Correlated real-time electronic charge migration dynamics using the density matrix renormalization group

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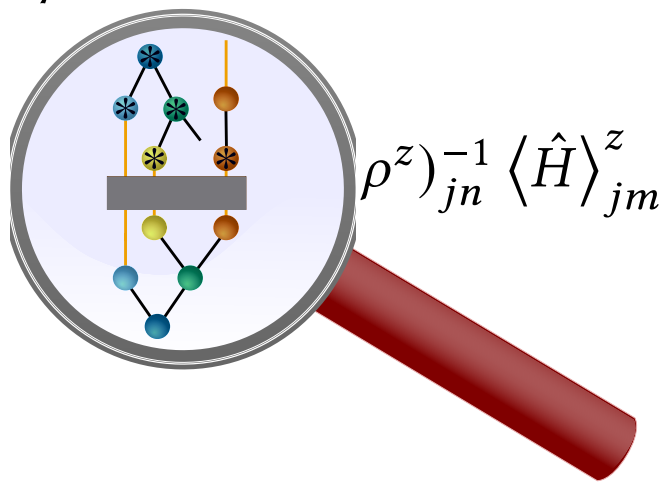
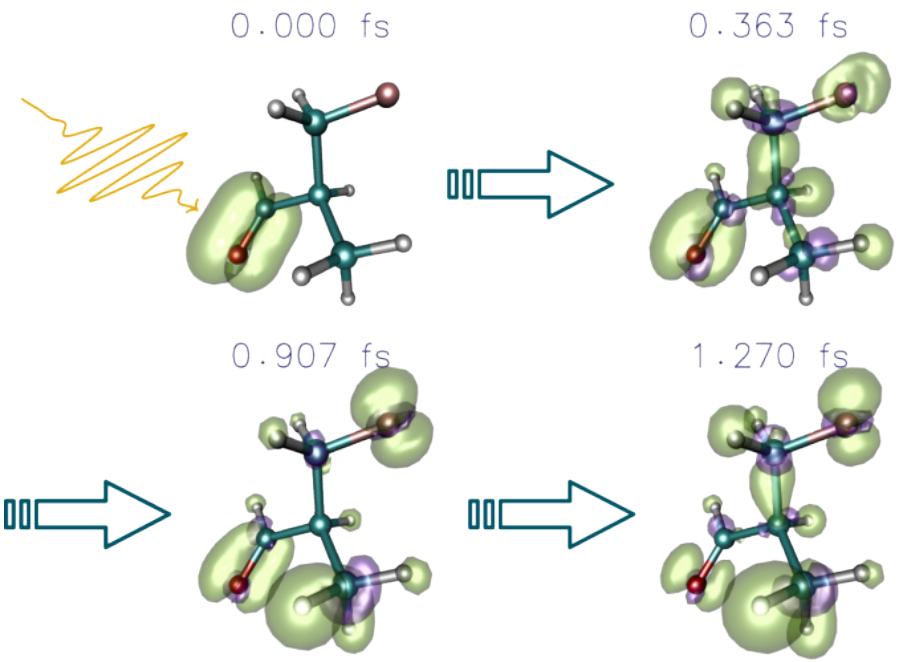
The Larsson quantum lab

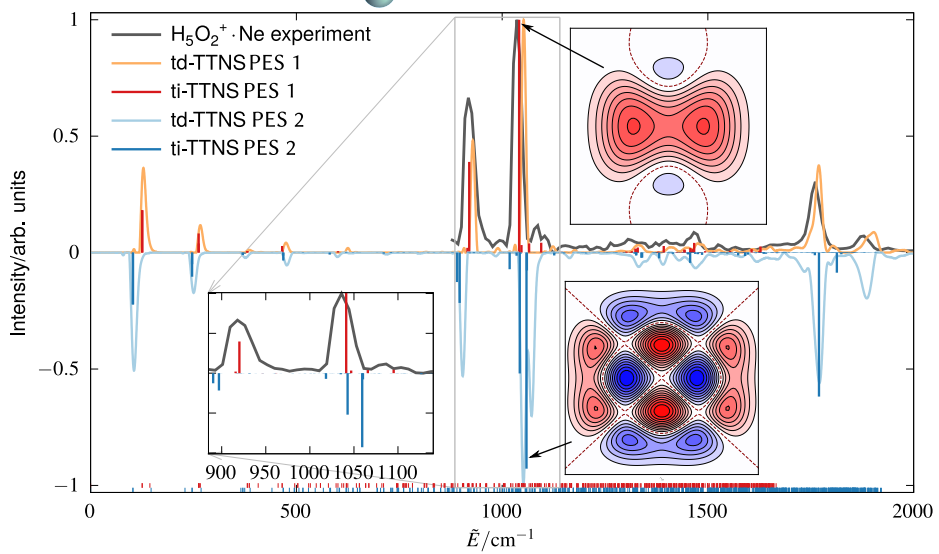
We apply tensor network states to complicated molecular quantum problems

