Libra/cp2k workflow application:

Modelling excited states in $(TiO_2)_4$

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Excited States and Nonadiabatic Dynamics CyberTraining Workshop 2023

Universitat de Barcelona / University at Buffalo

OUTLINE

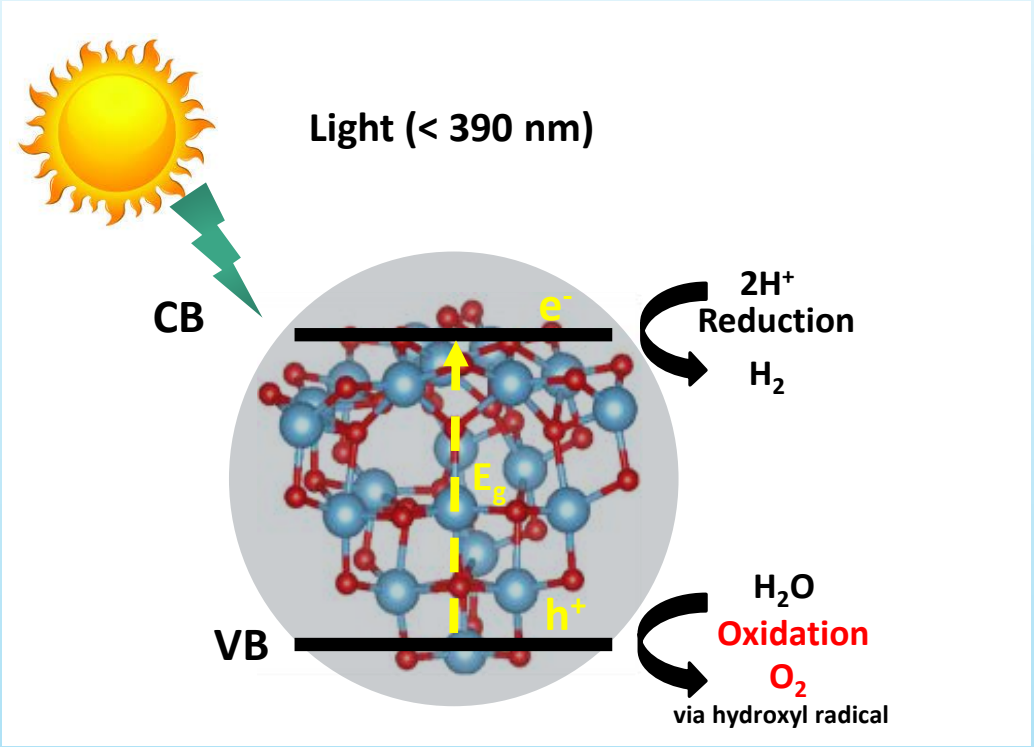
1. Motivation: TiO_2 NPs
2. Libra/cp2k workflow
    - Getting initial trajectory*
    - TDDFT excitations*
    - Computation of NACs and excitation energies
    - Run NAMD –> properties of interest
3. Conclusions

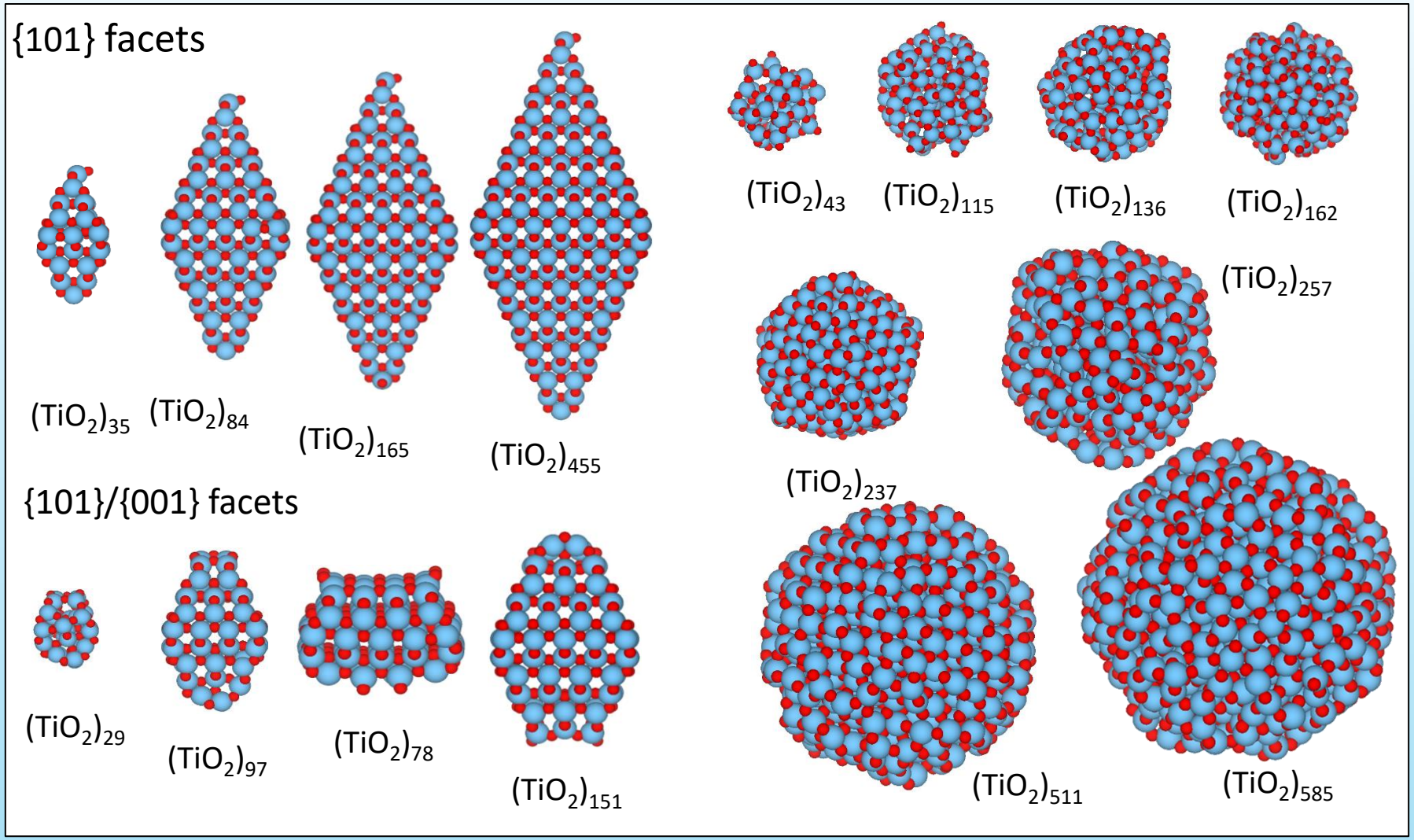
Titania (TiO_2) overview:

