Nonadiabatic molecular dynamics simulations in large scale nanomaterials and periodic solids

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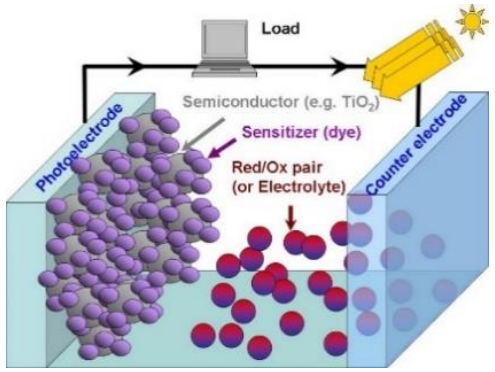
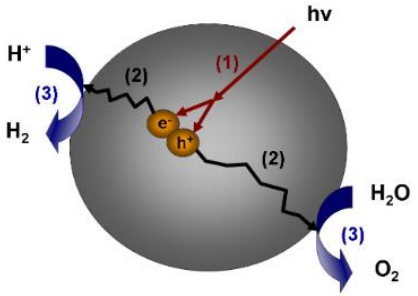
Motivation

- **Solar energy materials**

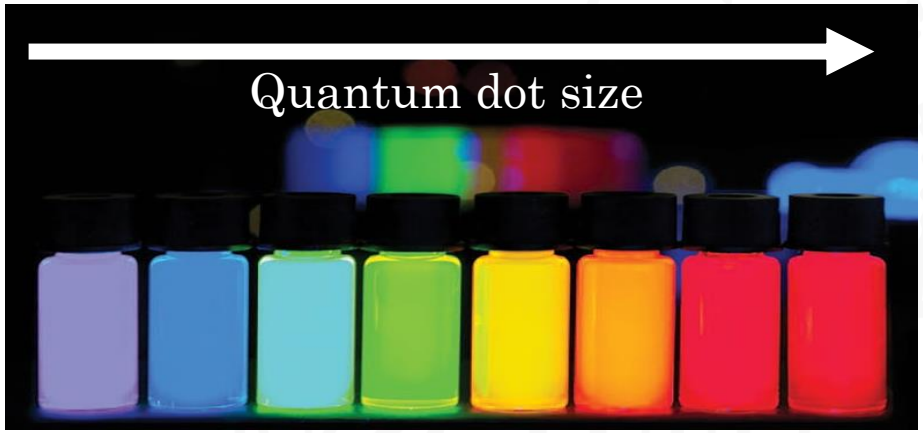


- **Photocatalysis**

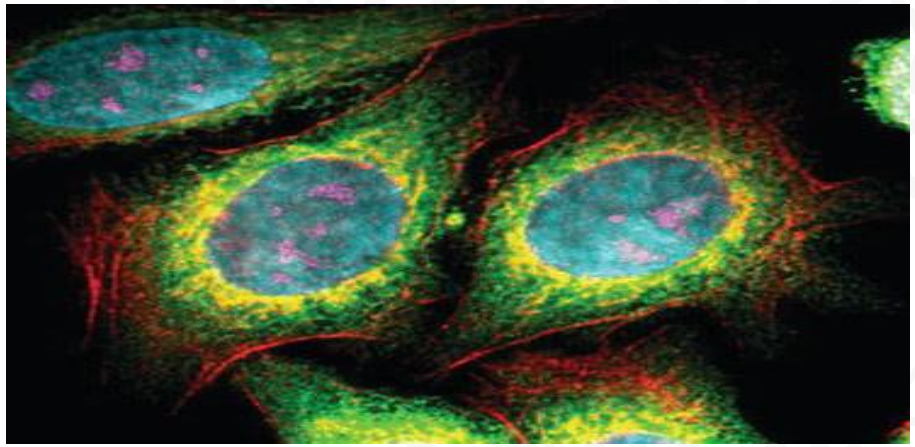
Artificial leaf



- **Light-emitting diodes**



- **Bio-imaging**



Nonadiabatic dynamics

- The total wavefunction:

$$\Psi(\mathrm{r},\mathrm{R(t)}) = \sum_i c_i(t)\psi_i(r,R(t))$$

$$H_{el}(r,R)\psi_i(r,R) = E_i\psi_i$$

- The evolution of the electronic amplitudes:

$$i\hbar\frac{\partial c_i(t)}{\partial t} = \sum_j \left(E_i(t)\delta_{i,j} - i\hbar d_{ij}(t)\right)c_j(t)$$

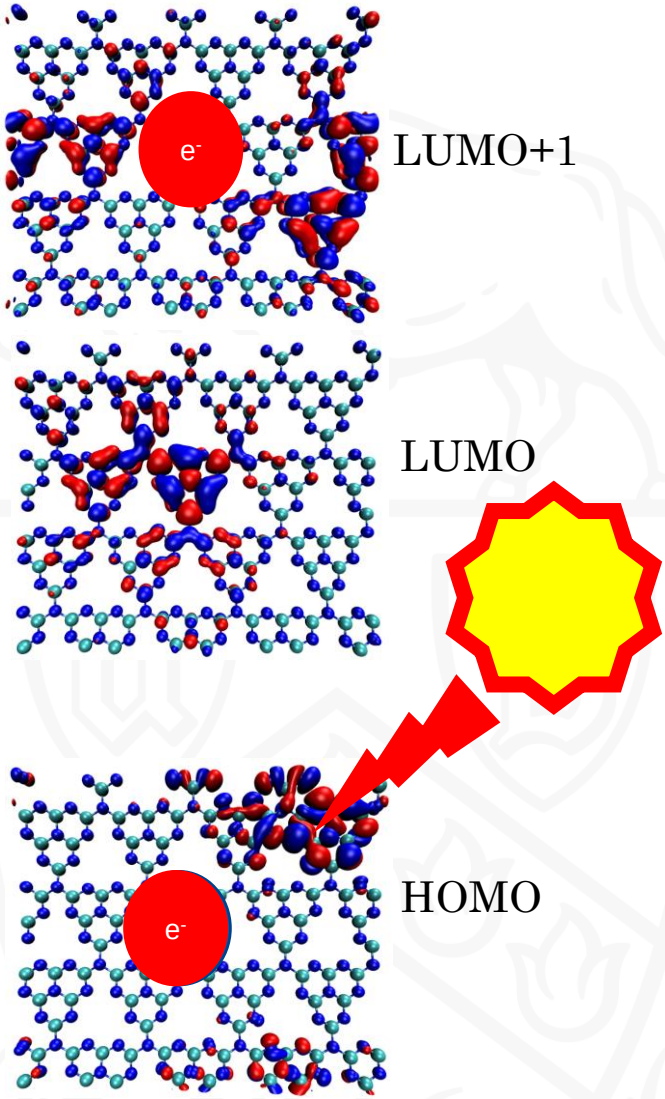
$$d_{ij}(t) = \langle\psi_i\left|\frac{\partial}{\partial t}\psi_j\right\rangle$$

- Hammes-Schiffer and Tully method:

$$d_{ij}\left(t+\frac{\Delta t}{2}\right) \approx \frac{\langle\psi_i(t)|\psi_j(t+\Delta t)\rangle - \langle\psi_i(t+\Delta t)|\psi_j(t)\rangle}{2\Delta t}$$

- Stochastic hop from state i to state j with the hopping probability:

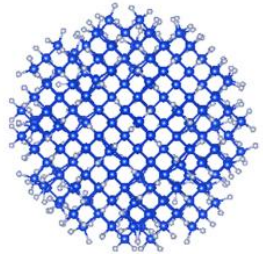
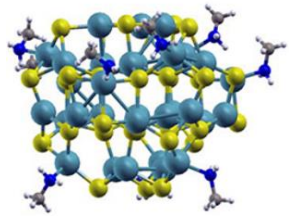
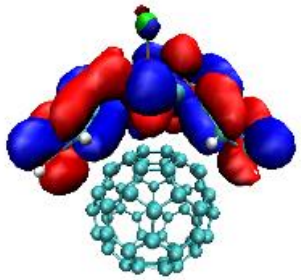
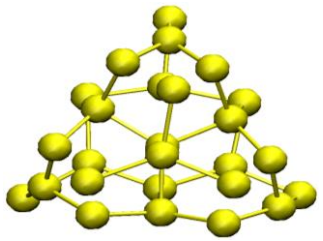
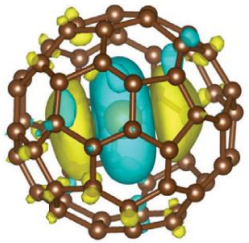
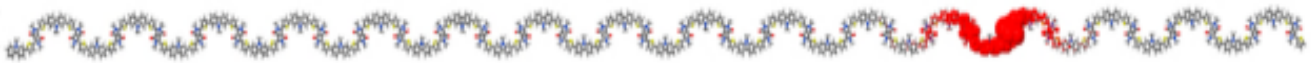
$$P_{i\to j}(t,t+\Delta t) = \max\left(0,\frac{\Delta t}{c_i c_i^*}\mathrm{Im}\left(c_i c_j^* d_{ji} - c_j c_i^* d_{ij}\right)\right)$$



