Excitons in Hematite Fe_2O_3

1- Electronic Structure

2- Short-time Dynamics from TD-DFT and non-Adiabatic Dynamics Theories

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Libra Workshop and Summer School on Excited States and Nonadiabatic Dynamics 2024

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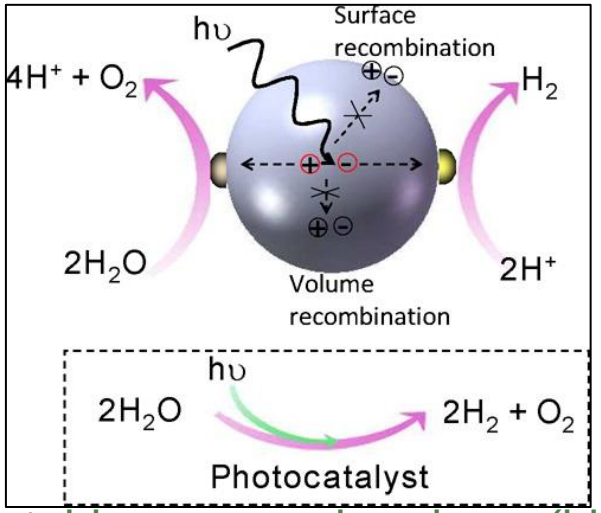
Introduction

PEC's mechanism[1]



- **Environmental challenges** → turn to **green energies**
- **Photoelectrochemical cells** (PECs) convert **solar energy to fuels** (chemical energy)
- Three phases of PECs:
  1. light absorption and charge carrier generation
  2. charge transport
  3. redox reactivity
- **Hematite = attractive photocatalyst:** abundant, cost-effective, chemically stable, narrow bandgap (high visible light absorption)
- **Limitations include high charge carrier recombination rate and low carrier mobility**
- **Experimental results** are available for hematite: **bandgap around 2.1 eV** for a bulk of hematite[2] and **lifetime around hundreds of ps** for a hematite film.[3,4]
- **Goal:** characterize, understand, and control carrier dynamics

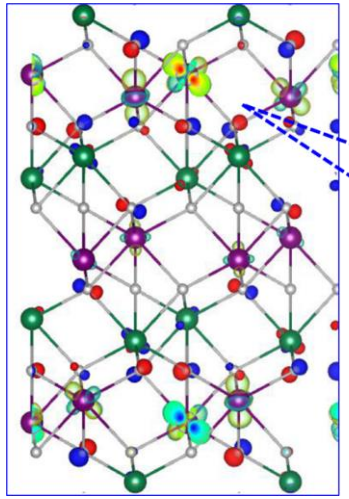
1- J. Yang *et al.*, *Accounts of Chemical Research*, 2013, 46, 1900.
2- S.I. Srikrishna Ramya, C.K. Mahadevan, *Journal of Solid State Chemistry*, 2014, 211, 37.
3- A.G. Joly *et al.*, *Journal of Applied Physics*, 2006, 99.
4- Z. Zhou *et al.*, *Journal of the American Chemical Society*, 2017, 139, 6707.

