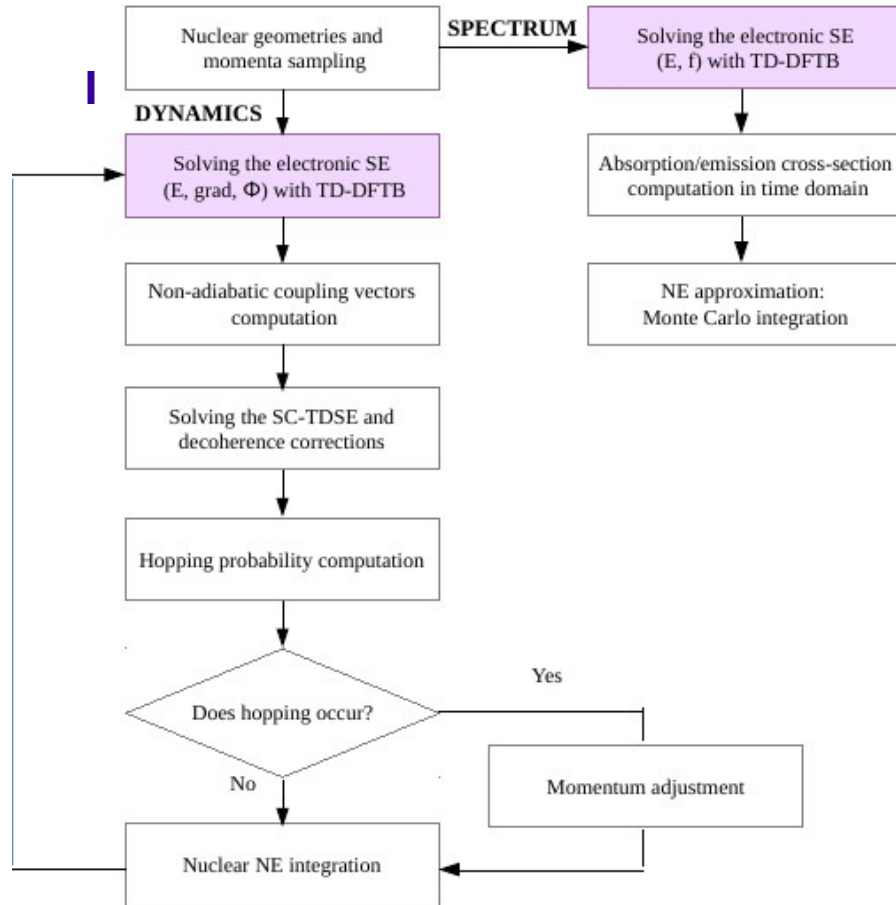# Fewest switches surface hopping with the TD-DFTB method (with the Newton-X code)
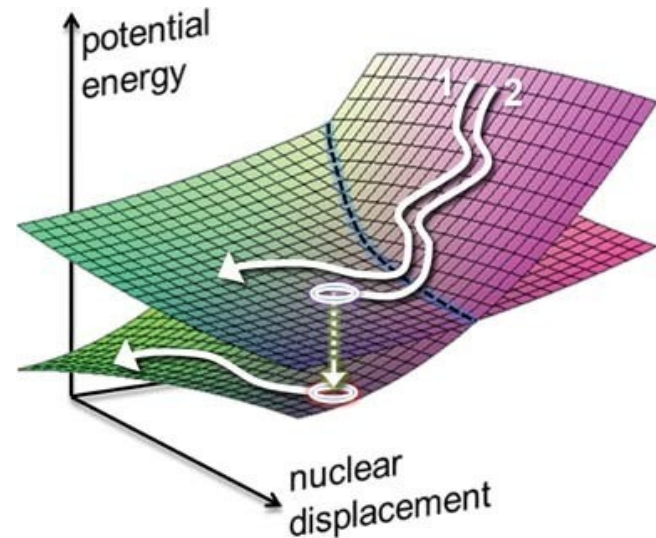
Instructor: Prof. Mario Barbatti