Tully, J. Chem. Phys. 1990, 93, 1061
Hammes-Schiffer, Tully, J. Chem. Phys. 1994, 101, 4657–4667

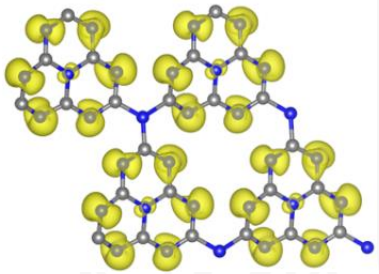
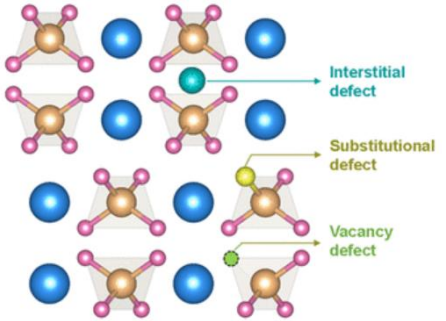
Challenges

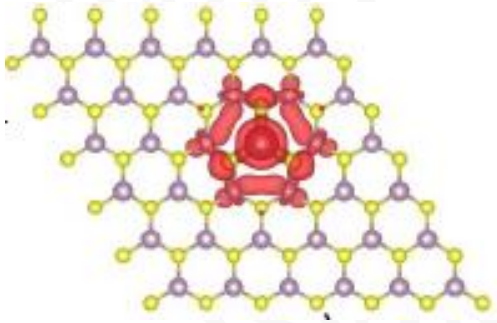
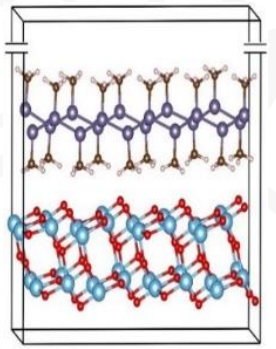
- NA-MD simulations are limited to small-medium sized structures
- Nonadiabatic coupling (NAC) calculations are computationally expensive to calculate for a large number of states

Goal

- To perform NA-MD calculations for large nanomaterials and periodic solids

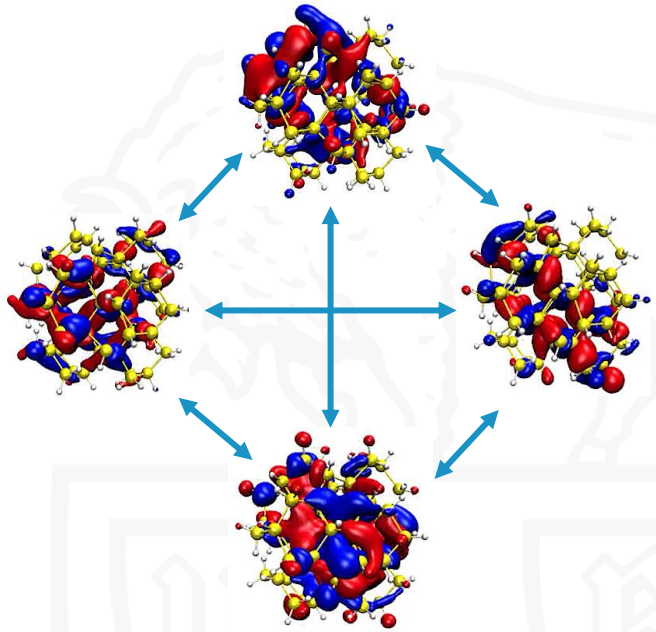
Time-overlap integration

- Grid-based approach using *.cube* files
  - Easy to implement
  - Most codes can output these file
  - Not suitable for large structures with large number of states

- Double-molecule approach
  - Easy to use and can be used in different codes
  - Very time-consuming for large structures
  - Not suitable for periodic structures

- Analytical approach
  - Suitable for large systems and large number of states
  - Recurrence relations for computing integrals: Libint2 package

$$S_{ij} = \int_{-\infty}^{\infty} \psi_i^* \psi_j dv$$



$$\boldsymbol{S^{MO} = c^T S^{AO} c}$$

$$\boldsymbol{S^{AO}} = \begin{bmatrix} \langle\psi_1|\psi_1\rangle & \cdots & \langle\psi_1|\psi_n\rangle \\ \vdots & \ddots & \vdots \\ \langle\psi_n|\psi_1\rangle & \cdots & \langle\psi_n|\psi_n\rangle \end{bmatrix}$$

LIBINT

Smith, Shakiba, Akimov, J. Chem. Theory Comp. 2021, 17, 678–693
Libint, Version 2.6.0 Edward F. Valeev, http://libint.valeyev.net.
Shakiba, Stippell, Li, Akimov, J. Chem. Theory Compu. 2022, 18, 5157-5180

Extending to periodic structures and K-points

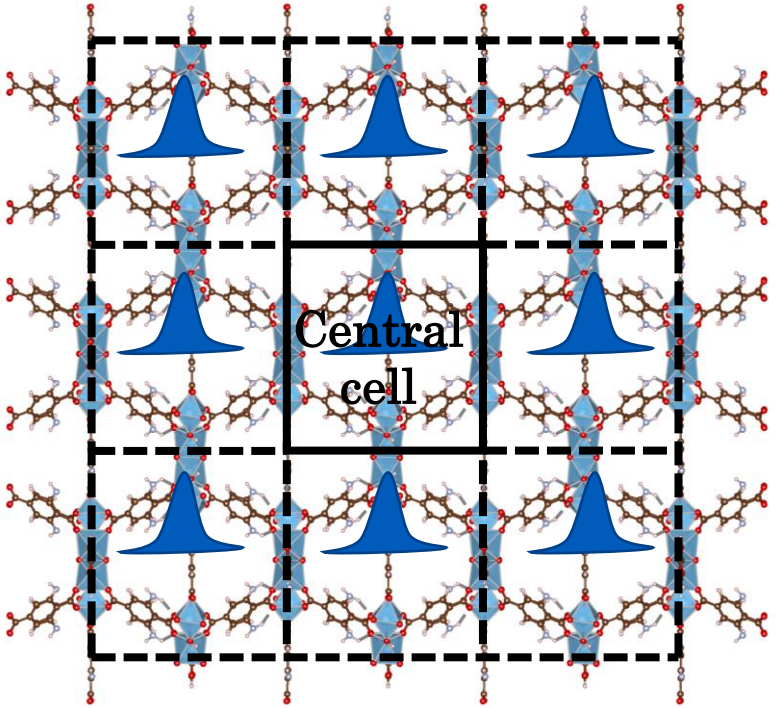
- The Bloch function for K-point in a periodic structure is defined as:

$$\beta_a^k(r) = \frac{1}{\sqrt{N}} \sum_R \varphi_a(r - R) e^{ikR}$$

- Overlaps between Bloch functions of two different K-points:

$$S_{a,b}^k = \langle \beta_a^k \middle| \beta_b^{k'} \rangle = \frac{1}{N} \int dr \sum_{R,R'} e^{-ikR} \varphi_a^*(r - R) e^{ik'R'} \varphi_b(r - R')$$

$$= \frac{1}{N} \int dr \sum_{R,R'} e^{i(kR - k'R')} \varphi_a^*(r - R) \varphi_b(r - R')$$

