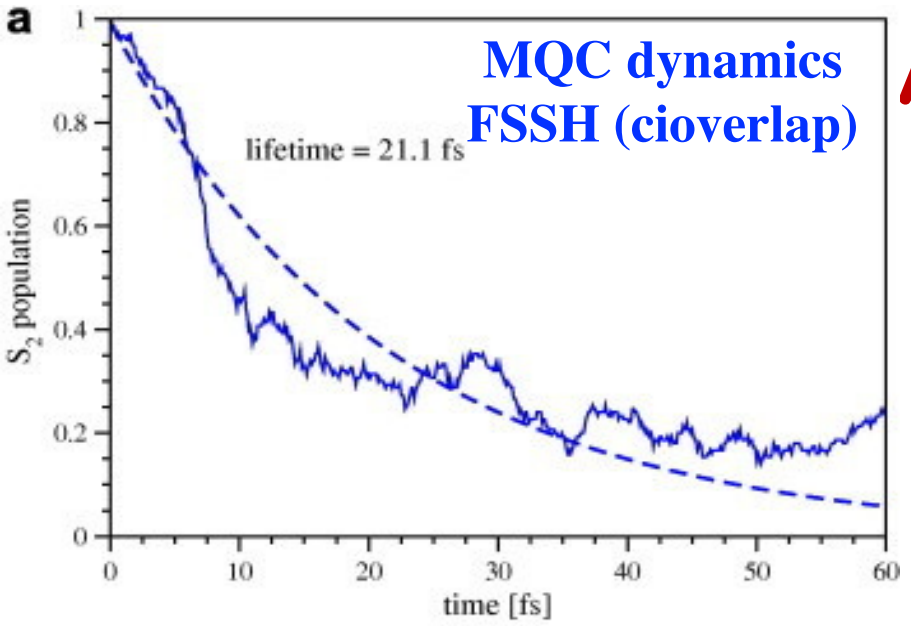
~ — saikat@data:~/QChem-Class/DYNAMICS/TRAJECTORIES — ssh saikat@147.94.185.212
tpsessions@data:~/tp6/saikat/DYN/TRAJECTORIES/TRAJ1 — ssh tpsessions@147.94.185.212
[tpsessions@data DYN]$ ls
auxnac.inp geom JOB_AD sh.inp
control.dyn initial_condition makedir.log TRAJECTORIES
DEBUG jiri.inp mkd.inp
[tpsessions@data DYN]$ cd TRAJECTORIES
[tpsessions@data TRAJECTORIES]$ ls
TRAJ1 TRAJ2
[tpsessions@data TRAJECTORIES]$ cd TRAJ1
[tpsessions@data TRAJ1]$ ls
auxnac.inp geom JOB_AD veloc
control.dyn jiri.inp sh.inp
[tpsessions@data TRAJ1]$ $NX/moldyn.pl > moldyn.out &