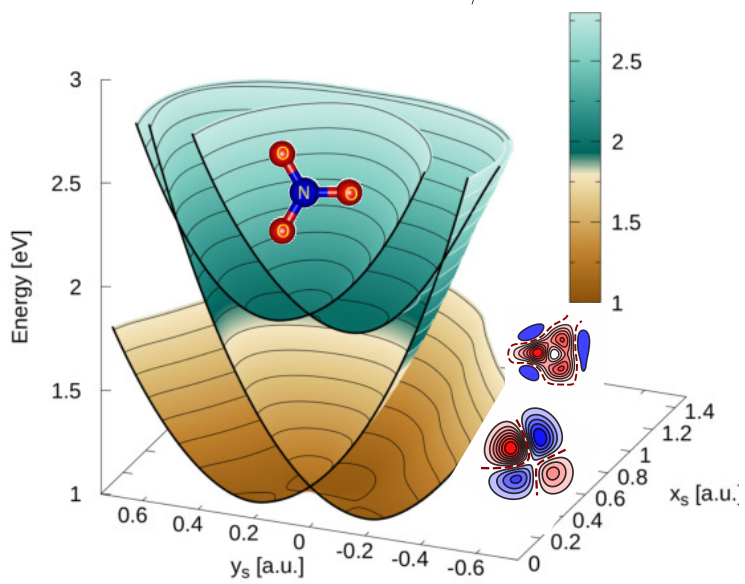
$$\mathrm{i}|\dot{\phi}_n^z\rangle = \rho^z)^{-1}_{jn} \left\langle \hat{H} \right\rangle^z_{jm} |\phi_m^z\rangle$$





1000 Eigenstates of the Zundel ion ($H_5O_2^+$)





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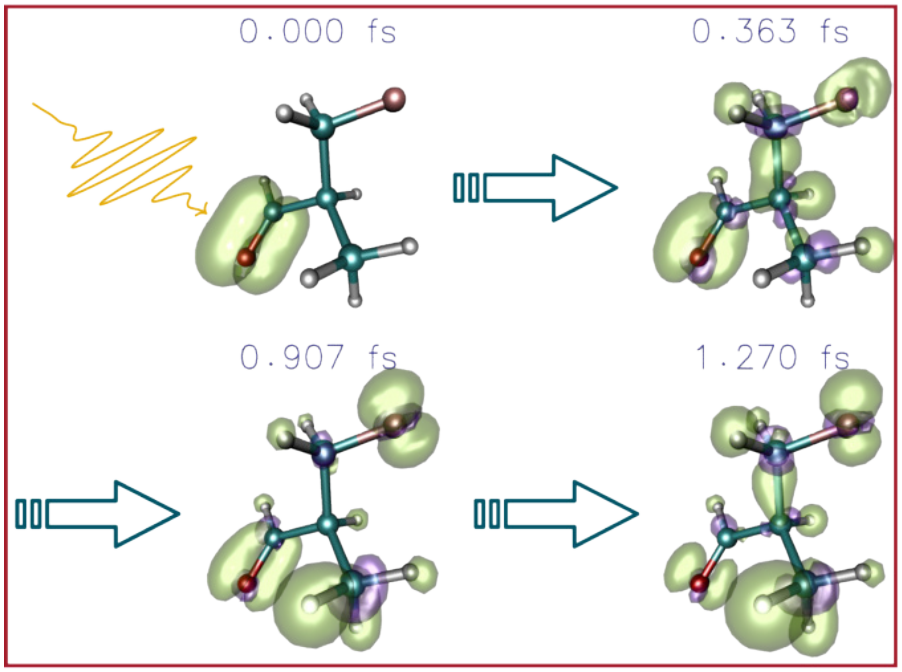