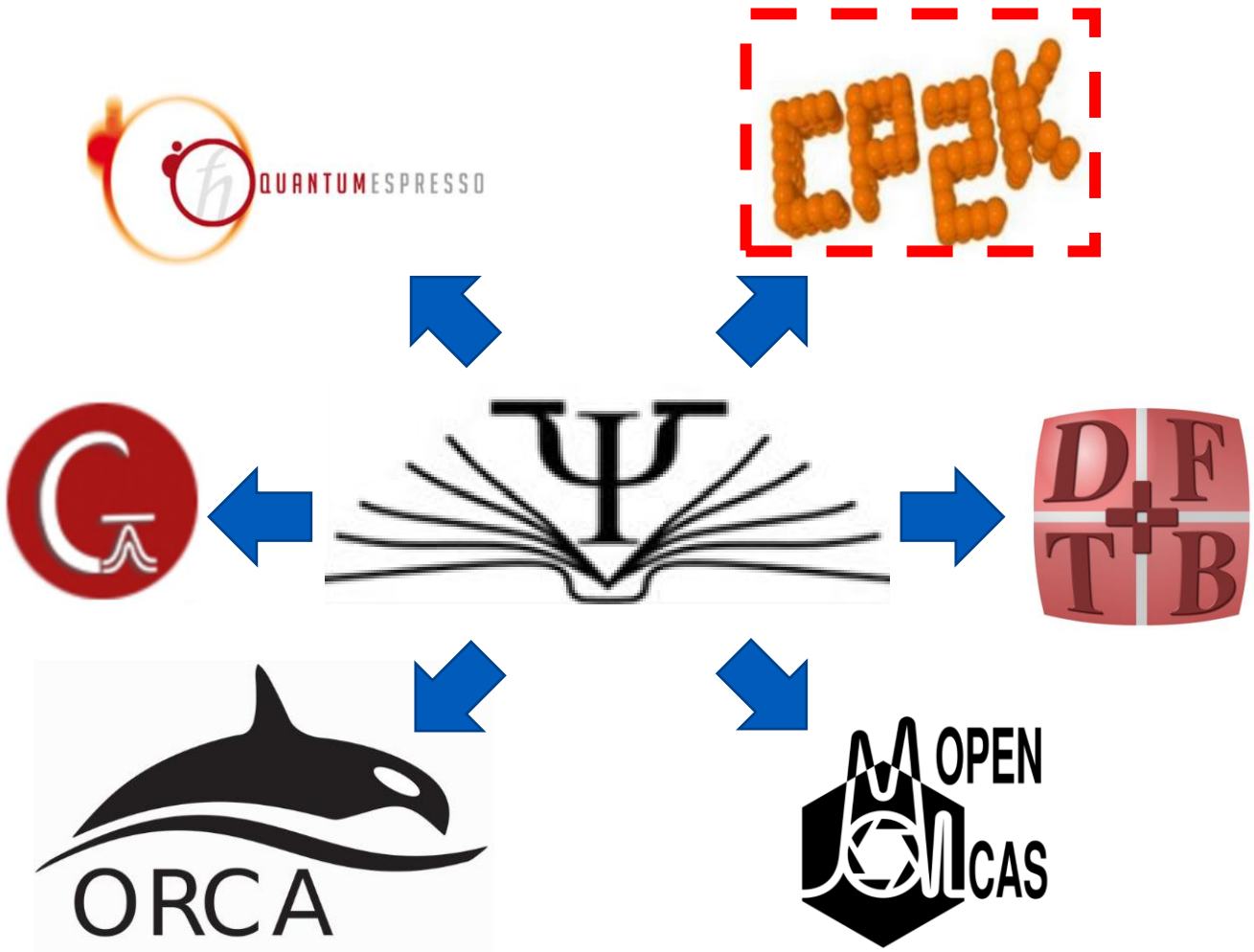


MIL-125-NH_2

Aradi, Hourahine, Frauenheim, J. Phys. Chem. A 2007, 111, 5678–5684

Shakiba, Stippell, Li, Akimov, J. Chem. Theory Compu. 2022, 18, 5157-5180

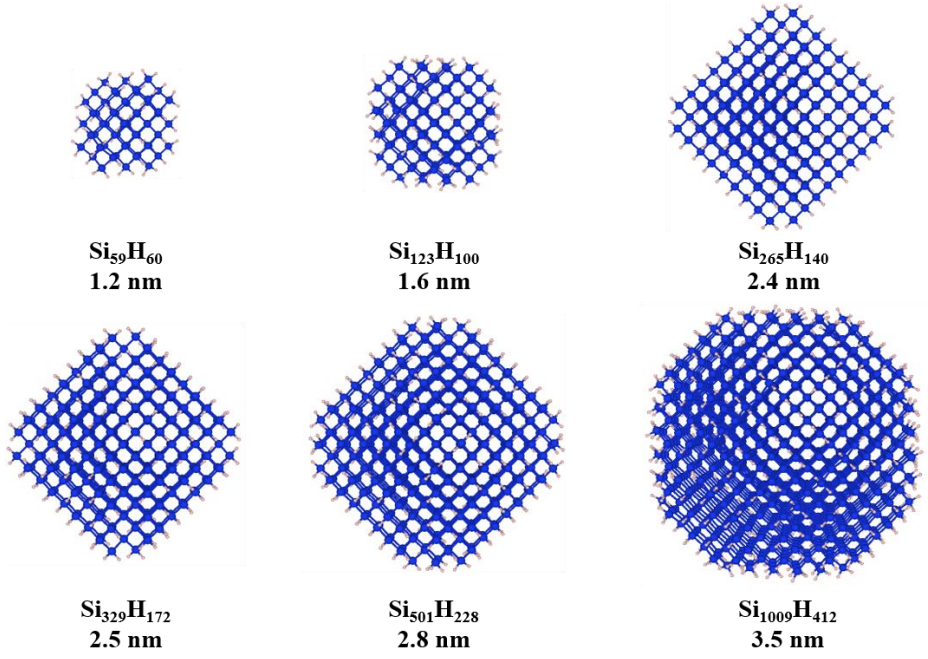
Implementation

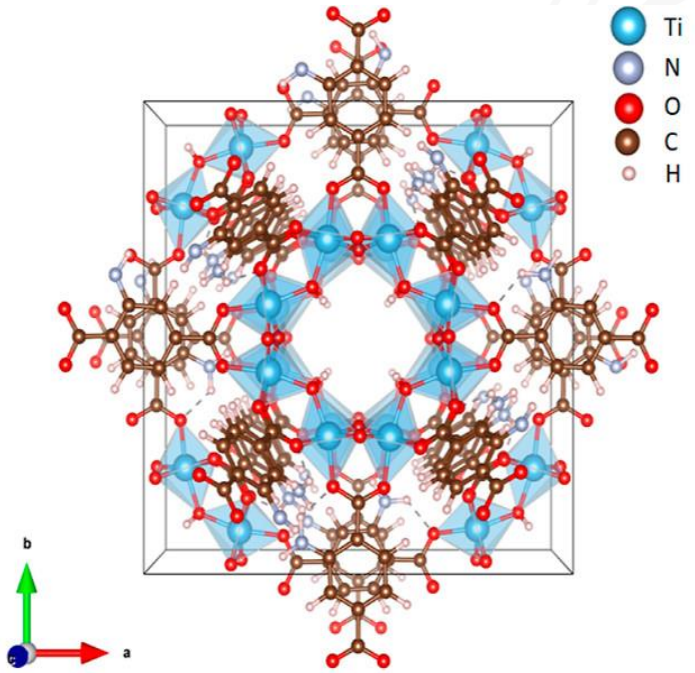


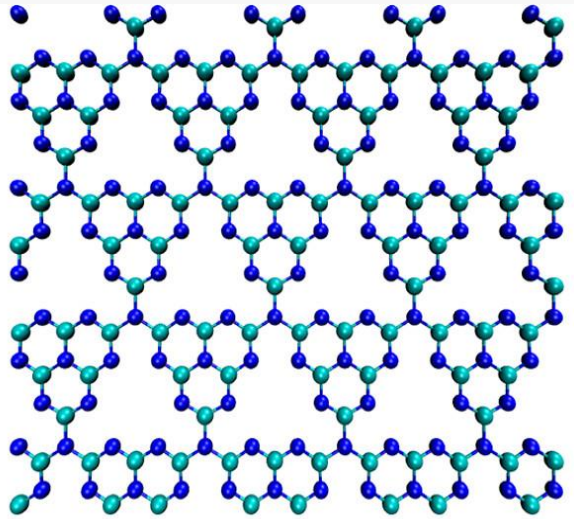

```python
import os
from libra_py import CP2K_methods
from libra_py.workflows.nbra import step2

# Setup the parameters
params = {'istep': 1, 'fstep': 2000, 'nprocs': 9, 'mpi_executable': 'srun',
          'lowest_orbital': 512-20, 'highest_orbital': 512+21,
          'res_dir': os.getcwd() + '/results',  'isUKS': False,
          'is_periodic': True, 'periodicity_type': 'XY'
          'is_spherical': True, 'isxTB': True, 'remove_molden': True,
          'cp2k_exe': 'cp2k.psmp', 'cp2k_ot_input_template': 'es_ot.inp',
          'cp2k_diag_input_template': 'es_diag.inp',
          'trajectory_xyz_filename': 'C3N4-2x2-pos.xyz',
          'cube_visualization': True, 'vmd_input_template': 'vmd.tcl',
          'vmd_exe': 'vmd', 'states_to_plot': [512,513],
          'plot_phase_corrected': True, 'remove_cube': True}

if params['is_periodic']:
    params['A_cell_vector'] = [28.483, 0.000, 0.000]
    params['B_cell_vector'] = [0.000, 24.669, 0.000]
    params['C_cell_vector'] = [0.000, 0.000, 15.000]
    # Set the origin and generate the translational vectors
    origin = [0,0,0]
    # Number of periodic images per each X, -X, Y, -Y, Z, and -Z directions
    num_periodic_images = [1,1,1]
    params['translational_vectors'] =
    CP2K_methods.generate_translational_vectors(origin, num_periodic_images,
                                                params['periodicity_type'])

# Run the calculations
step2.run_cp2k_libint_step2(params)
```