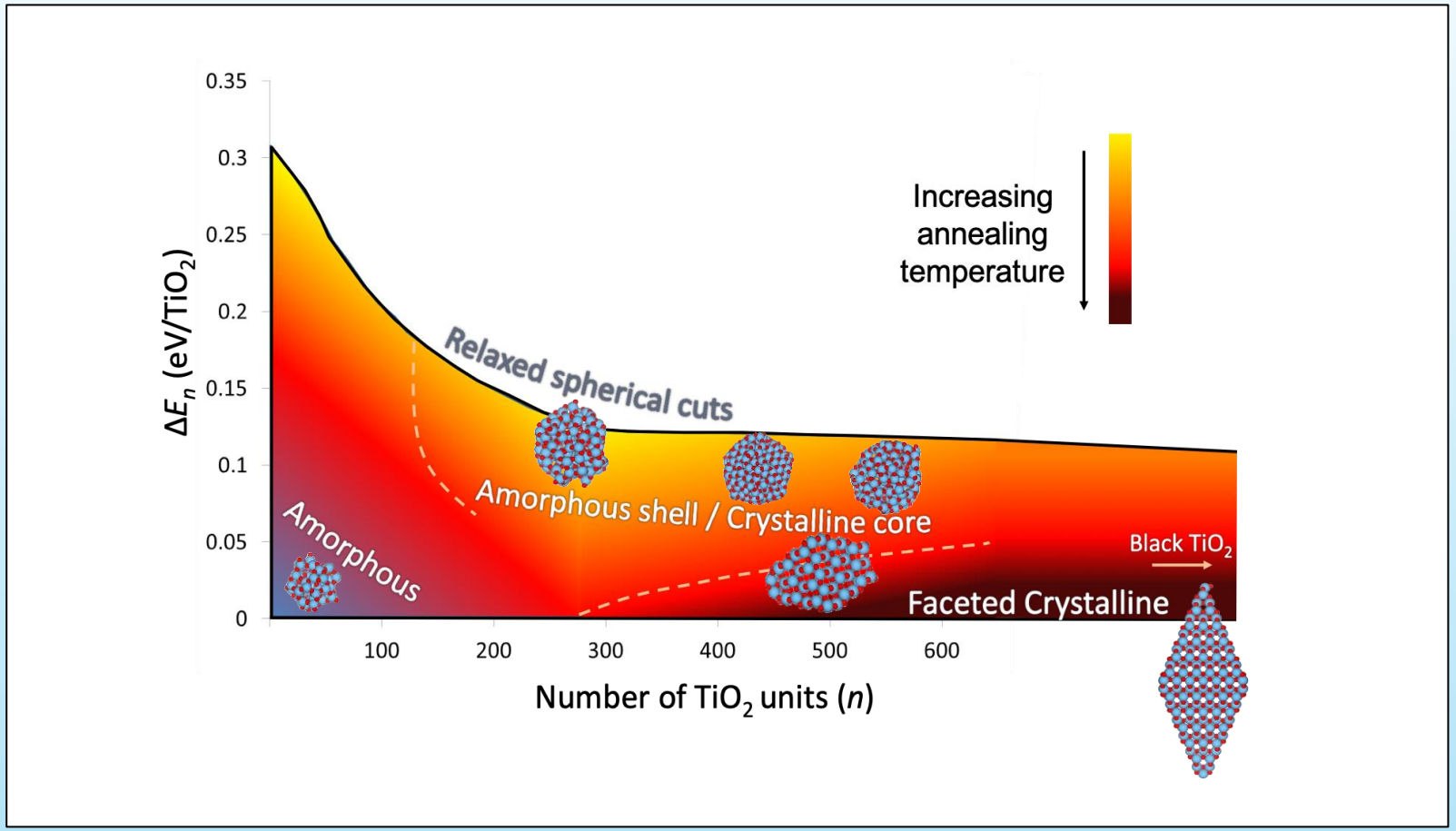
-Titania: wide-bandgap semiconductor

-5 decades since seminal discovery (~35000 citations) that anatase crystal TiO_2 is able to split water upon photoexcitation

-Limitations: short lifetime of such photogenerated species. Need of properly understanding charge carrier recombination dynamics.