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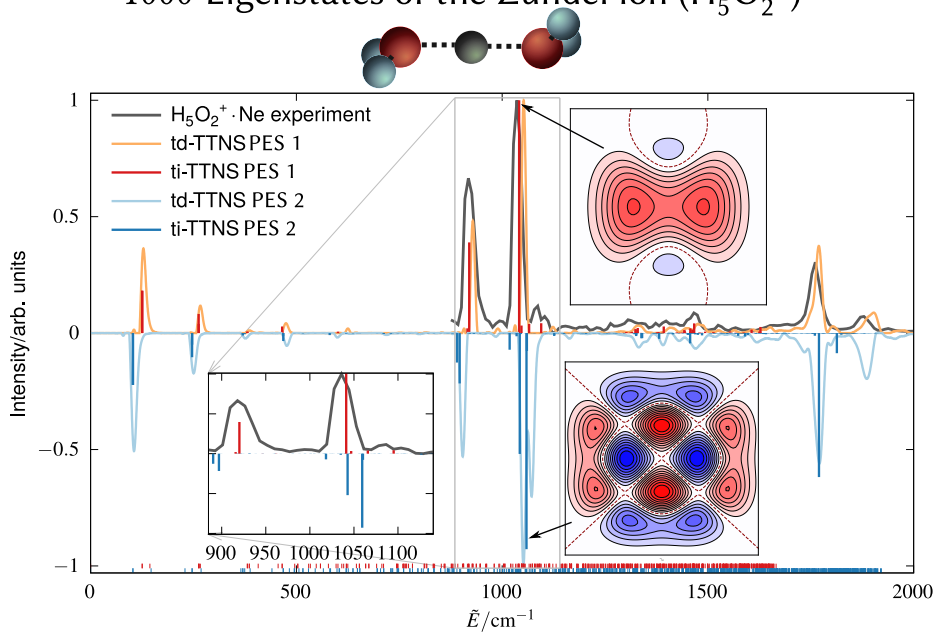
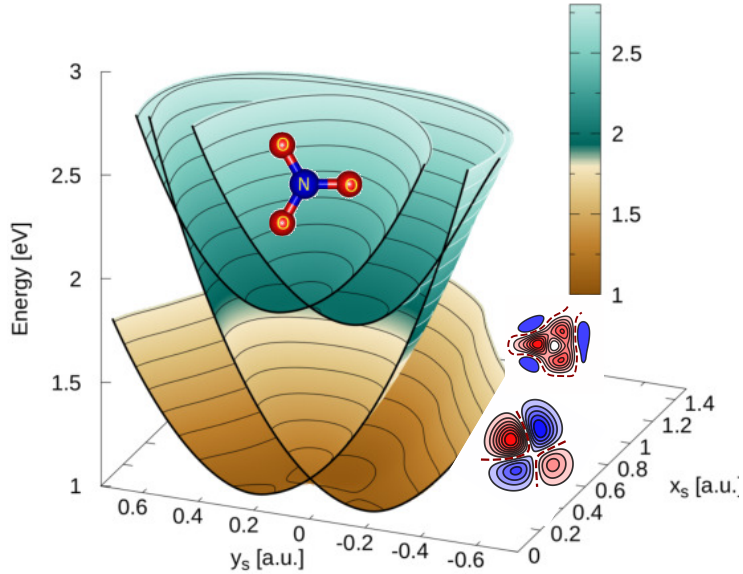