Applications

- Hot-electron cooling dynamics in silicon nanocrystals (Si NCs)
- Electron-hole recombination dynamics in metal organic frameworks and carbon nitride monolayers

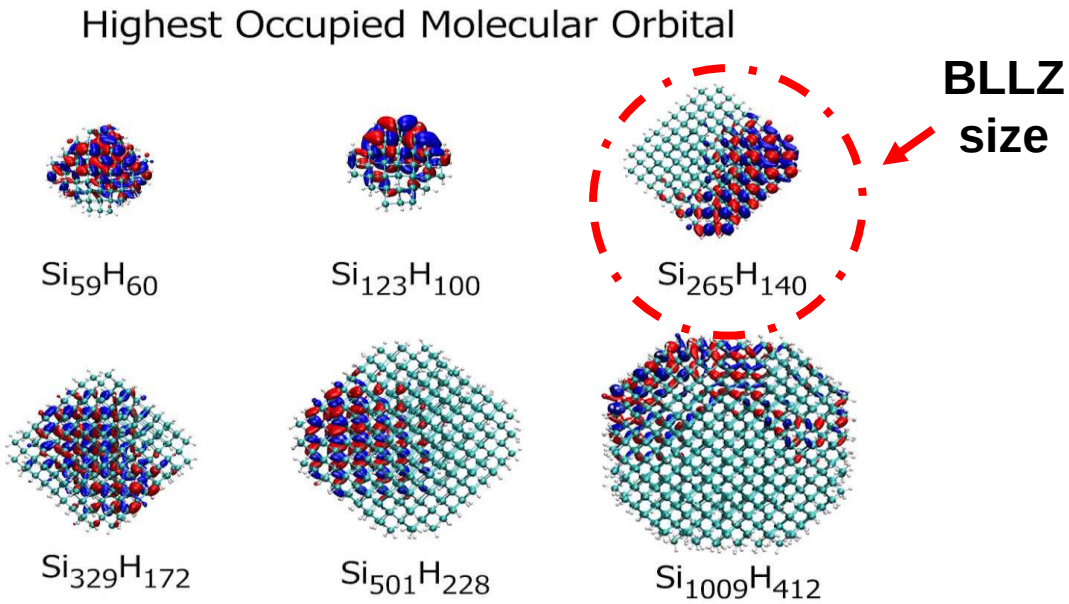






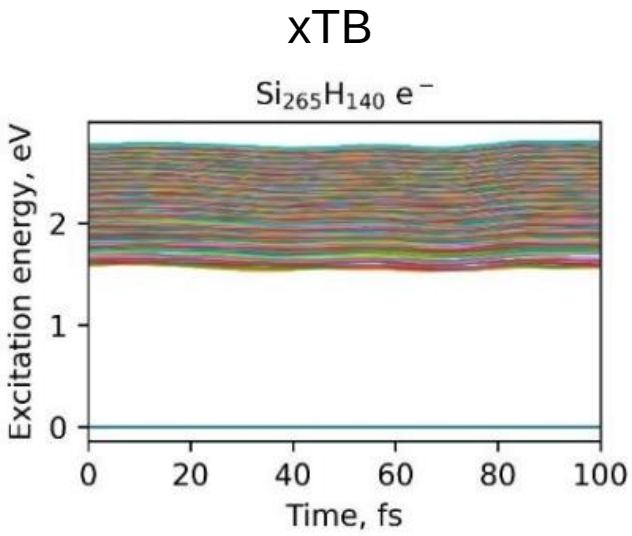
Shakiba, Stippell, Li, Akimov, J. Chem. Theory Compu. 2022, 18, 5157-5180