Aix-Marseille Universite

Co-instructor : Ljiljana Stojanovic
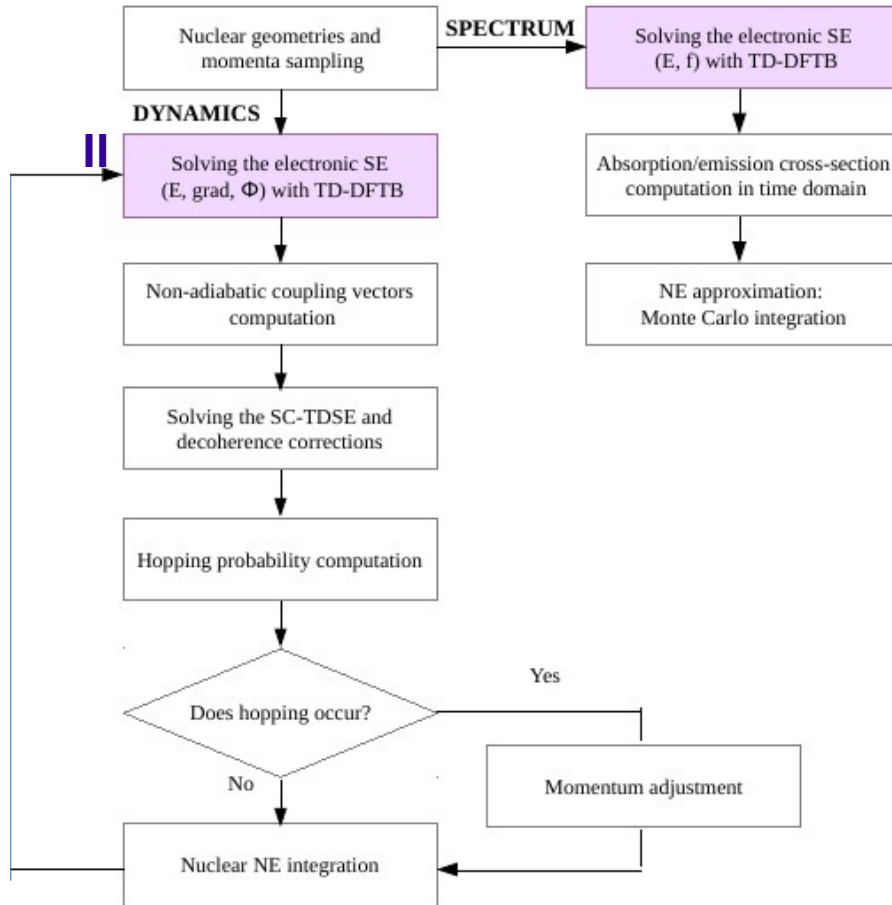
University College London

FSSH algorithm

I Initial conditions sampling
Wigner distribution

Barbatti, M. (2011), WIREs Comput Mol Sci, 1: 620-633.

A flowchart of the Newton-X code.

FSSH algorithm

A flowchart of the Newton-X code.

II Dynamics propagation

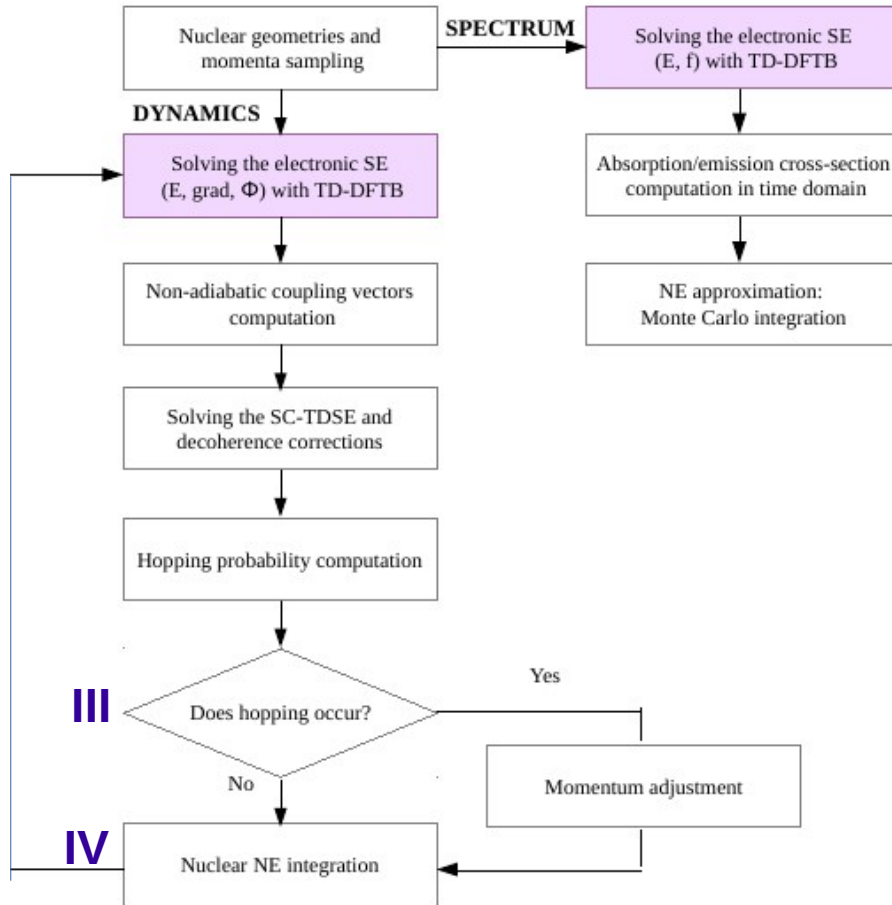$$\varphi\left(\mathbf{r},\mathbf{R}^c,t\right) = \sum_j c_j(t)\Phi_j\left(\mathbf{r};\mathbf{R}^c(t)\right)$$