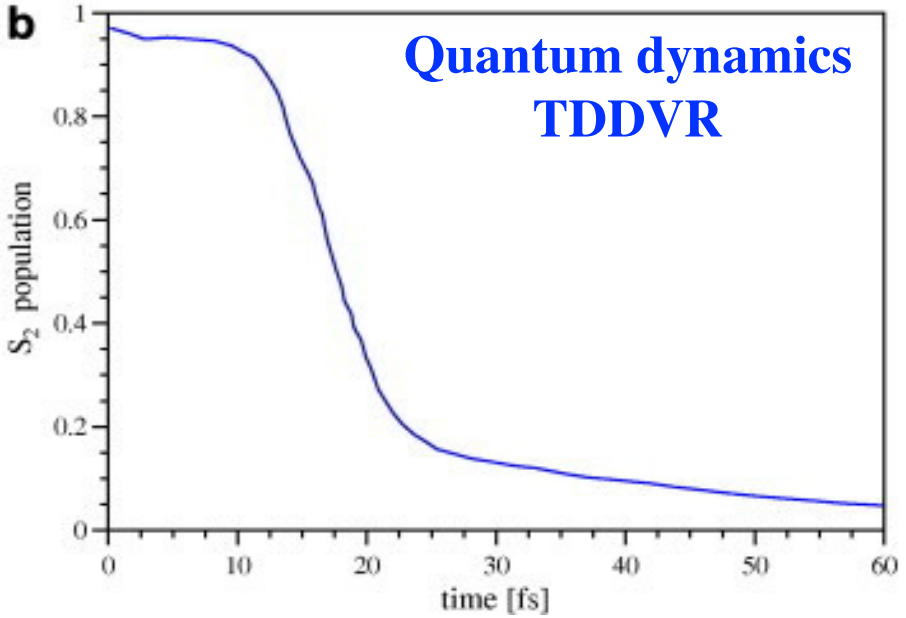
Analysis: Population Profile

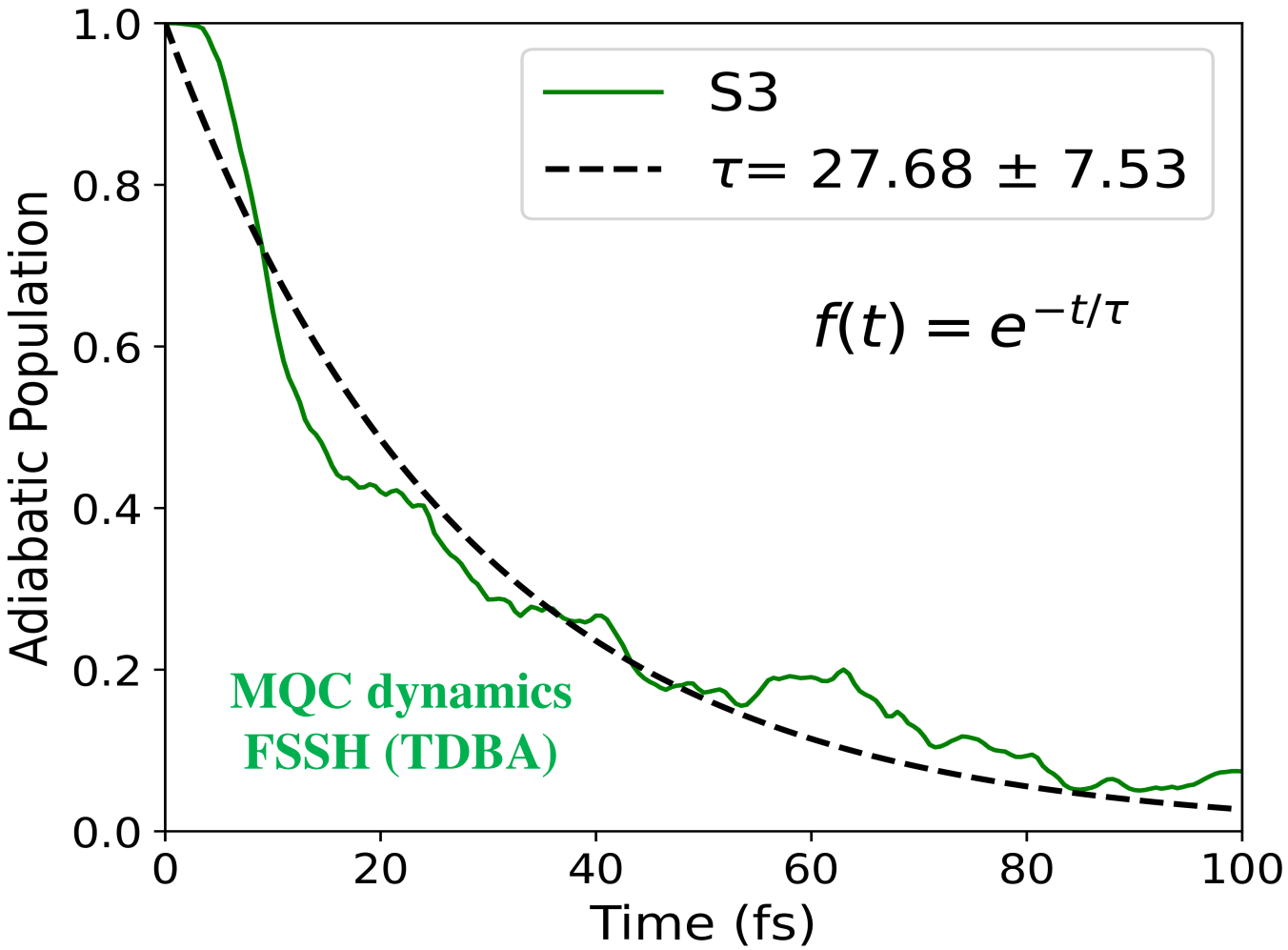
80 Trajectories



Analysis: S_3 Lifetime





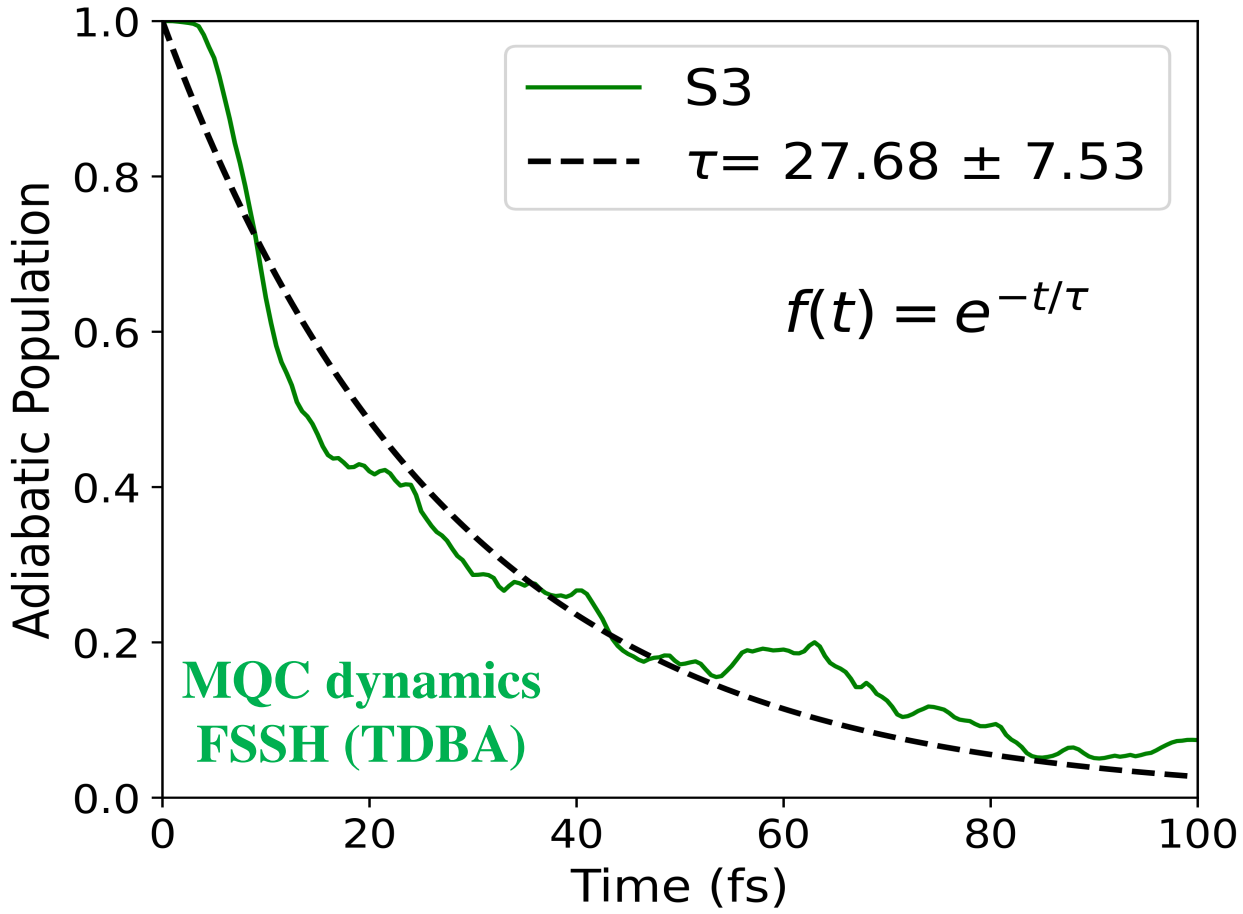


FSSH: U. Werner, R. Mitric, T. Suzuki, V. Bonacic-Koutecky, *Chem. Phys.* **349**, 319 (2008).

QD: P. Puzari, R. S. Swathi, B. Sarkar, S. Adhikari, *J. Chem. Phys.* **123**, 134317 (2005).