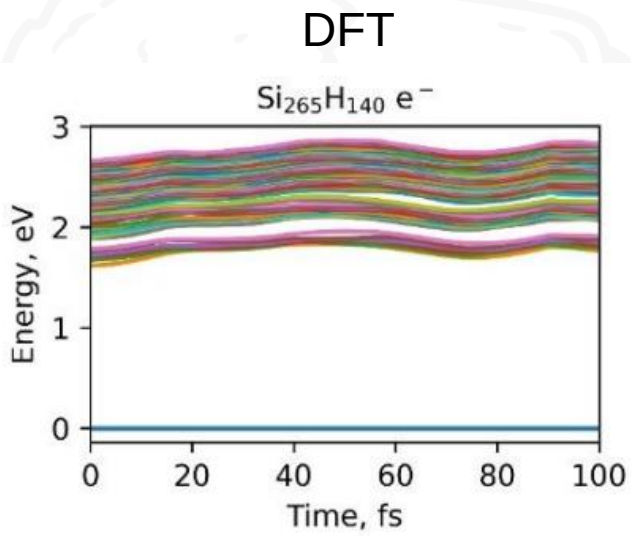
Hot-electron cooling dynamics in Si NCs

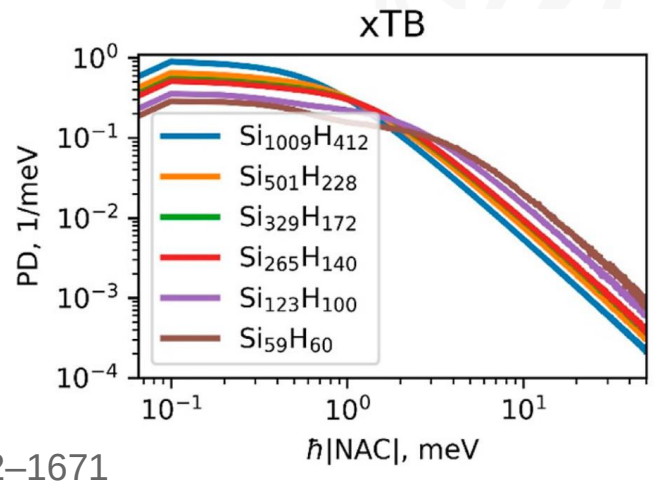


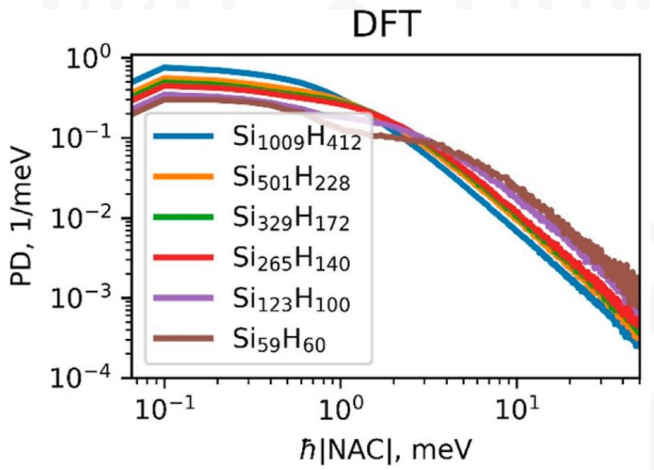
0

Size ↑ ↓ $\hbar|\mathbf{NAC}|$ **??**









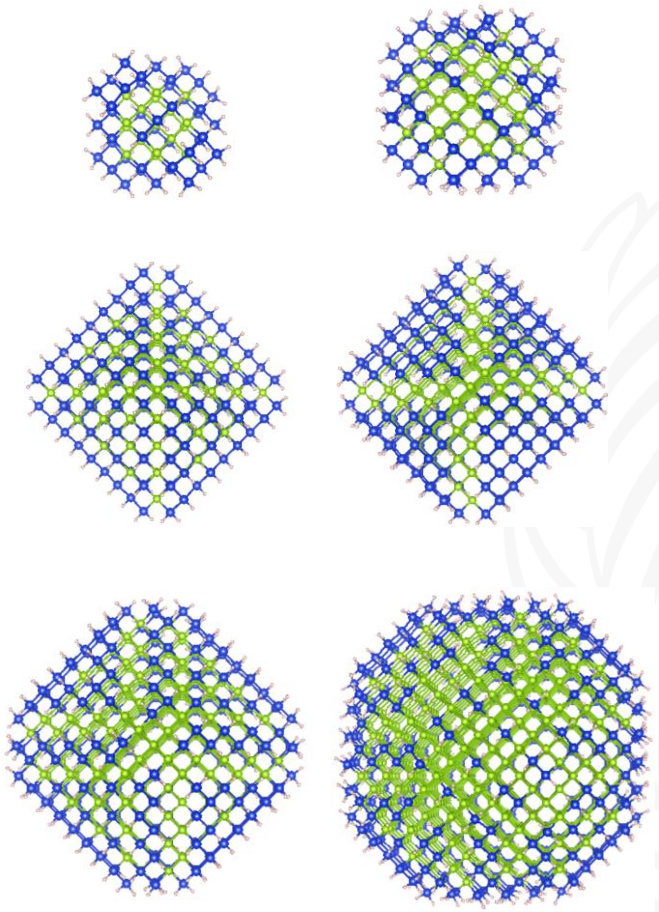
Bannwarth, Ehlert, Grimme, J. Chem. Theory Comput. 2019, 15, 1652–1671

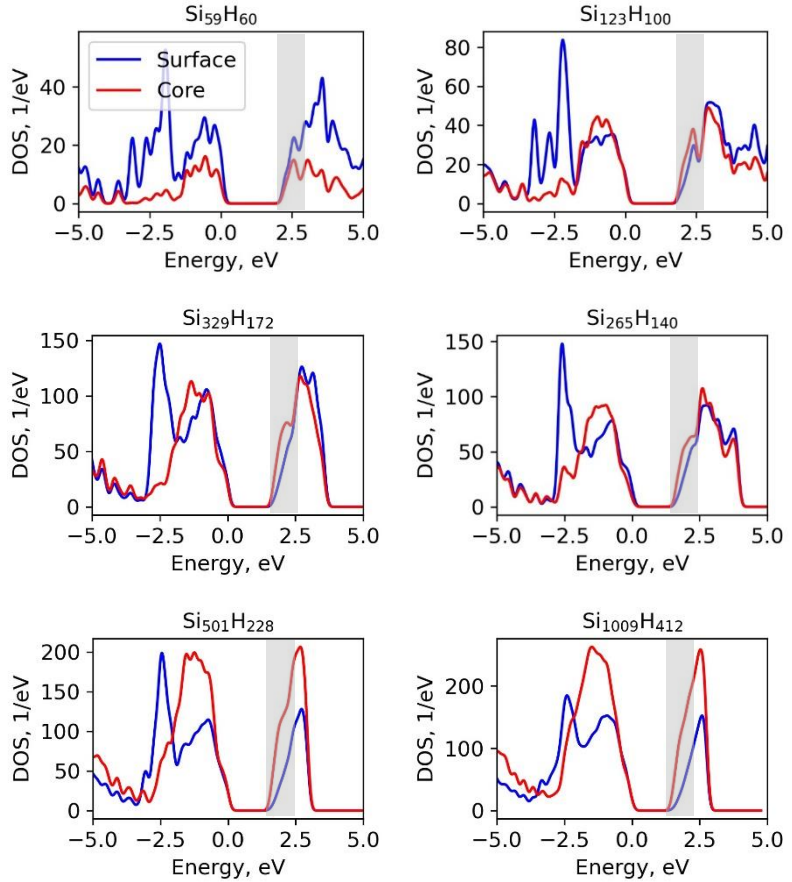
Core vs surface atoms

- By increasing size the surface/core DOS decreases
- Core atoms movements are slower than surface atoms

$$\sigma_i = \sqrt{\langle(\vec{r_i} - \langle\vec{r_i}\rangle)\rangle}$$

System	Si-surface	Si-core
$Si_{59}H_{60}$	0.273	0.172
$Si_{123}H_{100}$	0.152	0.113
$Si_{265}H_{140}$	0.144	0.114
$Si_{329}H_{172}$	0.186	0.141
$Si_{501}H_{228}$	0.262	0.190
$Si_{1009}H_{412}$	0.169	0.127

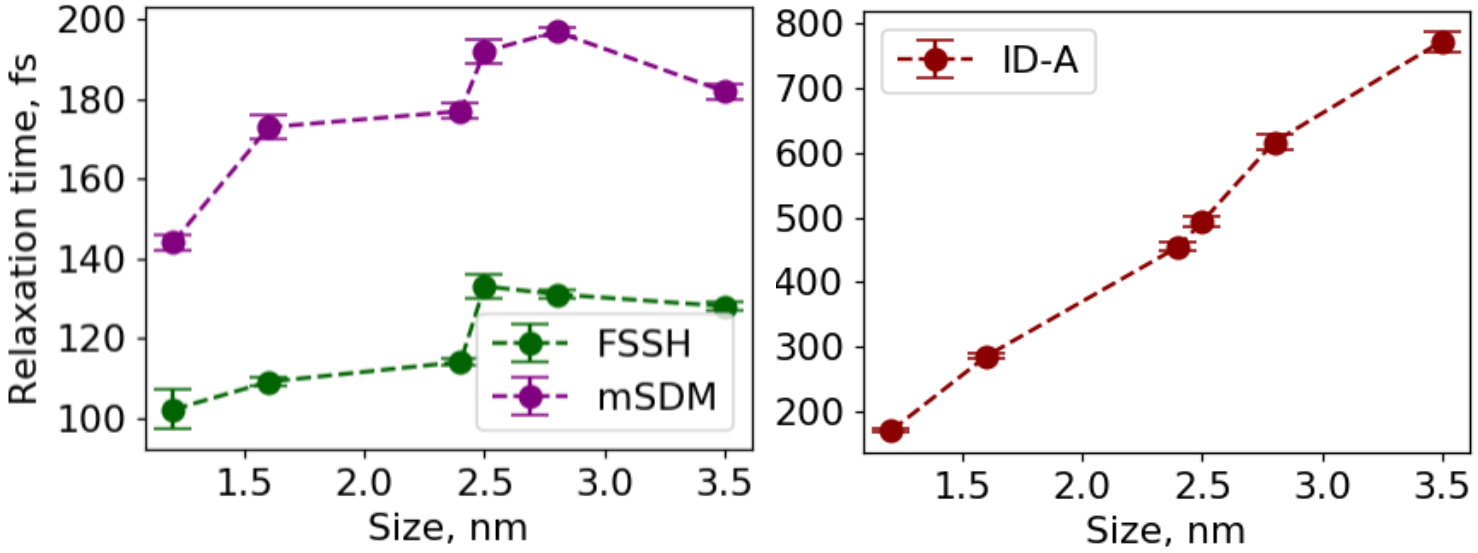




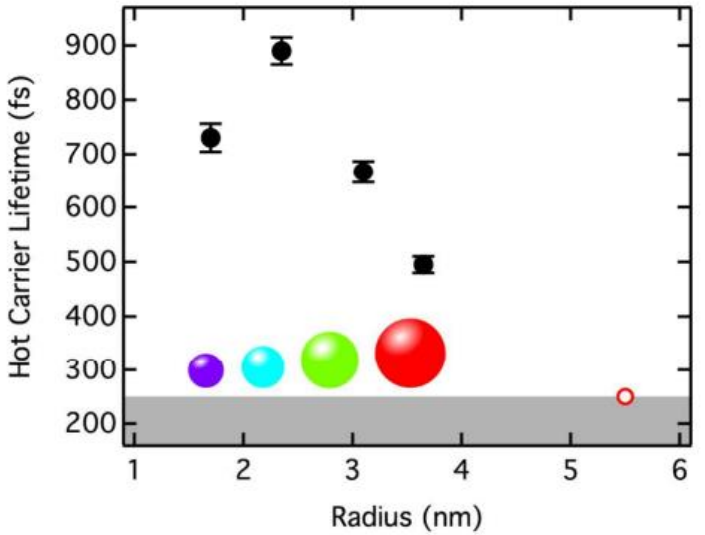
NA-MD results vs experiment

- Experimental data show a non-monotonic dependence of the relaxation time with respect to NC size
- FSSH and mSDM: Non-monotonic dependence of relaxation time on NC size
- ID-A: Monotonic dependence of relaxation time with increasing NC size