$$\left(i\hbar\frac{\partial}{\partial t} - H_e\right)\varphi(\mathbf{r},\mathbf{R},t) = 0$$

$$i\hbar\frac{dc_k}{dt} + \sum_j\left(-H_{kj}^c + i\hbar\mathbf{F}_{kj}^c\cdot\mathbf{v}^c\right)c_j = 0$$

$$\mathbf{F}_{kj}^{c,m} \equiv \left\langle\Phi_k\middle|\nabla_{\mathbf{R}_m}\middle|\Phi_j\right\rangle_{\mathbf{r}}\left\langle\Phi_k\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle_{\mathbf{r}} = \mathbf{F}_{kj}^c\cdot\mathbf{v}^c$$

Solutions are **c** coefficients.

FSSH algorithm

A flowchart of the Newton-X code.

III Hopping probabilities

$$\rho_{lk}(t) = c_l c_k^*$$

$$P_{l \to k} = \max\left[0, -\frac{2\Delta t}{\rho_{ll}} \operatorname{Re}(\rho_{kl}) F_{kl}^c \cdot v^c\right]$$

IV Newton equations propagation

$$\frac{d^2 \mathbf{R}_m^c}{dt^2} - \frac{\mathbf{F}_m^c}{M_m} = 0$$

Density functional tight binding (DFTB)

Density represented by Taylor expansion around reference density (atomic density)

$$E^{\mathrm{DFTB}}[\rho] =$$

$$\underbrace{\underbrace{E^0[\rho_0] + E^1[\rho_0, \delta\rho]}_{\text{DFTB1}} + E^2[\rho_0, (\delta\rho)^2] + E^3[\rho_0, (\delta\rho)^3] + \cdots}$$

DFTB2

DFTB3

Solutions: KS orbitals and orbital energies

Approximations:

1. Minimal STO atomic orbital set.

2. Only valence orbitals considered.

3. Non-diag. elements of $E[\rho_0]$ precomputed and stored. (SK files)

4. Diagonal el. Are precomputed atomic orbital E.

5. Mulliken approximation:
ρ fluctuations via atomic point charges.

6. Parameterization of the remaining Hamiltonian terms (Hubbard parameters).

Linear-response TD-DFTB

TD-DFTB equation

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}* & \mathbf{A}* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia\|jb)$$

$$B_{ia,jb} = (ia\|bj)$$

Approximation:

Mulliken approximation in orbital transition densities (in 2e integrals).

Solutions: |X+Y> vectors and excitation energies

Excited state wave function representation (Casida's Ansatz)

$$|\psi_J\rangle = \sum_{i,a} (X + Y)^J_{ia} |\Phi_{ia}\rangle$$

They are used in nonadiabatic couplings computations.

Number of terms in the expansion:

Nocc·Nvirt

Frozen core discarded

DFTB+ program - important features

- Second and third order expansion of electron density;

- GGA and long-range corrected functionals;

- Analytical gradients in the ground and excited states (for GGA and LC);

- Dispersion interactions (Lennard-Jones, Slater-Kirkwood, D3 correction);

- Analytical nonadiabatic coupling vectors (recent implementation);

- AIMD subroutines coupled with several thermostats and barostats.

Linear-response TD-DFTB

Advantages:

- Speedup in the energies and gradients computation (wrt the conventional TD-DFT, whereas the accuracy is similar);

- Speedup in the computation of nonadiabatic couplings

(due to decreased dimension of the excited states' wave functions);

- Possibility to use long-range corrected functionals;

- Analytic gradients available for both TD-DFTB and TD-LC-DFTB.