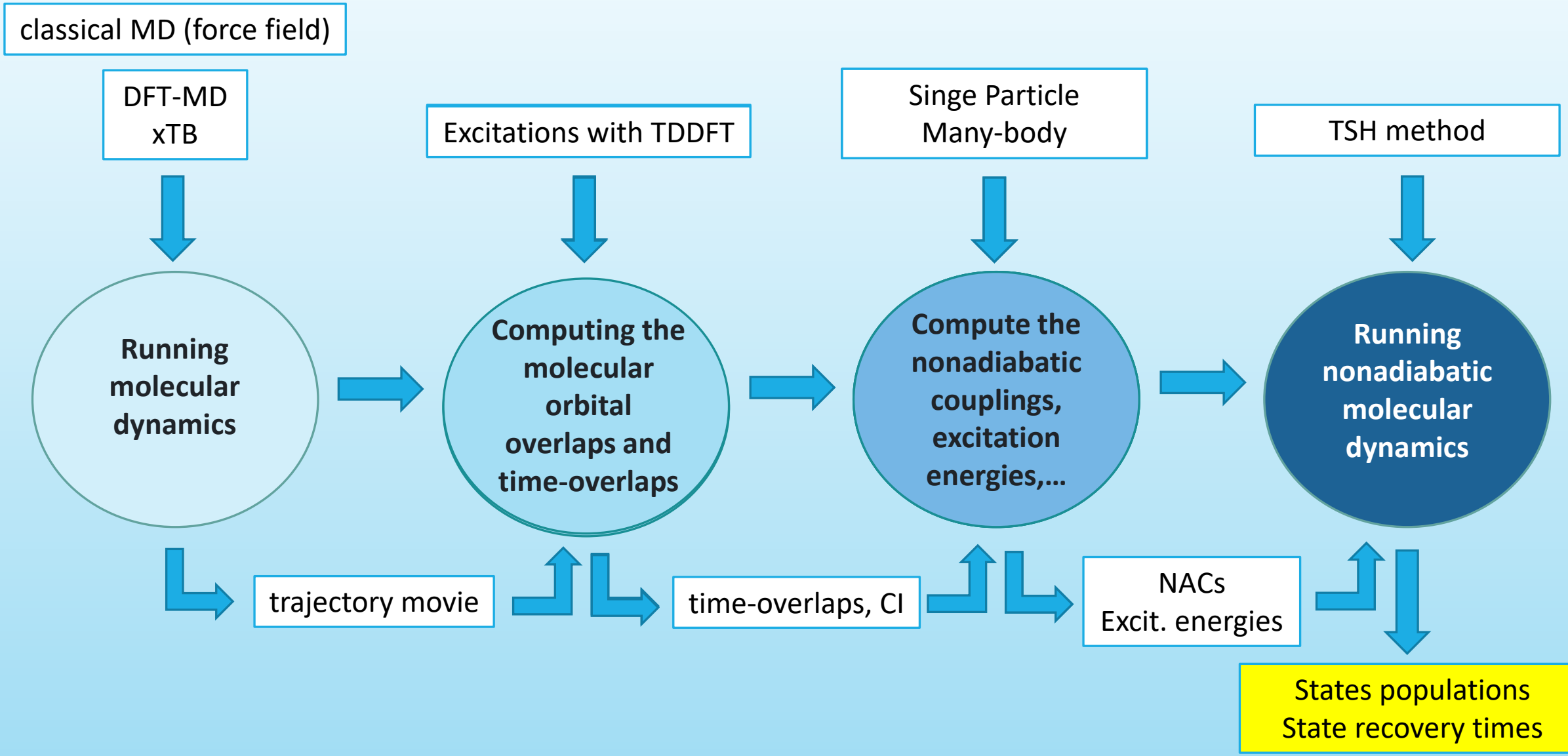

{101} facets
(TiO2)35
(TiO2)84
(TiO2)165
(TiO2)455
{101}/{001} facets
(TiO2)29
(TiO2)97
(TiO2)78
(TiO2)151
(TiO2)43
(TiO2)115
(TiO2)136
(TiO2)162
(TiO2)257
(TiO2)237
(TiO2)511
(TiO2)585



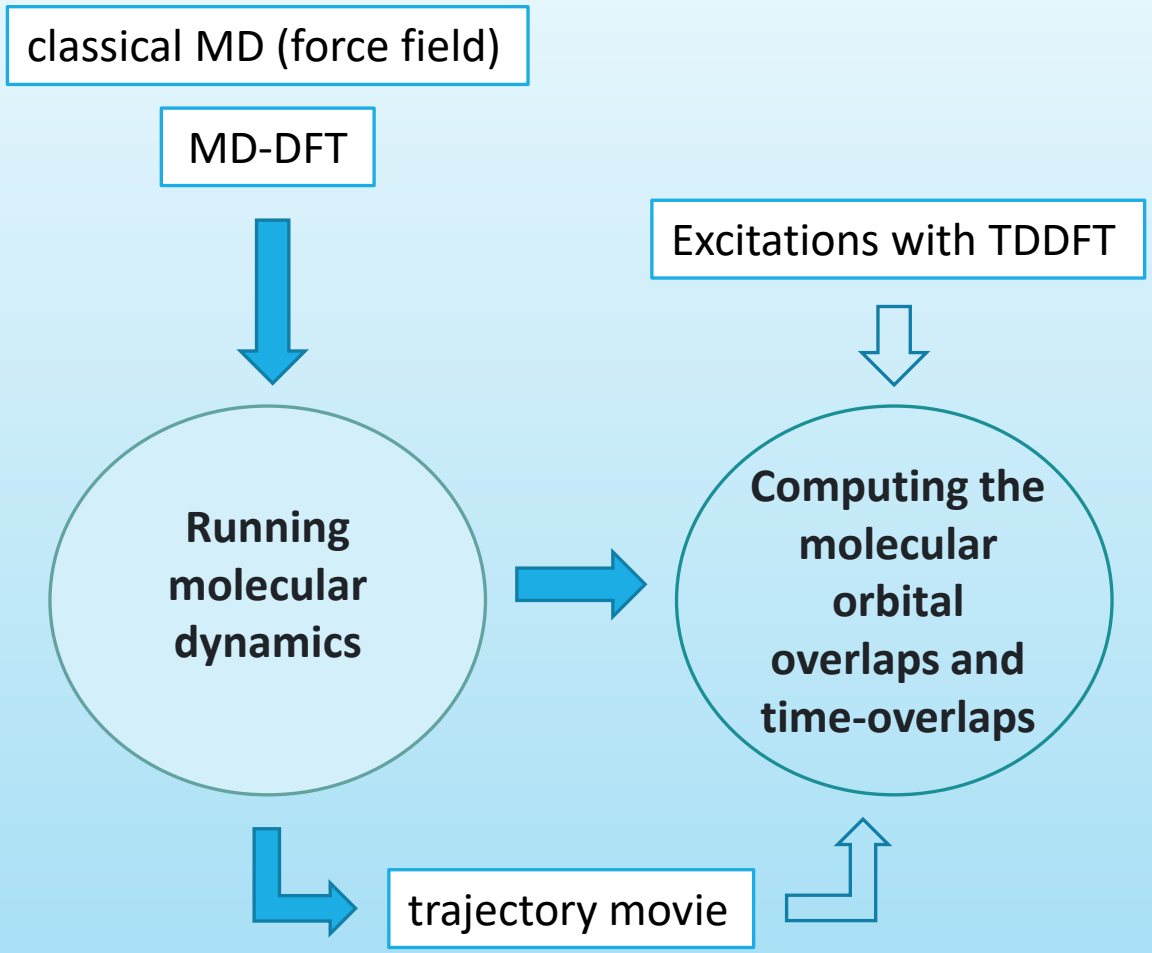
We have analyzed GS properties (energetics, structural, band gaps)…

What about the excited states???