Theory



Experiment



Bergren, Palomaki, Neale, Furtak, Beard, ACS Nano 2016, 10, 2316–2323

NA-MD results vs experiment

- By going to larger NCs, the possibility of relaxation happening through non-adjacent states increase
- NA-MD done with only adjacent state transition allowed does not decay for larger structures
- FSSH and mSDM show comparable results but mSDM timescales are larger
- mSDM and FSSH close timescales are due to relatively large dephasing times making correction to coherent amplitudes very small but the overall results are in a better agreement with experiments

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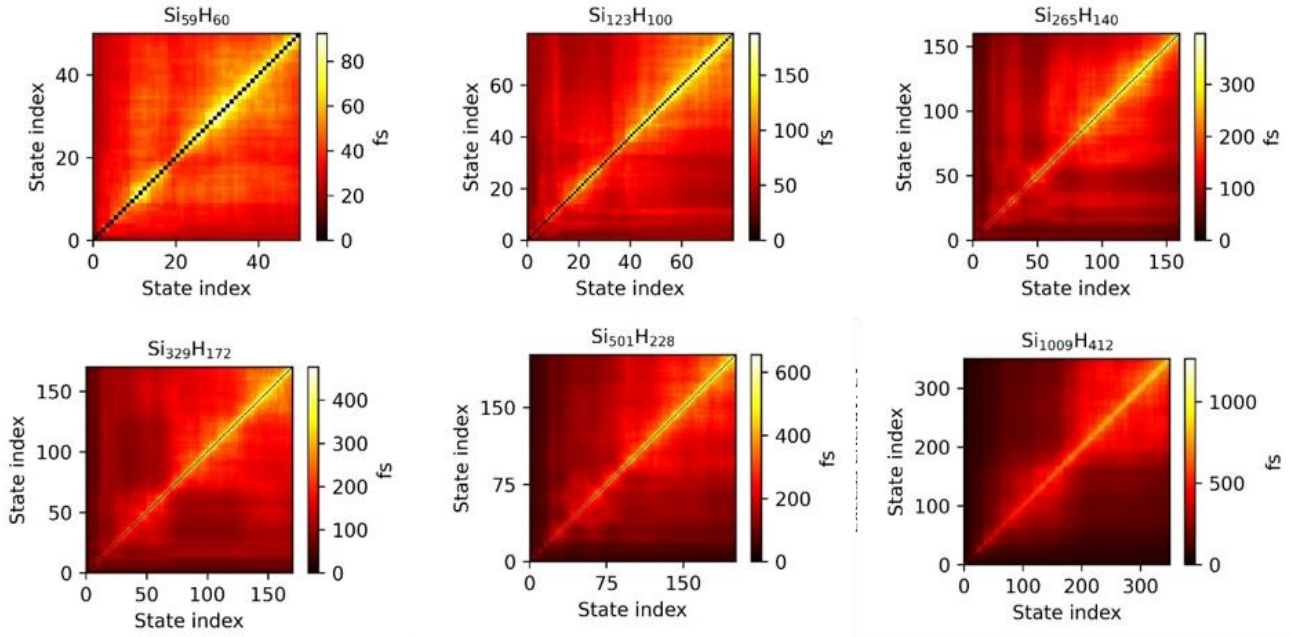
annels for non-adjacent state
ways by destroying the coherences
ncrease of the ID-A energy

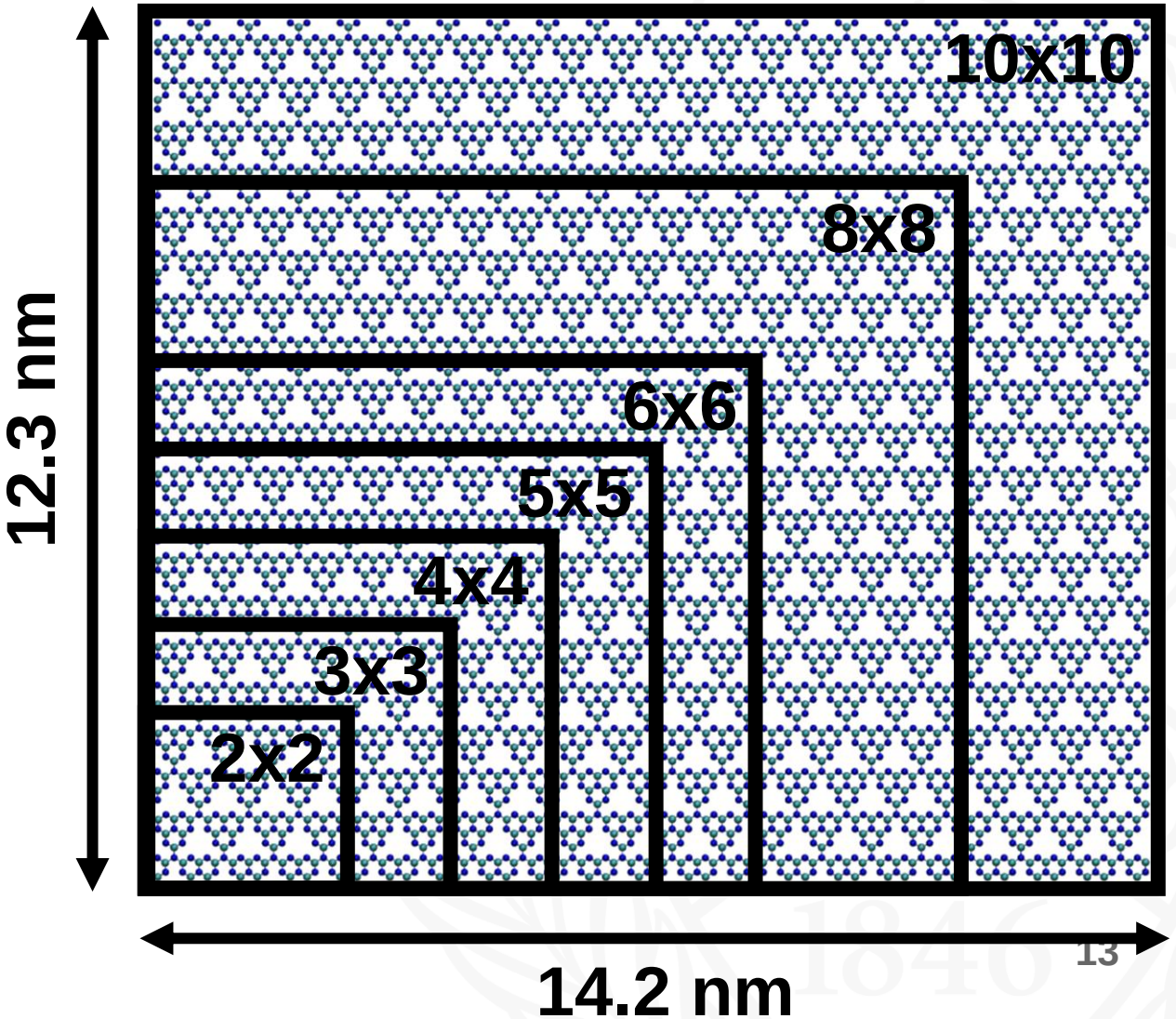


Charge carrier concentration in C_3N_4 monolayers

- Intrinsic charge carrier concentration in monolayers are in the range of ~10^{10}-10^{12} cm^{-2} in experimental studies
- Theoretical studies overestimate this value due to simulation of excited states in small cell size