Disadvantages:

- Single-determinant method

(instabilities in the case of ground state degeneracy, like Cis with the ground state);

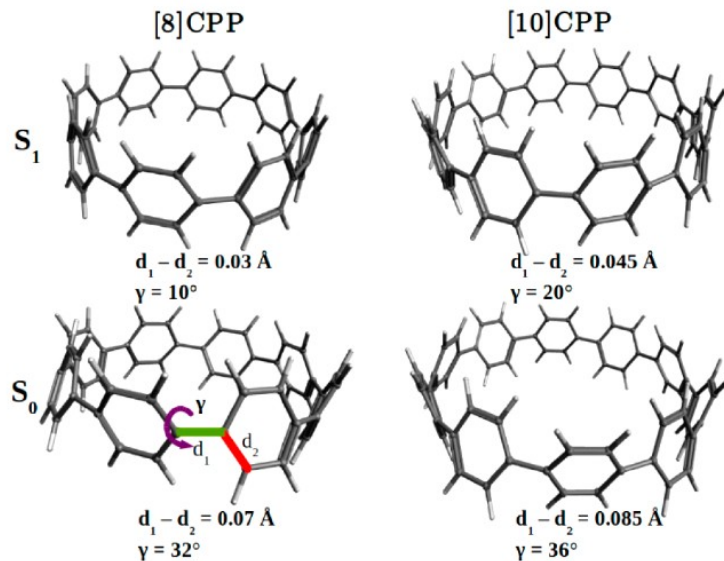- Number of excited states limited

Example: water molecule

Nocc = 4; Nvirt = 2; N(SPX) = 8

It is possible to compute only 8 excited states;

- Only GGA and LR-corrected functionals available.

Applications of the FSSH/TD-DFTB method

FSSH dynamics of cycloparaphenylenes

Due to the low computational cost it is possible to simulate extended systems for longer simulation times.

[8]CPP   [10]CPP

S_1

$d_1 - d_2 = 0.03$ Å
$\gamma = 10°$

$d_1 - d_2 = 0.045$ Å
$\gamma = 20°$

S_0

$d_1 - d_2 = 0.07$ Å
$\gamma = 32°$

$d_1 - d_2 = 0.085$ Å
$\gamma = 36°$

Time: 3ps
Number of excited states: 7
Number of atoms: 100 (80)

Other features:

- Analysis of exciton character (THEODORE code);
- Normal mode analysis during dynamics.

Stojanović; Aziz; Hilal; Plasser; Niehaus; Barbatti. *JCTC* **2017**, *13*, 5845

Test case: Spectrum and dynamics of tetrathiophene in vacuum

To be able to follow this tutorial, please:

1. connect to your accounts with ssh X forwarding:

ssh -X username@vortex.ccr.buffalo

2. load:

module load nx/2.2-B09

3. cp -rf /projects/academic/cyberwksp21/Software/inputs/tddftb_dynamics */your_folder*

or cp -rf /user/ub2036/tddftb_dynamics */your_folder*

Approach

Method / programs
- FSSH with Newton-X / DFTB+
(versions 17.1 and 2.2)

Electronic structure
- TD-DFTB/3ob-3-1 SK set

Initial conditions
- Uncorrelated Wigner sampling

Surface hopping
- Number of states: 1 and 5
- Initial state: S_1, S_5
- Classical timestep: 0.5 fs
- TDSE timestep: 0.5/20 fs
- Trajectory duration: variable
- DFTB+ interface
- Nonadiabatic couplings:
OD method
- Decoherence: SDM 0.1 au

Steps

1. Optimize ground state geometry and compute excited states

2. Prepare DFTB+ input for initial conditions

3. Compute initial conditions

4. Compute spectrum

5. Select initial conditions

6. Prepare DFTB+ input for dynamics

7. Prepare and run trajectories

8. Analyse

DFTB+ input for the initial conditions

```
Geometry = GenFormat {
 <<< "geom.gen"
}
```
→ Geometry section

```
Driver =  {}
```

```
Hamiltonian = DFTB {
  SCC = Yes
  Dispersion = LennardJones {
  Parameters = UFFParameters {}
  }
  SlaterKosterFiles = Type2FileNames {
  Prefix = "/home/ljiljana/Desktop/3ob-3-1/"
  Separator = "-"
  Suffix = ".skf"
  }
  MaxAngularMomentum {
    H = "s"
    C = "p"
    S = "d"
  }
  Filling = Fermi {
    Temperature [Kelvin] = 0.0
  }
}
```
→ Hamiltonian section

```
ExcitedState{
  Casida{
  Symmetry = Singlet
  NrOfExcitations = 10
  StateOfInterest = 0
  WriteTransitions = Yes
  WriteTransitionDipole = Yes
  }
}
Analysis{
}
Options {
WritedetailedOut = Yes
}
```
→ Excited state section

> The same from of input file used for the dynamics, but it is updated by NX/DFTB+ interface during simulations (gradients, current state).