Analysis: S_3 Lifetime

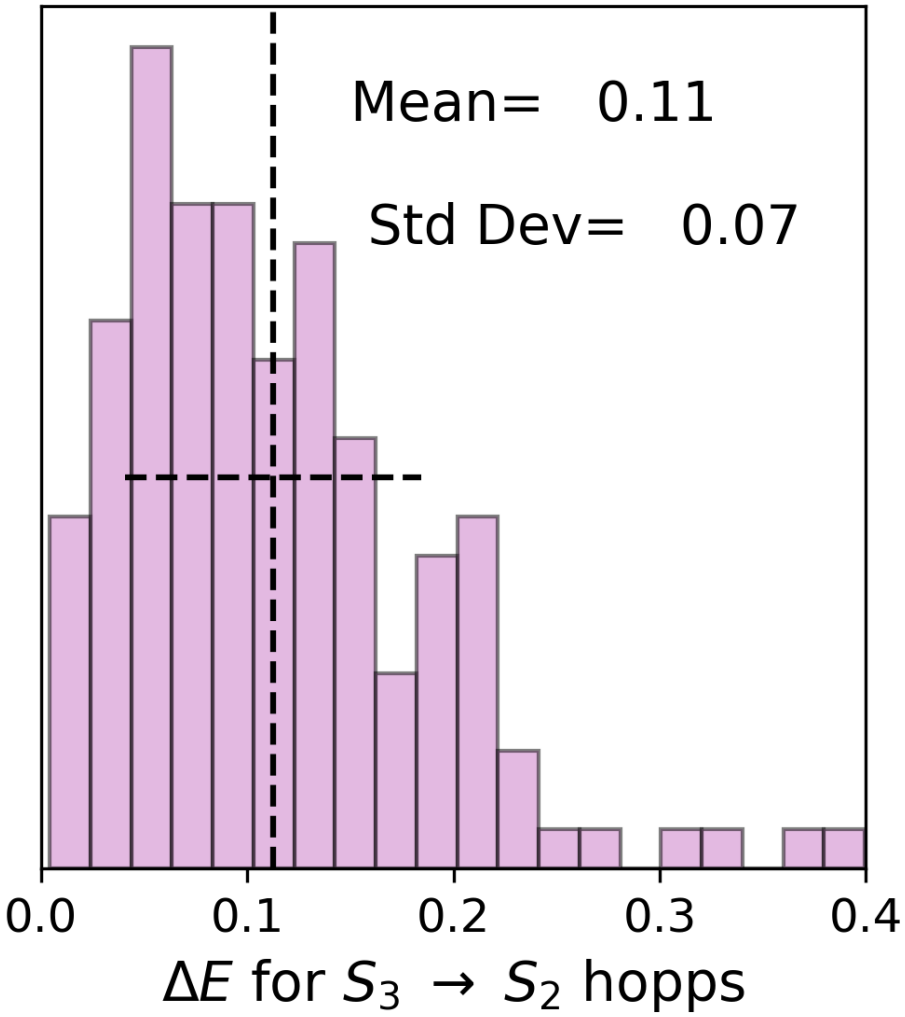
	S_3 Lifetime (fs)
Experiment	**20 ± 10**
FSSH (NAC – cioverlap)	**21.1**
FSSH (NAC – TDBA)	**28 ± 8**