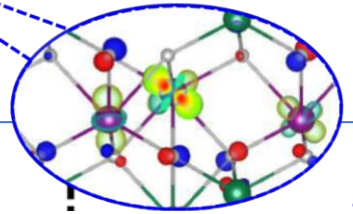
Methods

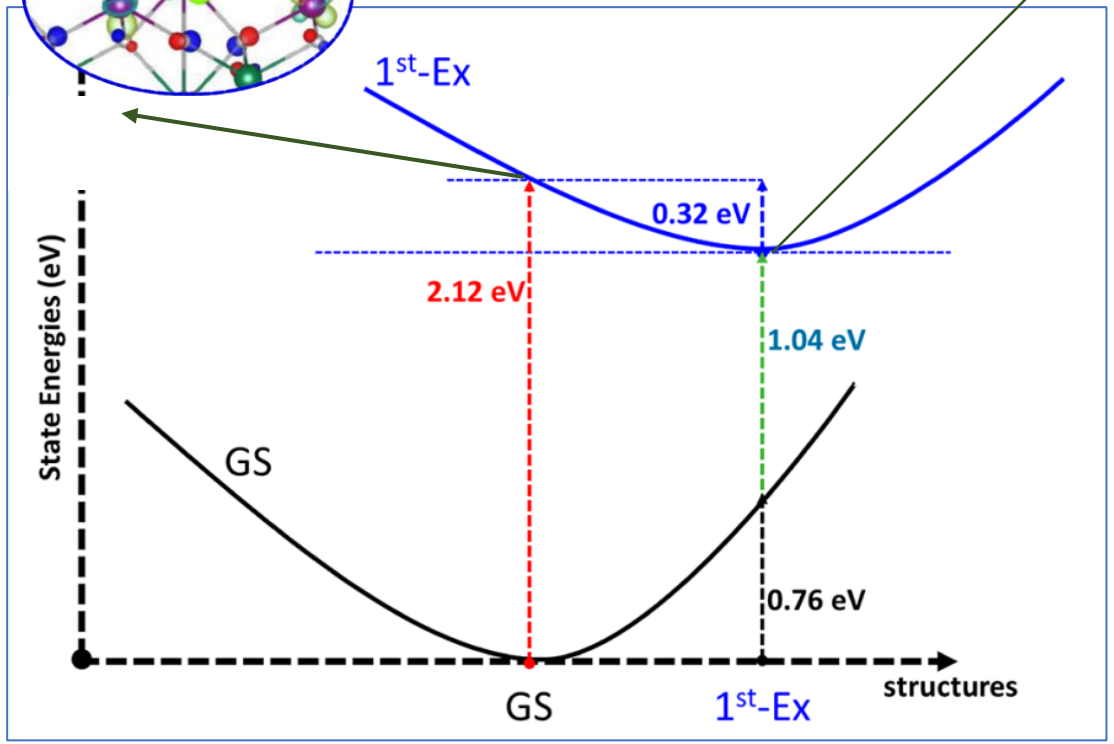
Cell optimization	• **Atomic positions and cell parameters of 2×2×1** • **Atomic positions of 2×2×3 cells**
AIMD	• **4 ps molecular dynamics after reaching the equilibrium (4000 steps with 1 fs timestep in NVT)** • **DFT and TDDFT at each time-step**
Periodic DFT	• **Functional: PBE+U(Fe,O)**
NAMD[1,2] (Libra[3,4] & CP2K)	1. **Molecular orbital overlaps and time-overlaps using Libra** 2. **Nonadiabatic couplings (NACs) between pairs of many-body excited states generated from TD-DFT calculations for each geometry in the MD trajectory.** 3. **Performing stochastic NAMD using the NACs on the many-body basis.**

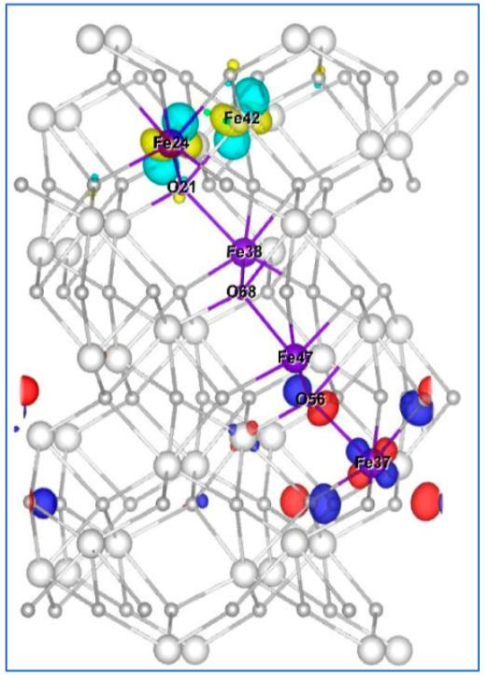
1- B. Smith, M. Shakiba, A. V. Akimov, *Journal of Chemical Theory and Computation*, 2021, 17, 678.
2- M. Shakiba *et al.*, *Journal of Chemical Theory and Computation*, 2022, 18, 5157.
3- A. V. Akimov, *The Journal of Chemical Physics*, 2021, 155, 134106.
4- A.V. Akimov, J. Comput. Chem, 2016, 37, 1626−1649.