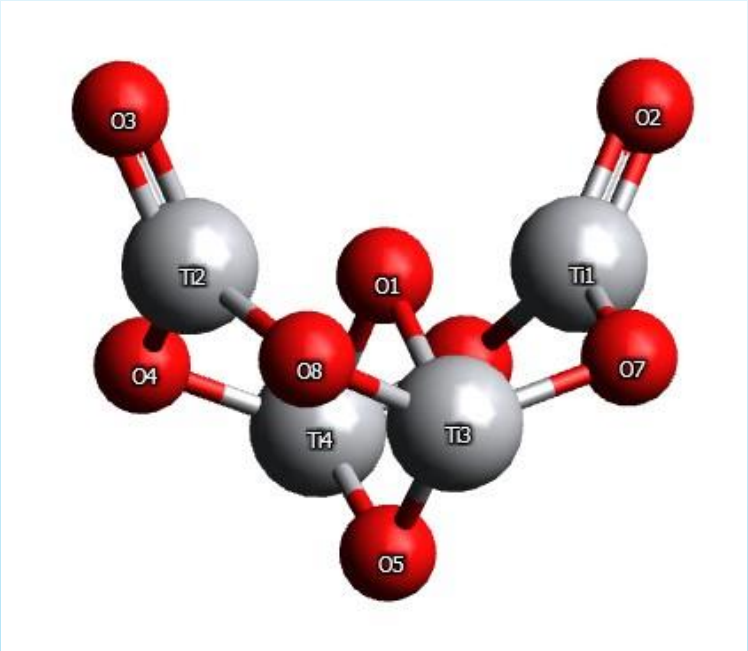
cp2k/Libra workflow overview:



cp2k/Libra workflows: step 1

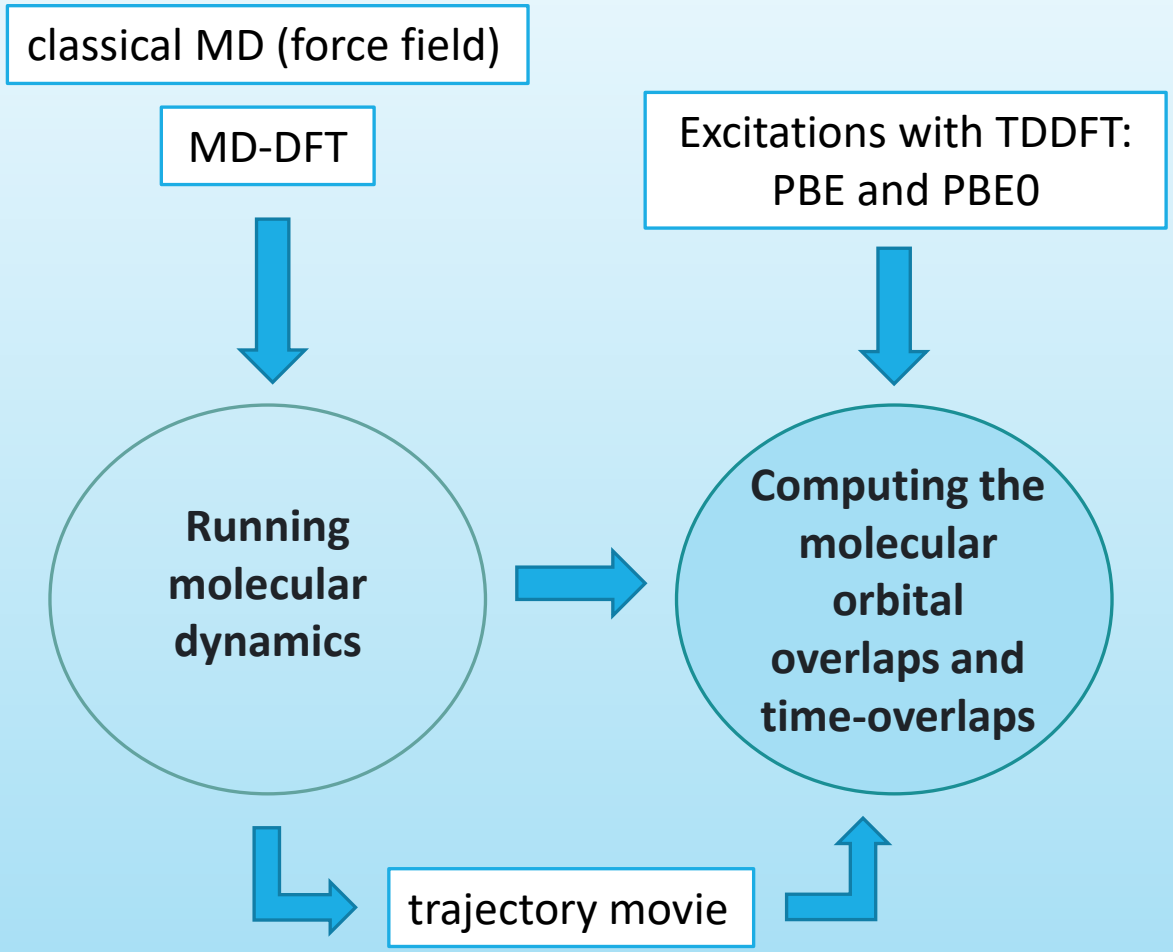


Test-system: globally optimized $(TiO_2)_{4NP}$



(MD) Simulations -> 1 ps trajectory at 300 K
GULP: Classical MD (NanoTiO IP)
CP2K: ab-initio MD (PBE)

cp2k/Libra workflows: step 2



After step 1 and step 2:

4 methodologies:

(i) IP MD + PBE TD-DFT

(ii) IP MD + PBE0 TD-DFT

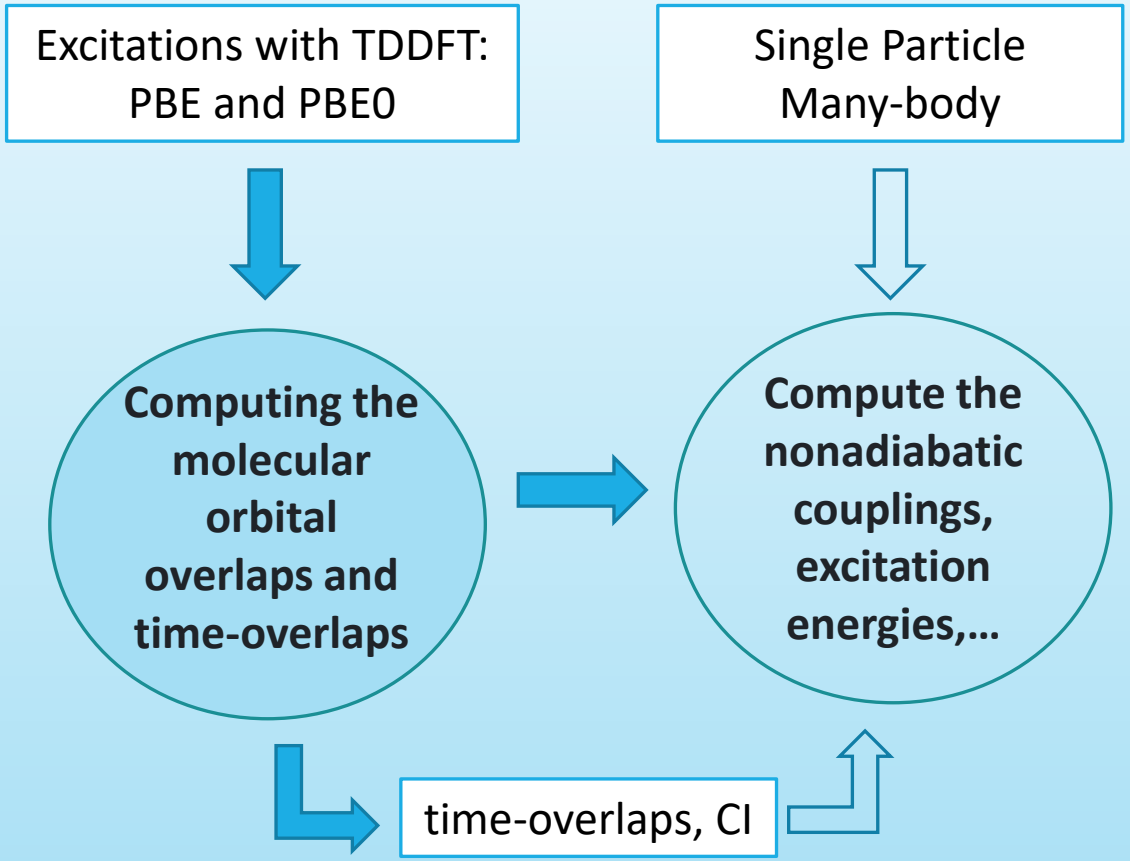
(iii) DFT MD + PBE TD-DFT

(iv) DFT MD + PBE0 TD-DFT

-Analyze the effect of the methodology for preparing our trajectoy file

-PBE vs PBE0 treatment of excitations

cp2k/Libra workflows: step 2



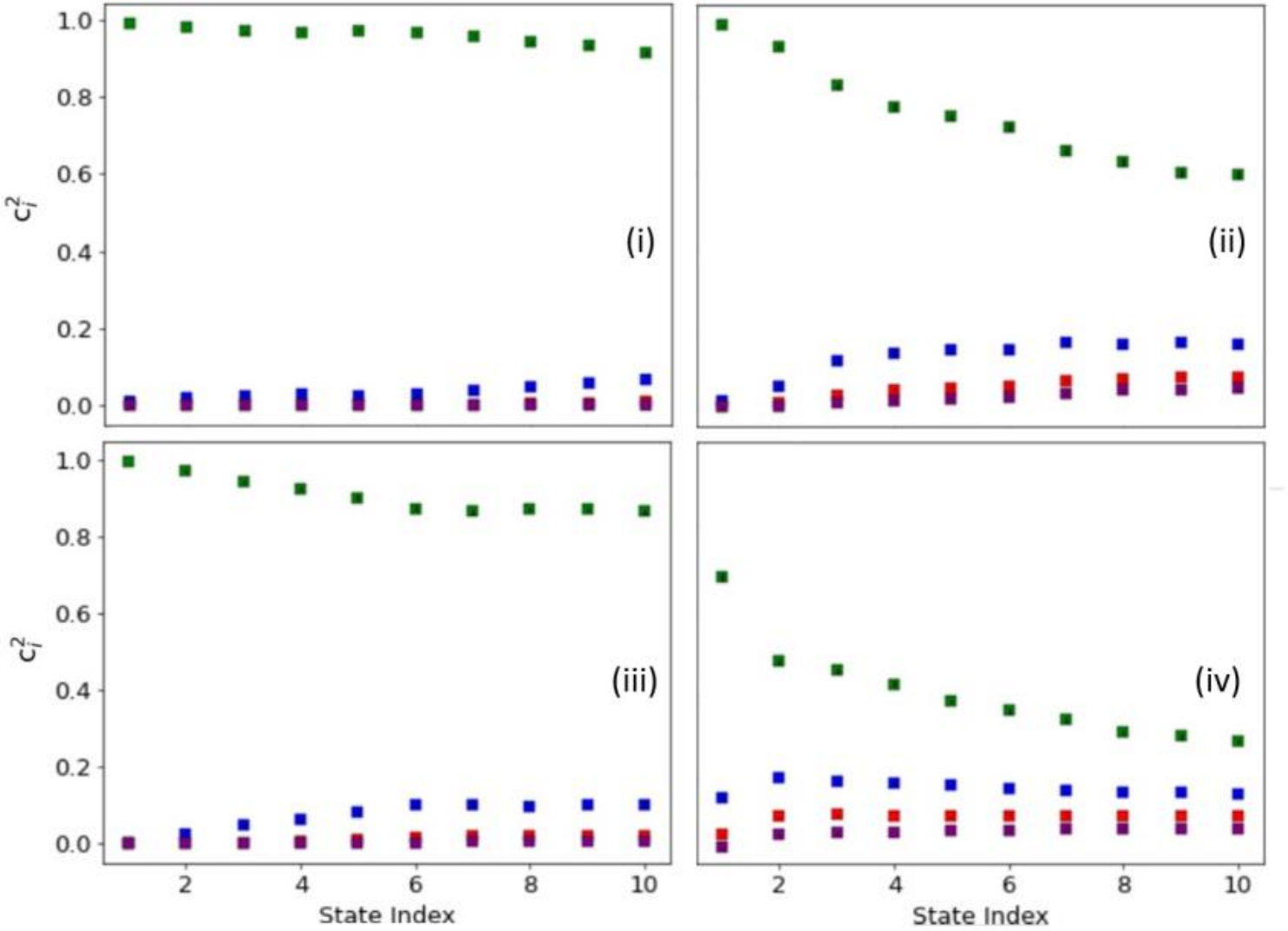
"Gaussian cubefile"-based approach to compute the MO overlaps and time-overlaps

Excited sates of nanoscale systems are multiconfigurational

Many-body effects play an important role

10 excited states composed by the squares of the configuration interaction (CI) coefficients.