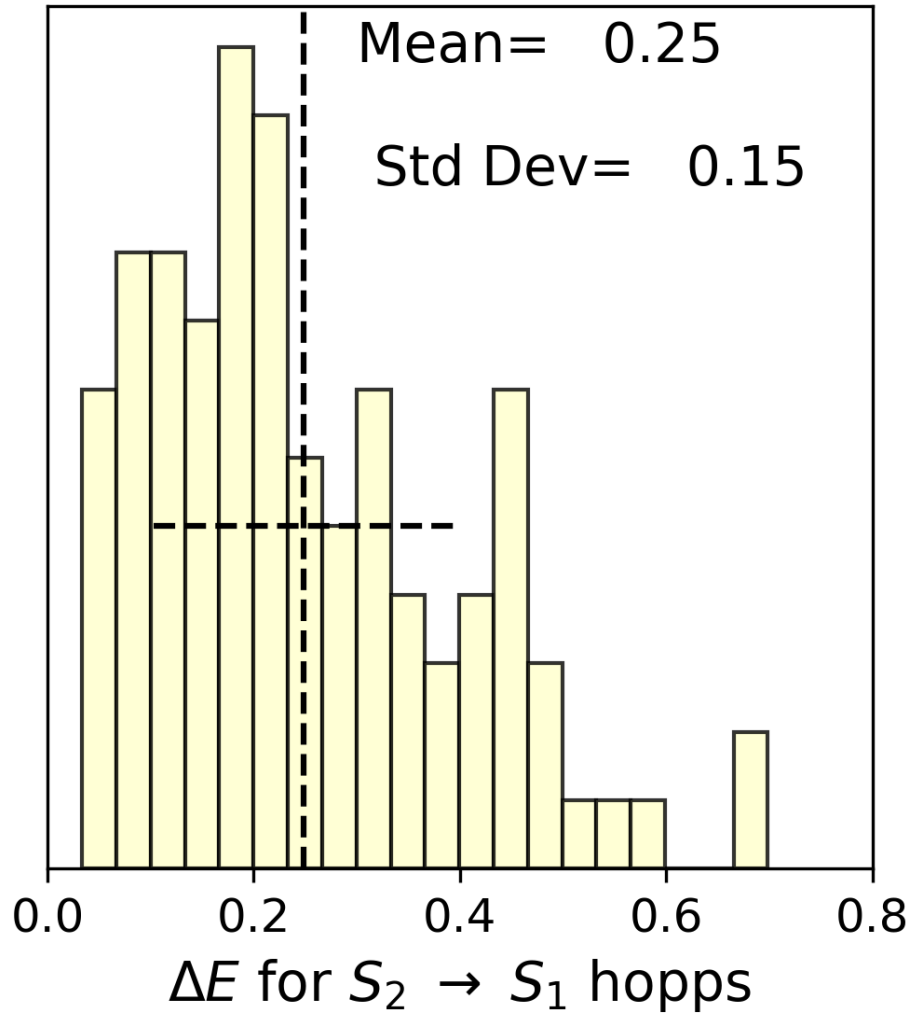


FSSH: U. Werner, R. Mitric, T. Suzuki, V. Bonacic-Koutecky, *Chem. Phys.* **349**, 319 (2008).
Expt.: V. Stert, P. Farmanara, W. Radloff, *J. Chem. Phys.* **112**, 4460 (2000).