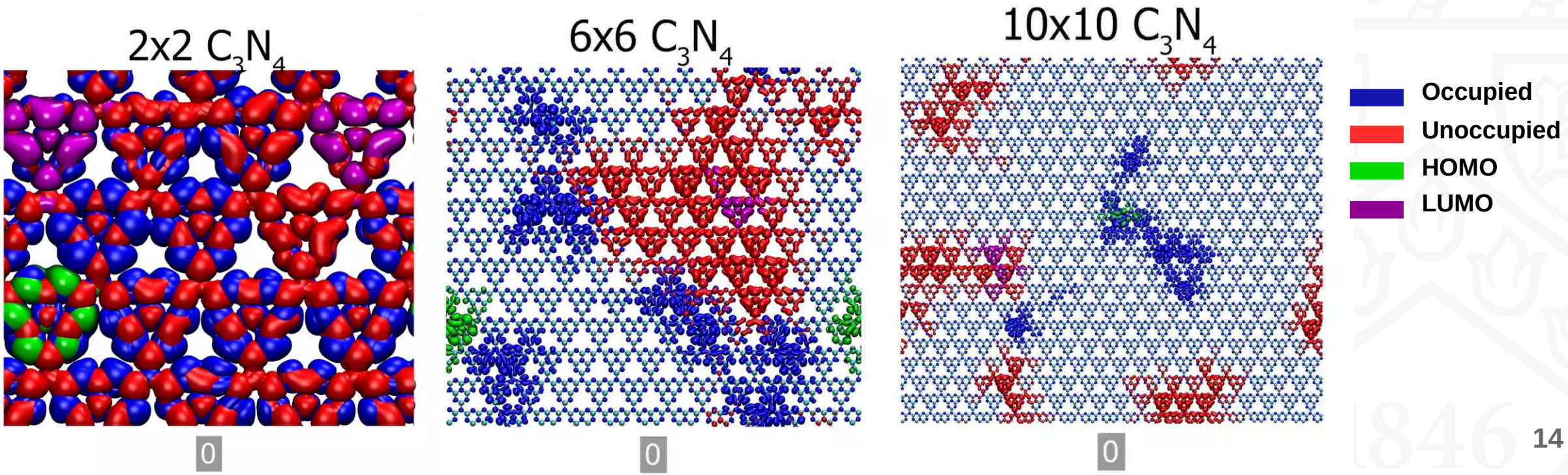
224 # Atoms 5600

512 # Orbitals 12800

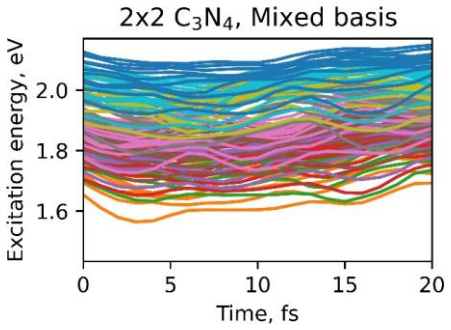


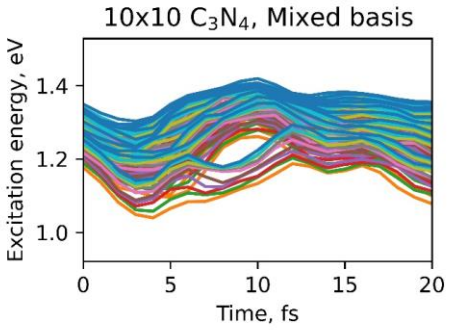
Molecular orbitals in C_3N_4 monolayers

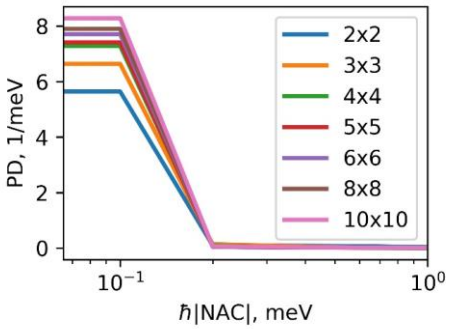
- Occupied orbitals are more localized on several melem (triangular repeated motif of 3 fused rings) units
- Unoccupied orbitals are delocalized over multiple connected melem units which is better observed in larger supercells

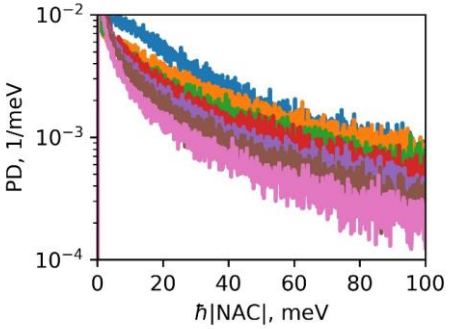


e-h recombination dynamics in C_3N_4 monolayers



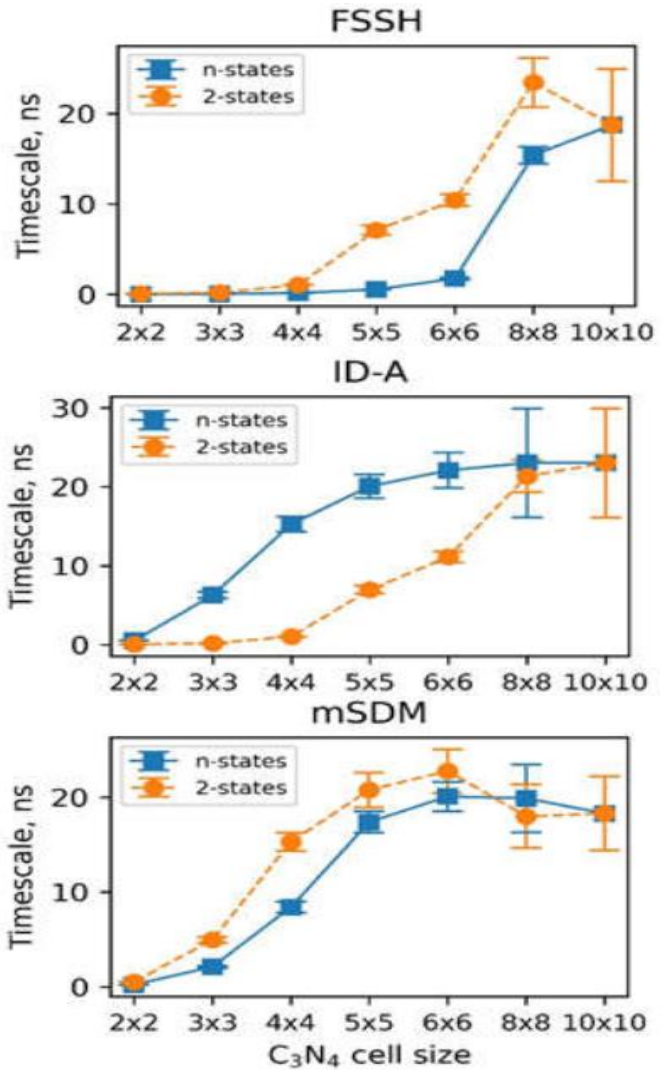




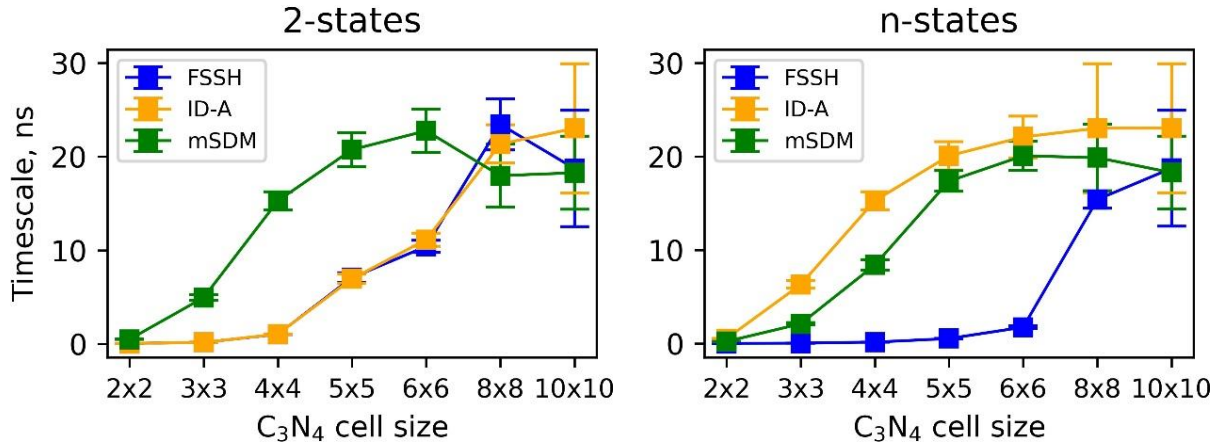


- 100 single-particle excitation states are built from all excitations from the first 10 occupied to the first 10 unoccupied molecular orbitals
- NAC values decrease by increasing supercell size
  - Small time-overlaps between molecular orbitals in large supercells
- Recombination dynamics becomes size-independent for all methods for very large supercell sizes
- For FSSH and mSDM, the dynamics accelerates in the n-states model due to presence of more nonradiative channels for recombination
- The dynamics is slower in ID-A in the n-states model due to presence of more nonradiative channels and therefore more frequent resets of the coherent amplitudes
- For larger supercells, the DOS does not play an important role and the 2- and n-states model show similar results