DFTB+ input for the initial conditions

```
Geometry = GenFormat {
 <<< "geom.gen"
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→ Geometry section

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}
Analysis{
}
Options {
WritedetailedOut = Yes
}
```
→ Excited state section

The same from of input file used for the dynamics, but it is updated by NX/DFTB+ interface during simulations (gradients, current state).

Excited states and absorption spectrum

Excited states at the FC geometry (EXC.DAT):

w [eV]	Osc.Str.	Transition			Weight	KS [eV]	Sym.
3.395	1.48761085	49	->	50	1.000	2.864	S
3.837	0.00000015	48	->	50	0.732	3.816	S
4.675	0.00059685	49	->	51	0.733	3.837	S
4.875	0.05366545	47	->	50	0.943	4.847	S
4.905	0.19709801	48	->	51	0.816	4.789	S
5.206	0.00000056	46	->	50	0.998	5.096	S
5.229	0.01537105	45	->	50	1.000	5.123	S
5.389	0.00007371	44	->	50	0.998	5.195	S
5.491	0.02525593	43	->	50	0.999	5.276	S
5.775	0.16757419	49	->	52	0.687	4.905	S
5.824	0.00000456	42	->	50	0.946	5.739	S
5.846	0.00000181	47	->	51	0.718	5.820	S
5.962	0.00008187	49	->	53	0.850	5.914	S
6.230	0.00336394	46	->	51	0.999	6.069	S
6.280	0.00002509	45	->	51	0.998	6.096	S
6.298	0.05246536	44	->	51	0.989	6.168	S

Excited states mostly dominated by a single determinant.

Excited states and absorption spectrum

Nuclear ensemble approach (400 IC with 15 excited states)
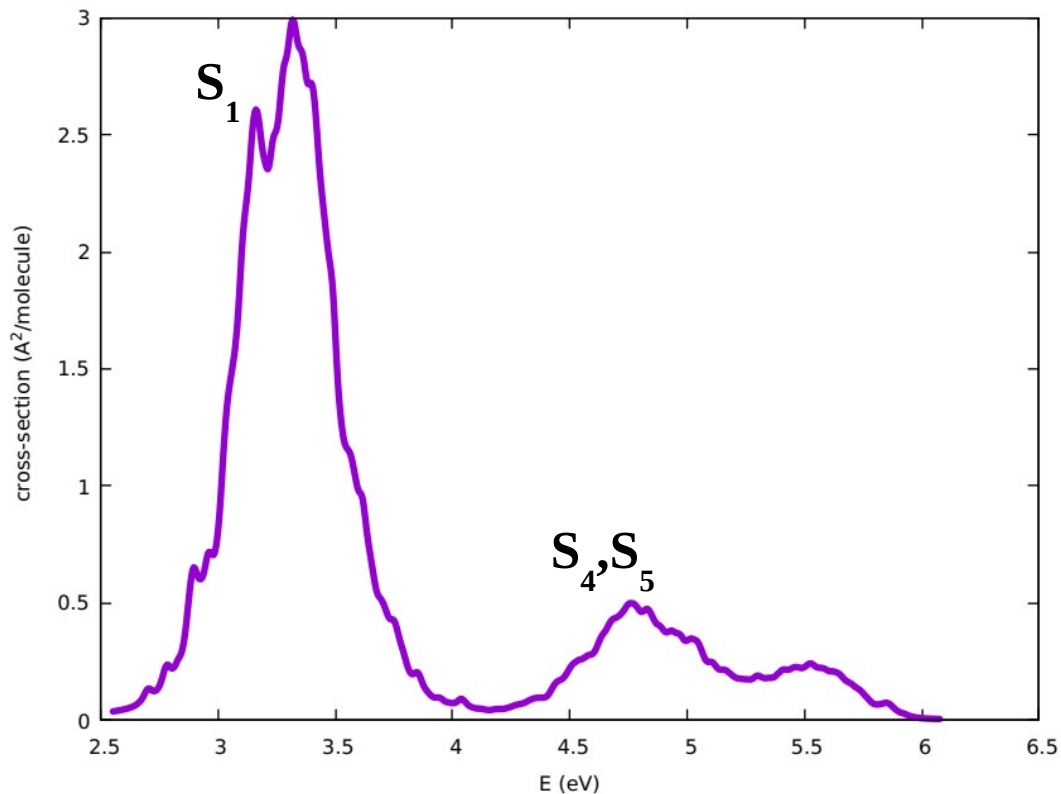
E(eV)	f
3.395	1.48761085
3.837	0.00000015
4.675	0.00059685
4.875	0.05366545
4.905	0.19709801
5.206	0.00000056
5.229	0.01537105
5.389	0.00007371
5.491	0.02525593
5.775	0.16757419
5.824	0.00000456
5.846	0.00000181
5.962	0.00008187
6.230	0.00336394
6.280	0.00002509
6.298	0.05246536