Analysis: Hopping

80 Trajectories

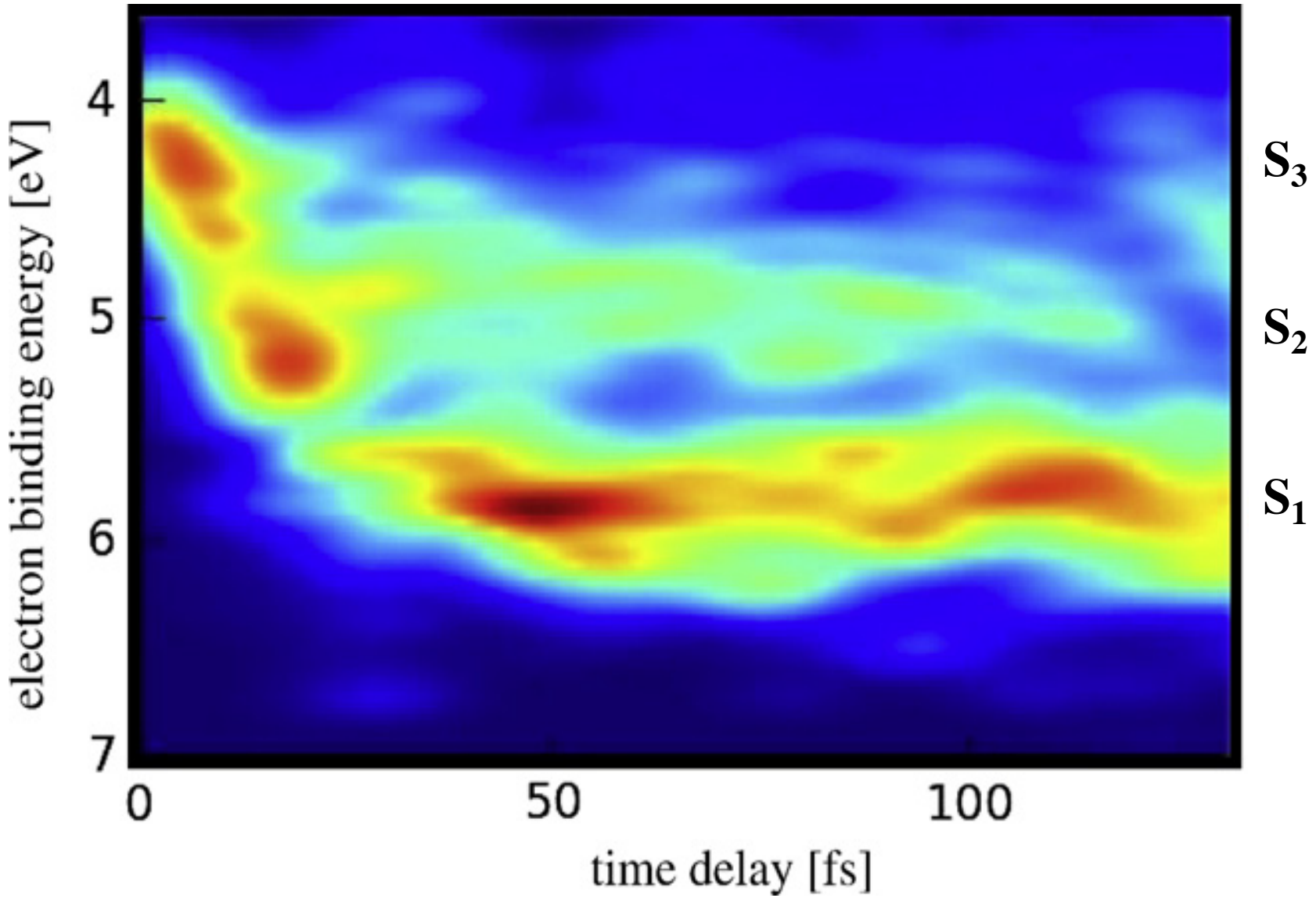




Exponential Distribution
S_3/S_2 Conical Intersection

Gaussian Distribution
S_2/S_1 Avoided Crossing

Analysis: Calculated TRPES

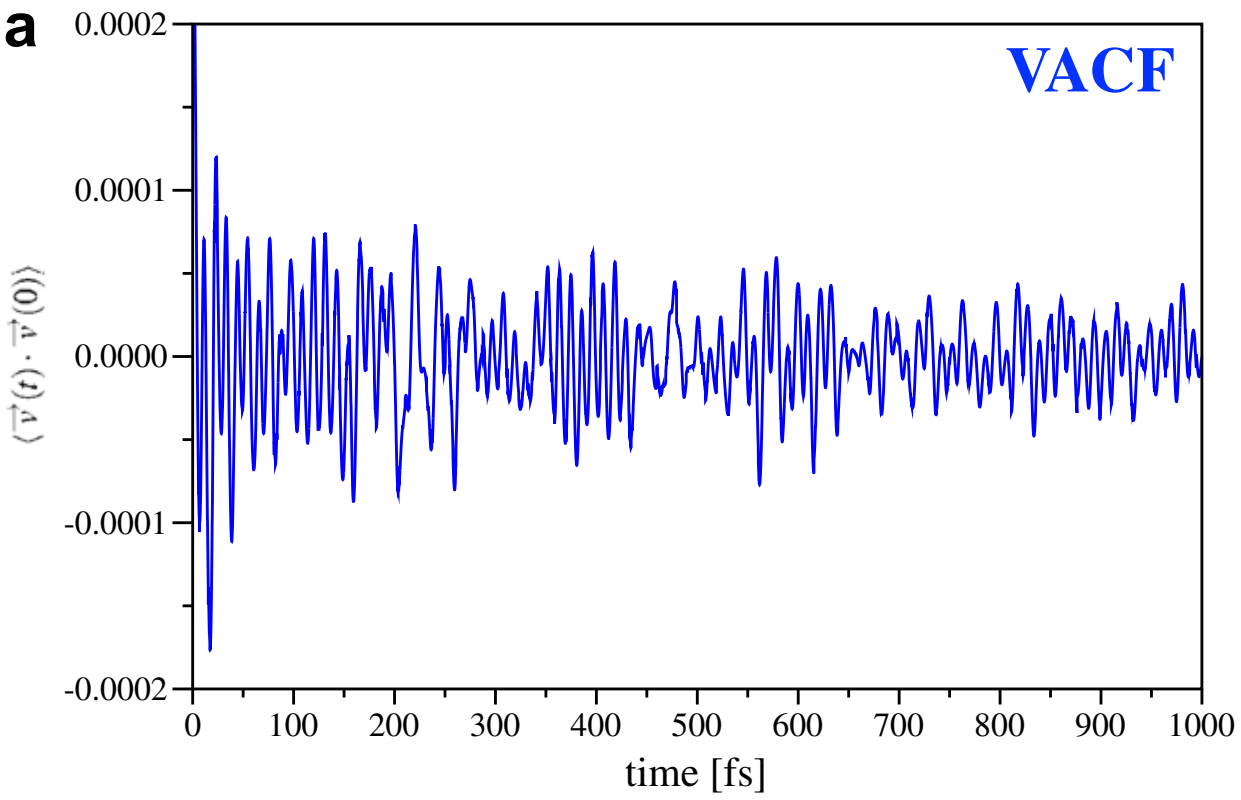


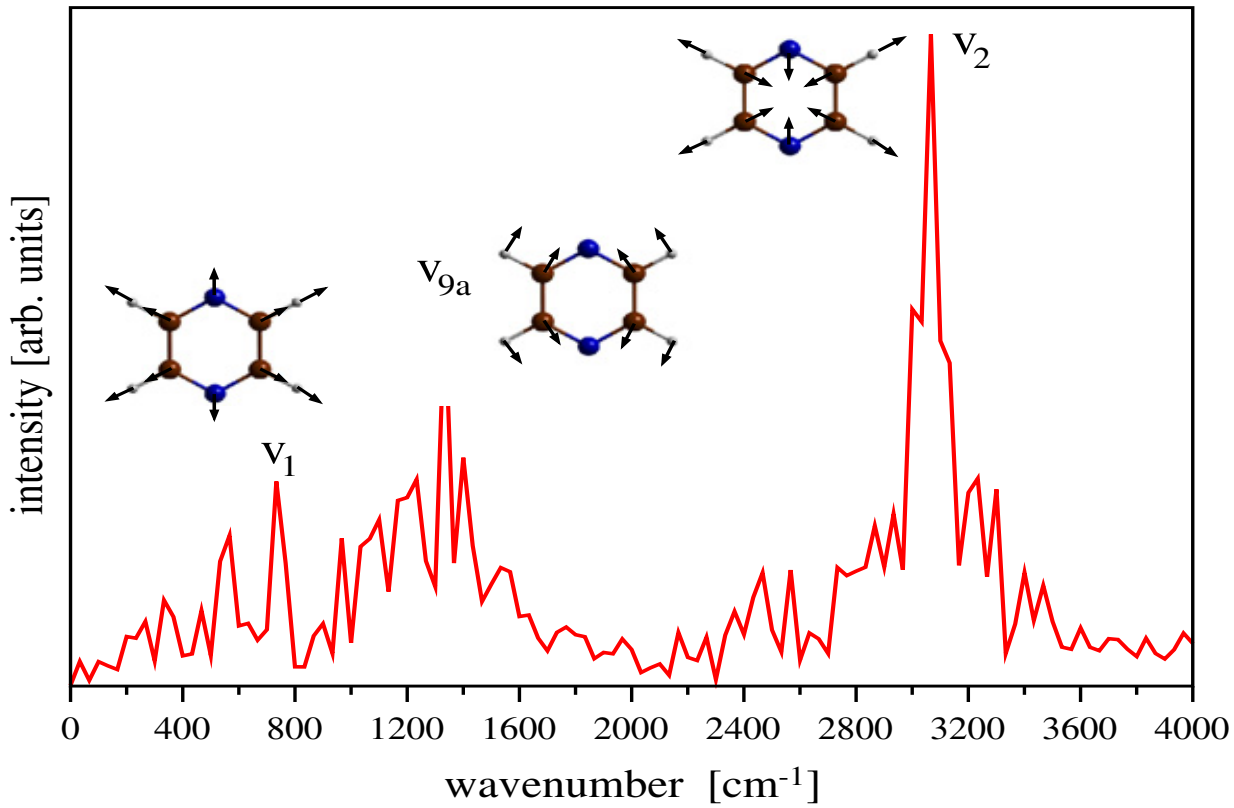
U. Werner, R. Mitric, T. Suzuki, V. Bonacic-Koutecky, *Chem. Phys.* **349**, 319 (2008).

Analysis: Power spectrum

Power Spectra:
Fourier transform of the velocity autocorrelation function

$$P(\omega) = \int \langle v(\tau)\, v(\tau + t) \rangle_{\tau} e^{-i\omega t}\, dt$$





U. Werner, R. Mitric, T. Suzuki, V. Bonacic-Koutecky, *Chem. Phys.* **349**, 319 (2008).

Thank You

Happy Simulating !!!