Results: Exciton Structure in small cell









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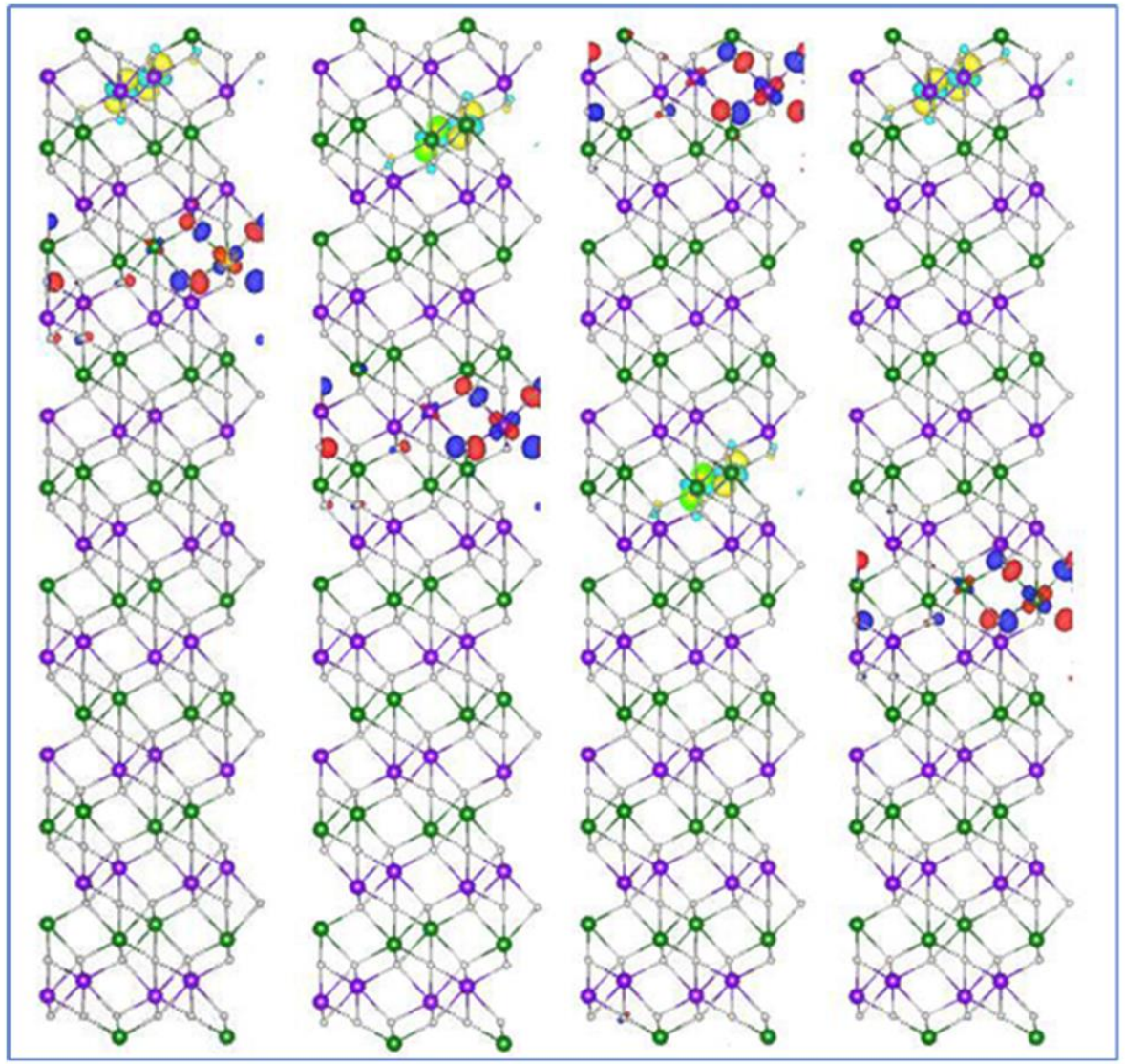
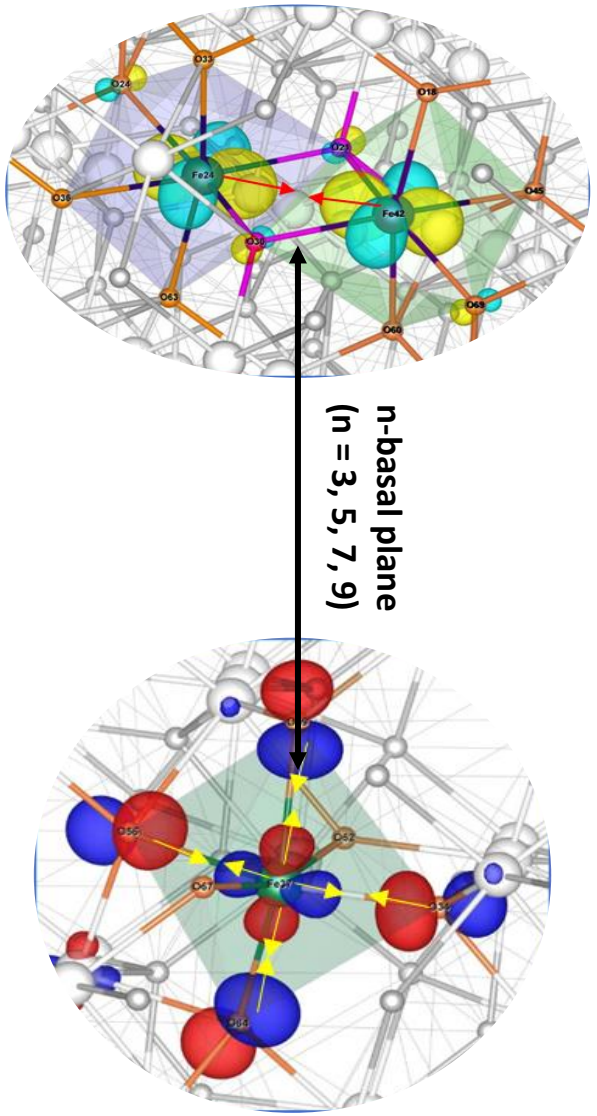
Results: Exciton Structure in 2×2×3 supercell