Selecting initial conditions for dynamics
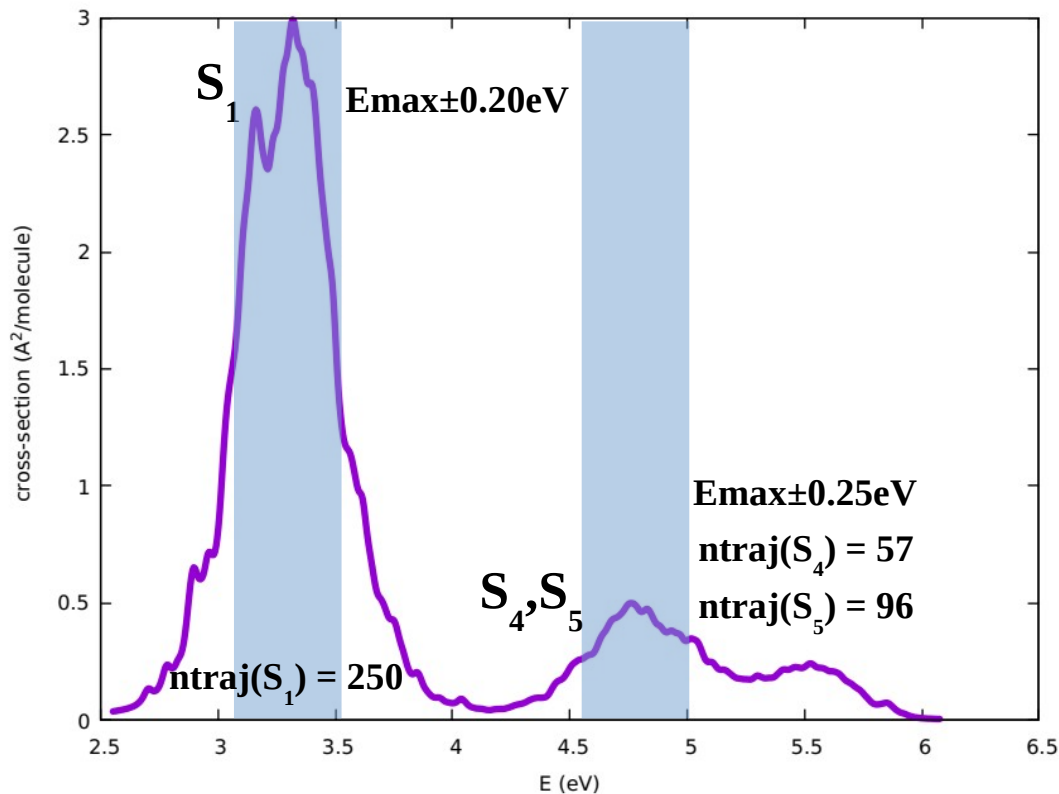
1. Energy windows applied to filter the ICs for dynamics around maxima of the bands.