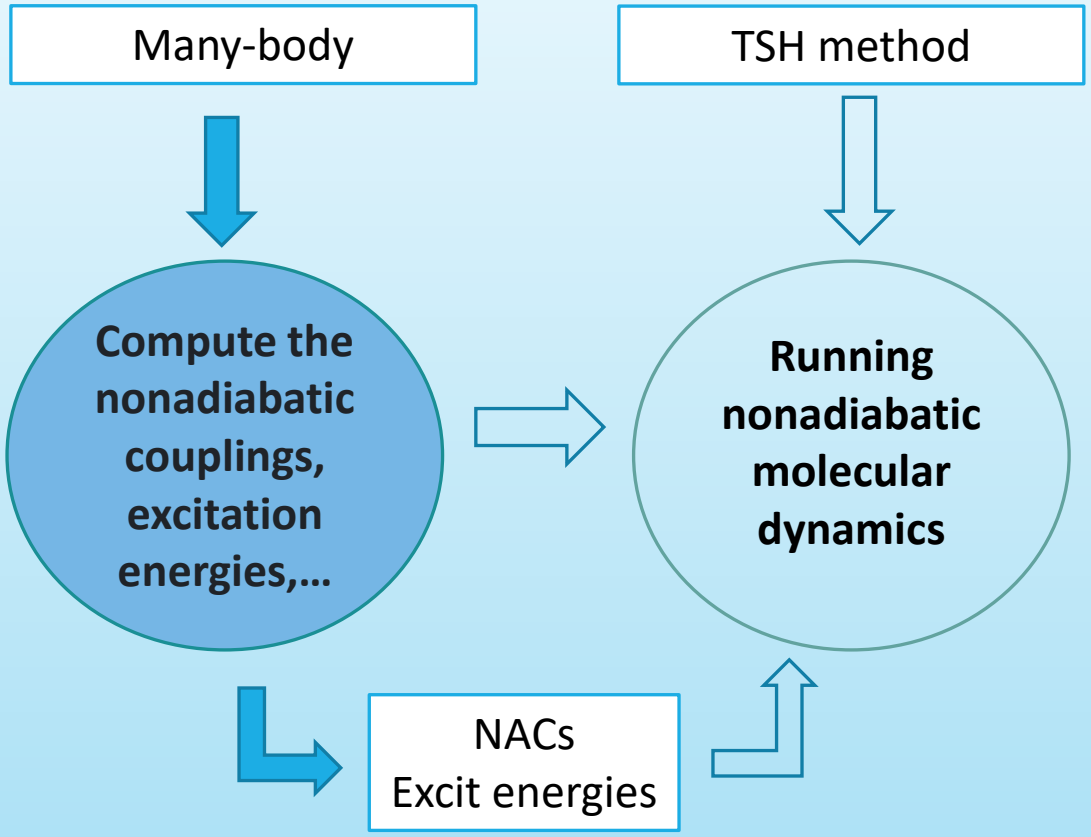
cp2k/Libra workflows: step 2

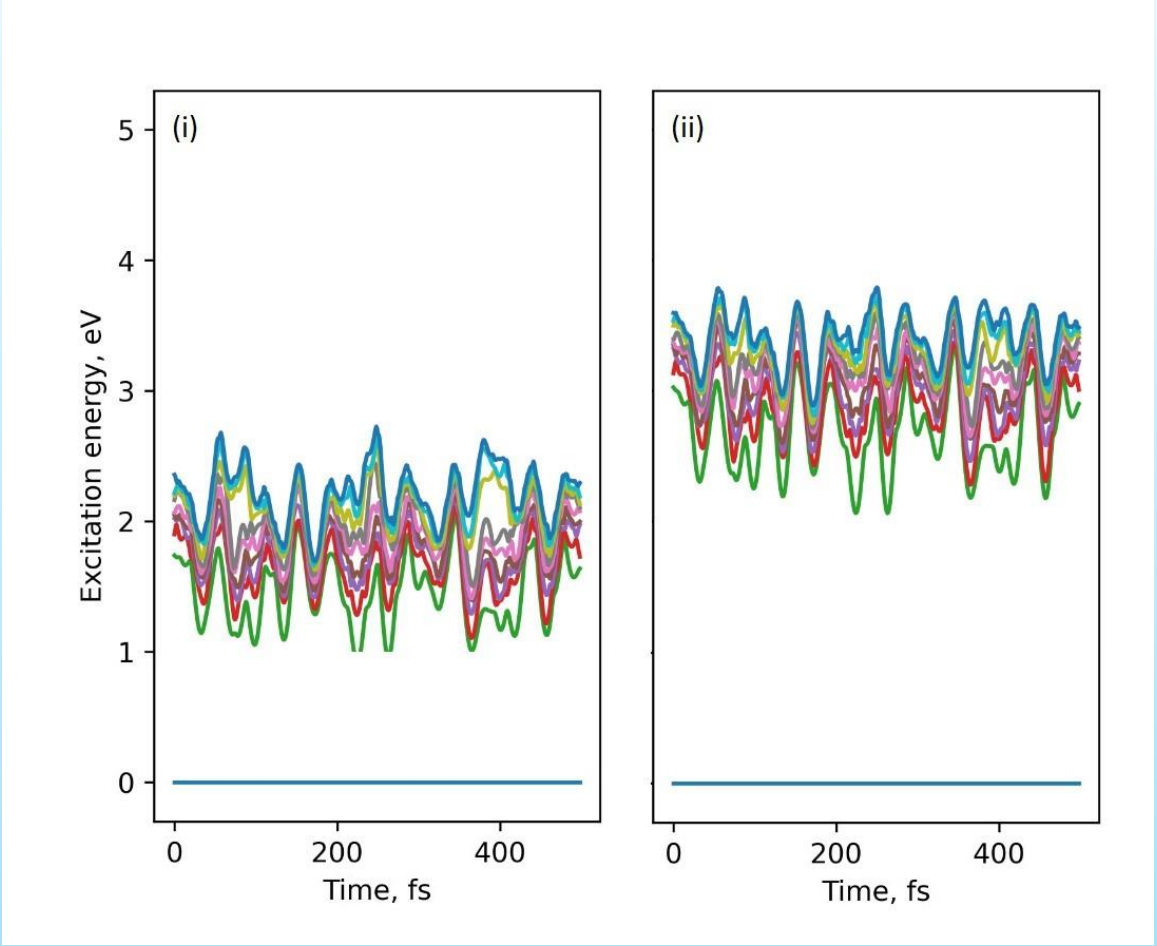


(i), (iii): single SD excitation dominance that starts to slowly break down. No big differences between using classical or AIMD