CB_{min} = Fe(3d)

electron LUMO localization (~80%) over two Fe atoms at the centers of two edge-sharing octahedra belonging to a basal plane

in-phase (bonding)shortening

VB_{max} = O(2p)

hole HOMO localization (~ 50%) over the four equatorial O atoms of an FeO_6 octahedron

out-of-phase (anti-bonding) shortening

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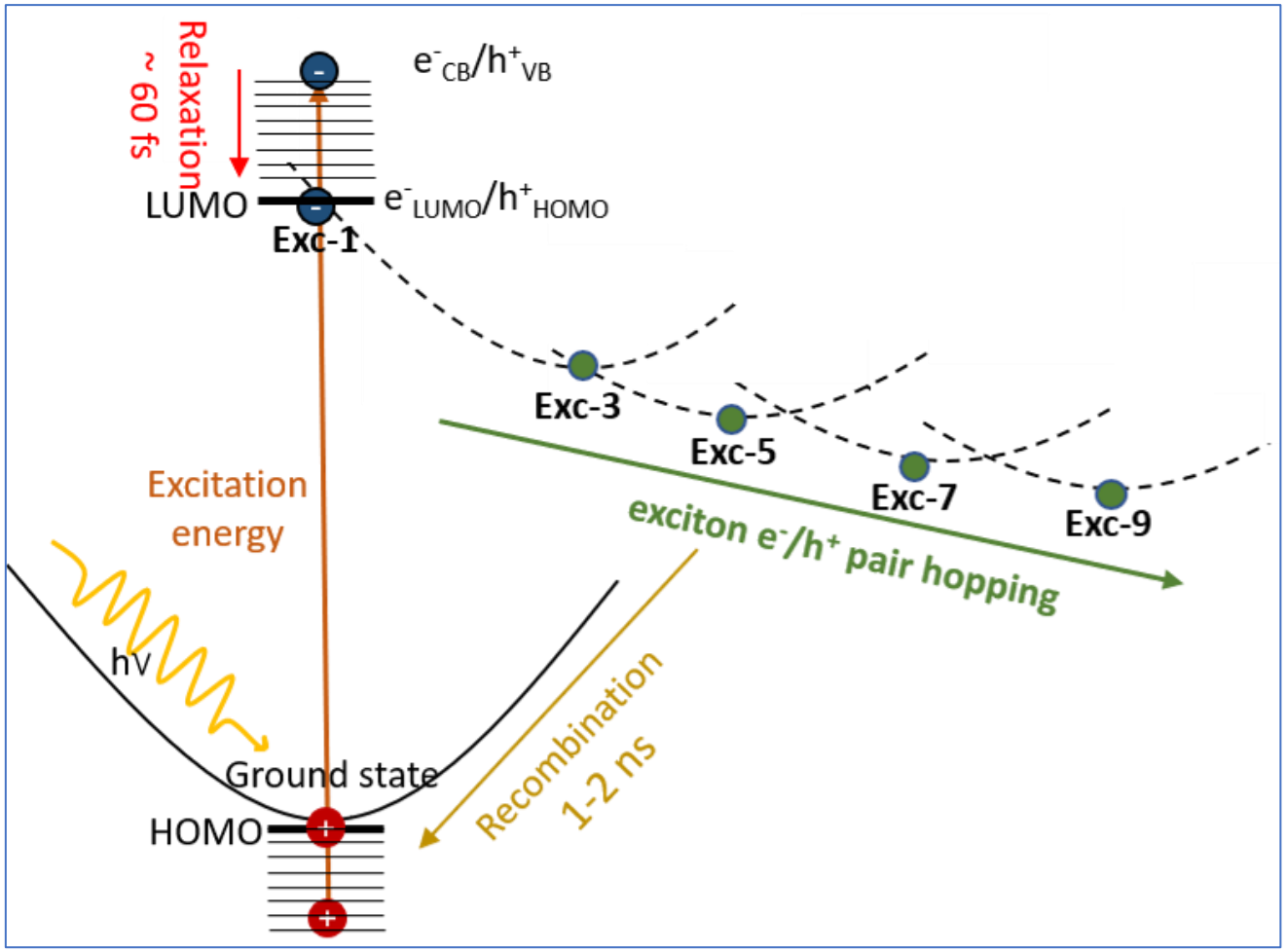
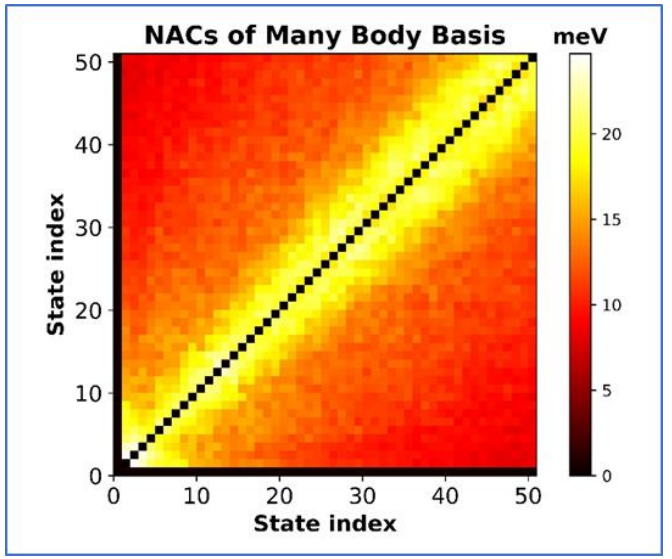
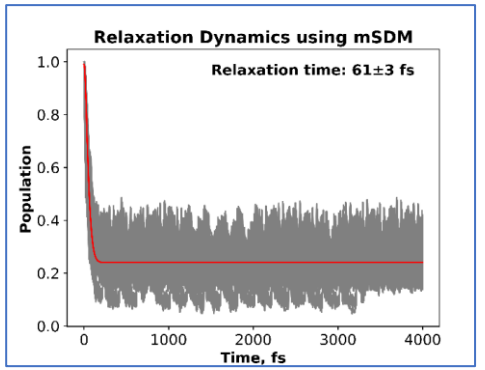
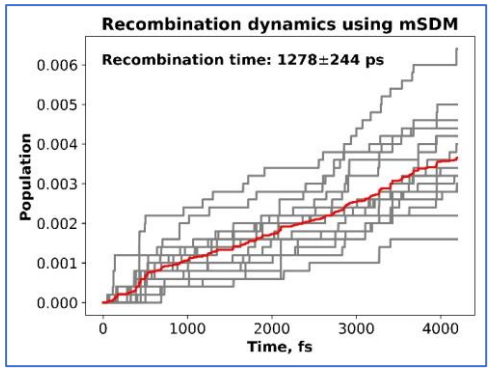
Results: Dynamics of Exciton using Libra