2. The first band mainly arises in transition to the S_1 state. (dynamics from S_1)
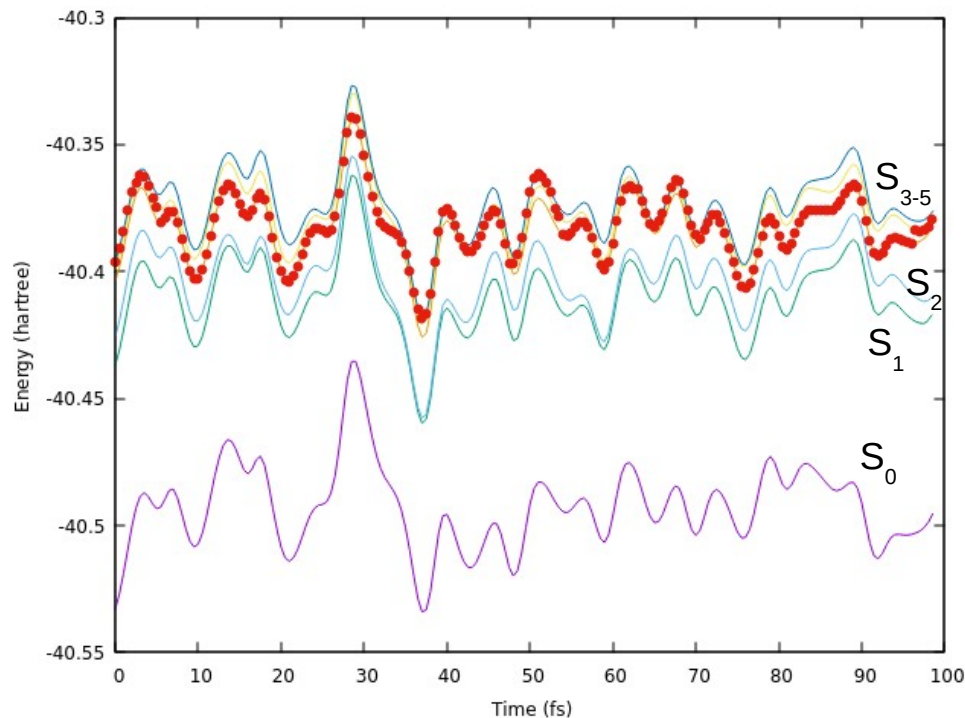**Adiabatic dynamics**
(the S_0-S_1 gap criterion)

3. The S_4 and S_5 states mainly contribute to the second band.
(dynamics from S_4 and S_5)
Nonadiabatic dynamics

FSSH dynamics from the S$_5$ state

Ground and excited state energies during dynamics **in a single trajectory**.

The first 100 fs of dynamics initiated from the S$_5$ state.

- During the first 100 fs of dynamics, 4T remains on the S$_3$-S$_5$ manifold (mostly in the S$_3$ state);

- S$_1$ and S$_2$ states are separated from the higher S$_3$-S$_5$ manifold;

- Longer simulation times necessary to reach the population of the lower excited states;

- This is in agreement with the simulated spectrum (two bands are well-separated).
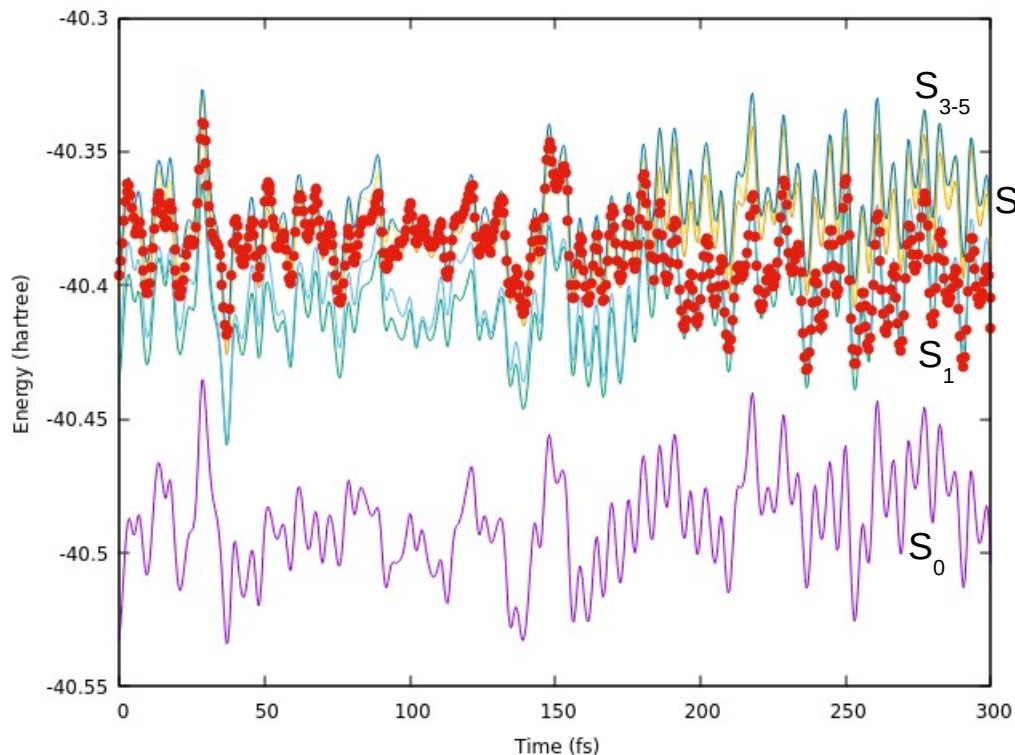
Visualization:

$NX/plot

(input RESULTS/en.dat)

FSSH dynamics from the S$_5$ state

Ground and excited state energies during dynamics **in a single trajectory**.