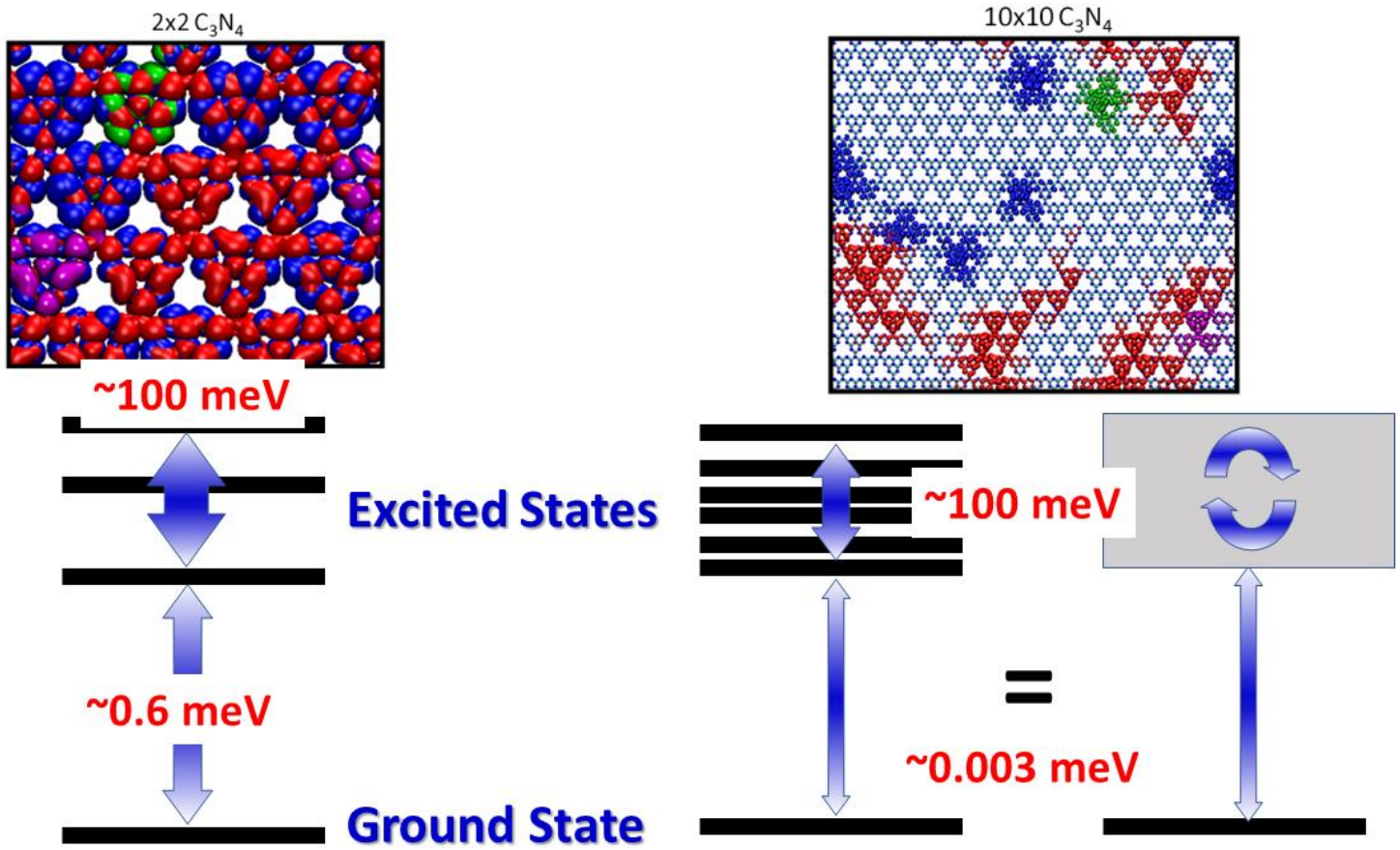
e-h recombination dynamics in C_3N_4 monolayers

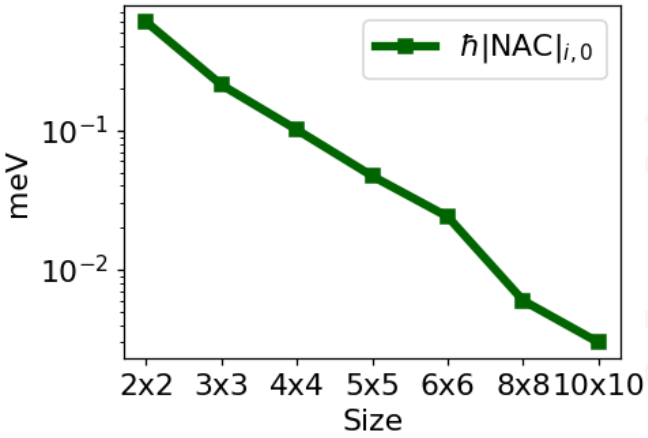


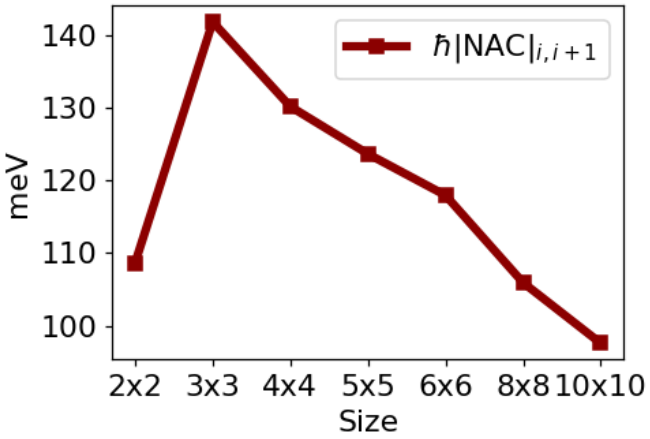
- 100 single-particle excitation states are built from all excitations from the first 10 occupied to the first 10 unoccupied molecular orbitals
- NAC values decrease by increasing supercell size
  - Small time-overlaps between molecular orbitals in large supercells
- Recombination dynamics becomes size-independent for all methods for very large supercell sizes
- For FSSH and mSDM, the dynamics accelerates in the n-states model due to presence of more nonradiative channels for recombination
- The dynamics is slower in ID-A in the n-states model due to presence of more nonradiative channels and therefore more frequent resets of the coherent amplitudes
- For larger supercells, the DOS does not play an important role and the 2- and n-states model show similar results



e-h recombination dynamics in C_3N_4 monolayers







Summary

- A new methodology for NA-MD simulations in large nanostructures and periodic solids is implemented in the open-source Libra code
- The NAC values decrease by increasing Si NC size and C_3N_4 monolayer supercell size
- A non-monotonic dependence of hot-electron relaxation dynamics on Si NC size was observed in FSSH and mSDM in agreement with experiment
- Non-adjacent transitions play an important role in the relaxation dynamics in Si NCs
- FSSH and mSDM showed similar dynamics in Si NCs due to high dephasing times
- ID-A showed a monotonic dependence of the relaxation time on NC size which was due to multiple coherence resets in the dynamics
- By varying charge carrier concentration using different supercell sizes, a saturation of the recombination timescale was observed showing the size-independence of recombination dynamics in very large structures
- The results of the dynamics in the 2-states and n-states model showed that the inclusion of more states in the dynamics increases the recombination rate by providing more nonradiative channels for the dynamics in the FSSH and mSDM methods
- ID-A showed slower dynamics in the n-states model compared to 2-states model due to frequent coherence resets in the dynamics

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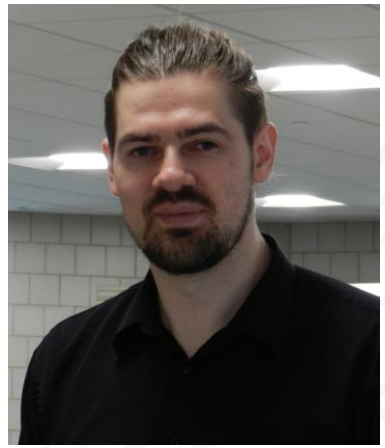

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Thank You!

Questions?