Conclusion

- Electron excitation from O 2p states to Fe 3d
- Exciton self-traps into stable electron-hole pair
- Hole localization on $(FeO_6)^+$ octahedral in HOMO
- Electron localization on $(FeFe)^-$ in accordance with previous computational studies [1]
- Computed recombination time is 1210 ps
- Computed relaxation time is in fs range

1- C.S. Ahart, K.M. Rosso, J. Blumberger, *Journal of the American Chemical Society*, 2022, 144, 4623

Libra Tutorials

https://github.com/compchem-cybertraining/Tutorials_Libra/tree/75701a6114782d1597cf5b1931c0cce42096b9e0/6_dynamics/2_nbra_workflows

https://github.com/compchem-cybertraining/Tutorials_Libra/blob/master/VIDEOS.md

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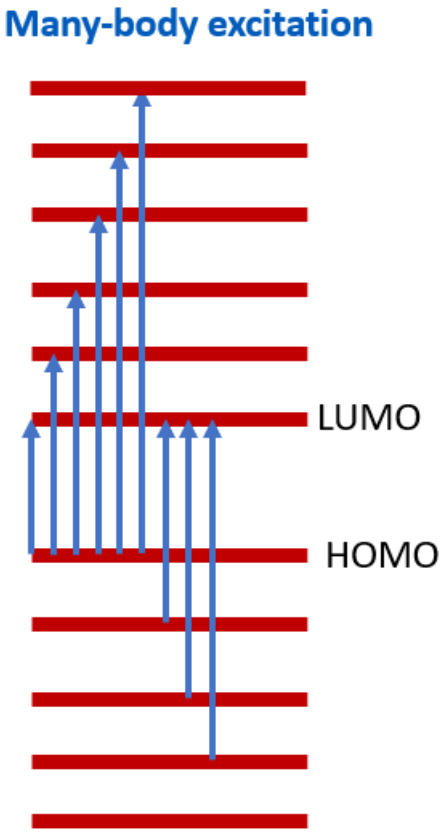
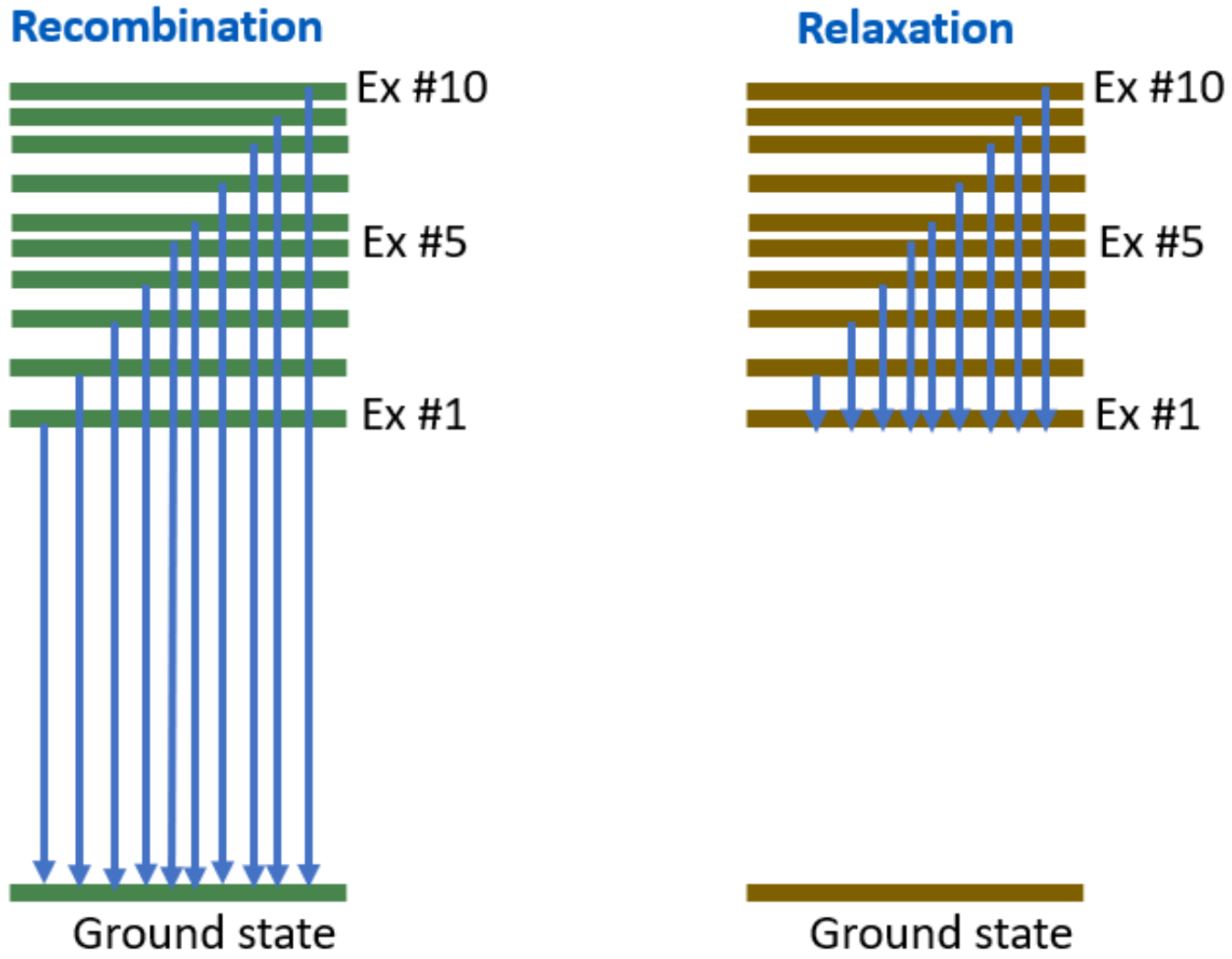
Many-body excitation

The non-adiabatic coupling coefficients between excited states were calculated based on many-body (MB) treatment of excited states rather than single particle (SP) treatment. The MB approach provides a more accurate treatment of excited states because the SP approach neglects the interaction between electronic states and relies on the properties of single-electron molecular Kohn-Sham orbitals to calculate state energies and NACs. In contrast, the MB approach involves a linear combination of single-particle excitations for each excited state, considering the weight of different contributions. Since the excited states of small molecules are almost always multiconfigurational, even for low-lying excited states, the SP description is inadequate, and many-body effects must be considered.



neglect-of-back-reaction approximation: NBRA

During excitation and relaxation, the electronic states change, but the NBRA neglects the effect of new electronic states (electronic state transitions) on nuclear evolution


Recombination
Ex #10
Ex #5
Ex #1
Ground state
Relaxation
Ex #10
Ex #5
Ex #1
Ground state