A 300 fs trajectory initiated from the S$_5$ state.

- After 150 fs of dynamics, the lower excited states start to populate;

- S$_1$ state becomes the most dominantly populated in the last 100 fs;

- The internal conversion to the ground state does not occur during the firat 300 fs of dynamics;
(the S0/S1 gap is approx. 2 eV by the end of dynamics)

- It is possible to visualise molecular motions during dynamics.

Useful information from the NX output files

RESULTS/en.dat - energies of all states during dynamics.

```
0.00   -40.532823   -40.436870   -40.425699   -40.403833   -40.399496   -40.396262   -40.396262   -40.269910
0.50   -40.527020   -40.431031   -40.419455   -40.398434   -40.393951   -40.390864   -40.390864   -40.269990
1.00   -40.518937   -40.423205   -40.411335   -40.391049   -40.386603   -40.383993   -40.383993   -40.269960
1.50   -40.509622   -40.414441   -40.402387   -40.382800   -40.378427   -40.376112   -40.376112   -40.269886
2.00   -40.500551   -40.406142   -40.394014   -40.375199   -40.370825   -40.368584   -40.368584   -40.269787
```

RESULTS/dyn.out - Information about hopping, geometries, velocities, energies, real and imaginary parts of wf for each time step.

```
STEP      6   Molecular dynamics on state  5   TIME =      3.00 fs
Type of dyn. =   4   N. of hoppings =   1   N. of rejec. Hoppings =   0

Time   Etot       Ekin       Epot E0,    E1, ...
%      3.00   -40.269726    0.092451   -40.488521   -40.396170   -40.384079   -40.366954   -40.362177   -40.359788

  Wave function state  1:      0.00000000000000      0.00000000000000
  Wave function state  2:     -0.00922517920283     -0.00506322662525
```

RESULTS/sh.out - Information about integration of TD Schrodinger equation.

```
|v.h|=   0.000000   0.000000  -0.000759   0.000000  -0.000137   0.001141   0.000000   0.000144   0.000518   0.003257   0.000000   0.000383  -0.000474  -0.000207  -0.002456
    181      10    5   0.000000000   1.000000000
                        0.000005922
                        0.003064893
                        0.337904351
                        0.575519351
                        0.083505482
```

Useful information from the NX output files

RESULTS/typeofdyn.dat - current excited state and energy separation from lower/higher state.

```
Time =    1.50  Threshold=****  PES = 6  DE_inf = 0.06  DE_sup = -----  Type = 2  Next type = 2
Time =    2.00  Threshold=****  PES = 6  DE_inf = 0.06  DE_sup = -----  Type = 2  Next type = 2
Time =    2.50  Threshold=****  PES = 5  DE_inf = 0.12  DE_sup = 0.06  Type = 2  Next type = 4
Time =    3.00  Threshold=****  PES = 5  DE_inf = 0.13  DE_sup = 0.07  Type = 4  Next type = 4
Time =    3.50  Threshold=****  PES = 5  DE_inf = 0.14  DE_sup = 0.08  Type = 4  Next type = 4
Time =    4.00  Threshold=****  PES = 5  DE_inf = 0.14  DE_sup = 0.10  Type = 4  Next type = 4
```

RESULTS/report.ci - All state pairs with Ediff smaller than a threshold during dynamics.

```
Report points with energy gap smaller than  0.200 eV
Time (fs) =    0.00  State I = 5  STATE J = 4  |DE| (eV) = 0.118
Time (fs) =    0.00  State I = 6  STATE J = 5  |DE| (eV) = 0.088
Time (fs) =    0.50  State I = 5  STATE J = 4  |DE| (eV) = 0.122
Time (fs) =    0.50  State I = 6  STATE J = 5  |DE| (eV) = 0.084
Time (fs) =    1.00  State I = 5  STATE J = 4  |DE| (eV) = 0.121
```

RESULTS/tprob - Random seed and hopping probabilities at all electronic substeps.

Statistical analysis of trajectories

For a set of finished trajectories:

1. $NX/diagnostic.pl

2. $NX/nxinp (option 6)

$NX/analysis.pl > analysis.log

Interactive analysis for the test case of pentacene dynamics.

Thank you very much for your attention :) !