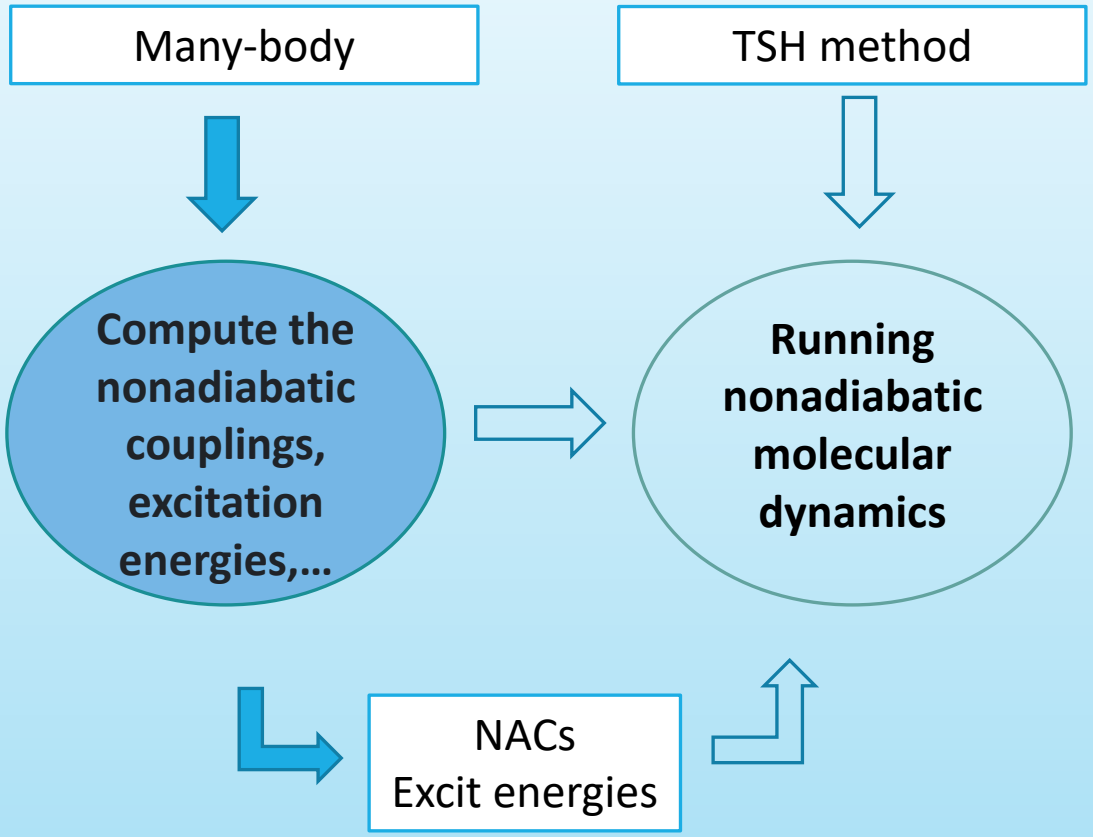
(ii), (iv) Using PBE0 for computing the TDDFT excitations leads to a stronger multiconfigurational description of our excited states.

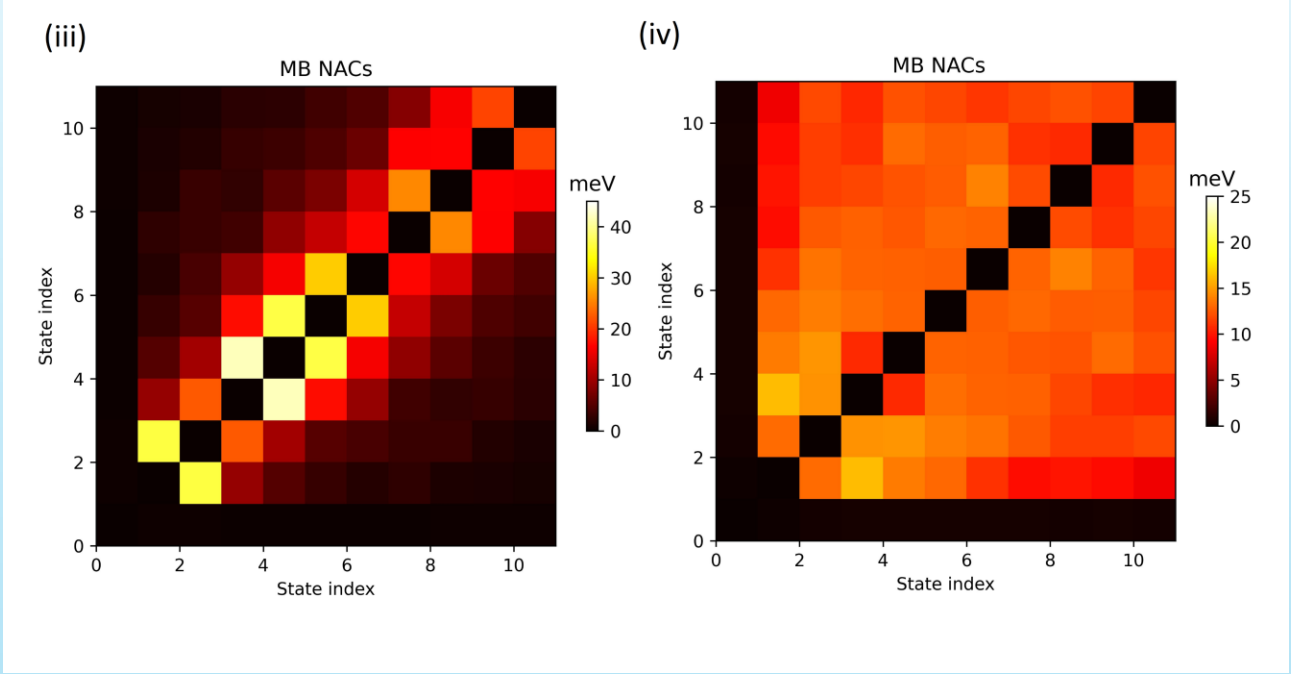
cp2k/Libra workflows: step 3



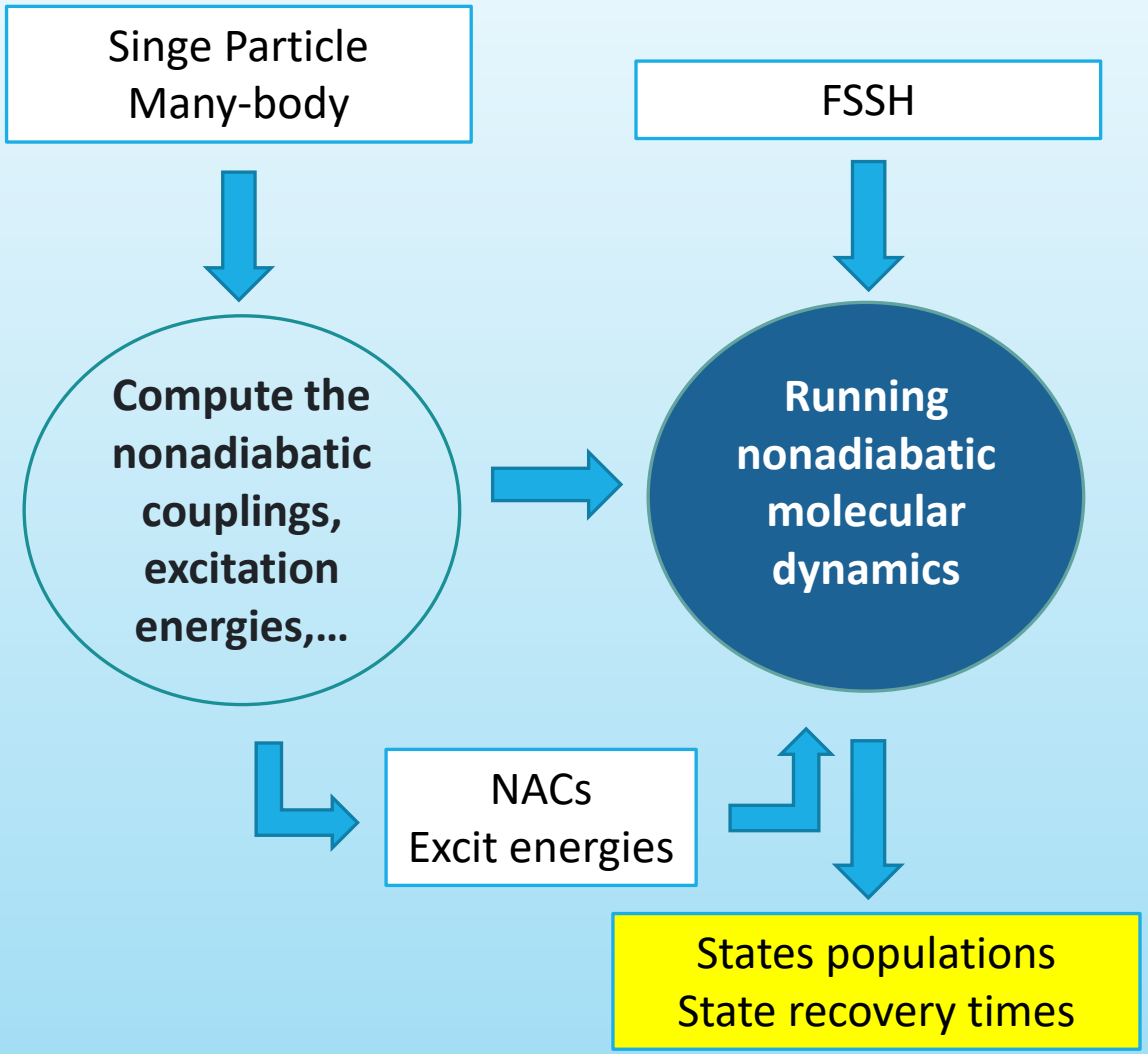


cp2k/Libra workflows: step 3





cp2k/Libra workflows: step 4



we pick ten geometries of our MD runs (step 1) as starting points

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we use 40 different sets of initial conditions for our FSSH trajectories

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Run 400 nonadiabatic dynamics of 1000 fs

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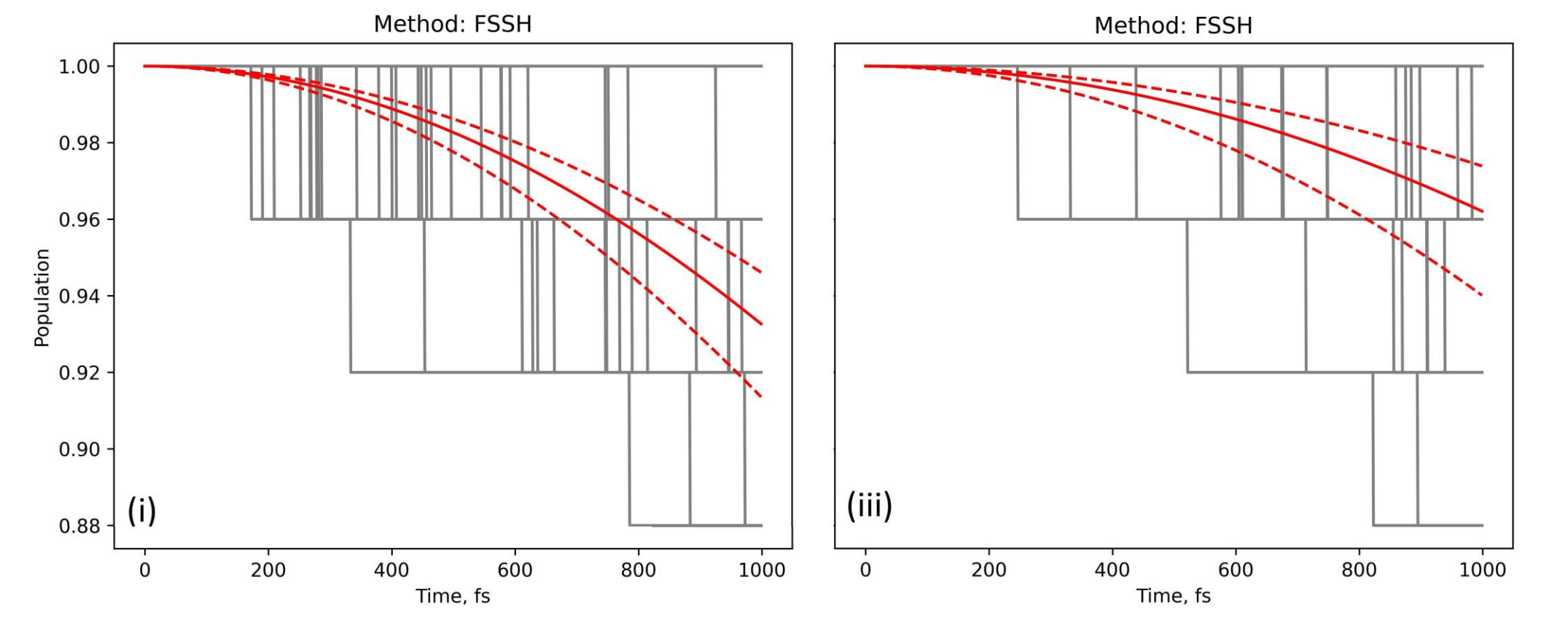
calculating magnitudes of interest (population recovery times)

cp2k/Libra workflows: step 4



Exponential fit for the average population recovery time (red solid line) among all trajectories

Longer recovery time in AIMD preparation case.

The faster decay of ground state in figure (i) will point towards the use of classical MD in step 1.

CONCLUSIONS

- Implementation of Libra/CP2K workflow to a small TiO_2 NP
- We obtained quantities of interest (recovery times).
- Further analysis and connection to charge recombination times is needed.
- Use of classical and ab-initio MD for getting initial trajectory
- PBE vs PBE0 treatment of excitations
- Use larger simulation times, introduce decoherence,… REKS?


THAT'S ALL
THANKS!!
CENTER FOR THE ARTS
Slee Hall