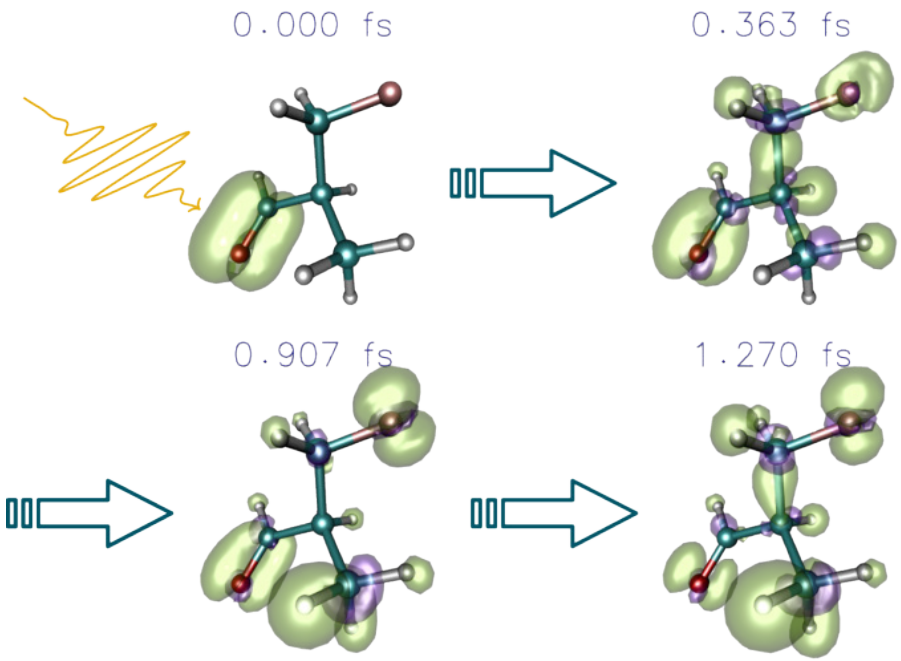
Charge migration dynamics[1]

- Central problem: Understand evolution of the hole density following ionization

$$h(\mathbf{r}, t) = \rho_{\text{neutral}}(\mathbf{r}) - \rho_{\text{cation}}(\mathbf{r}, t),$$

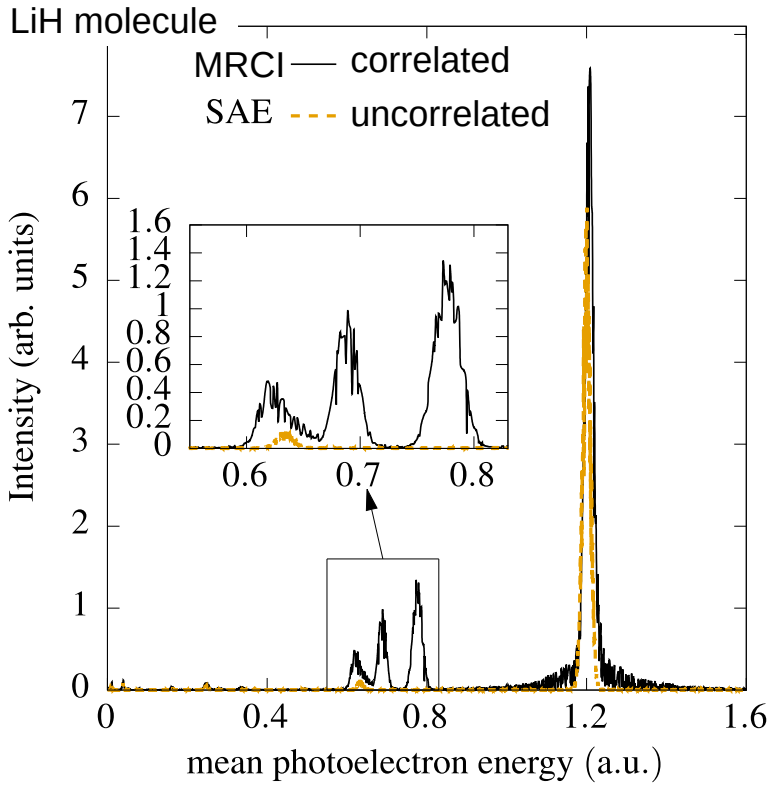
$\rho(\mathbf{r}, t)$: one-particle reduced densities

- Electron-electron repulsion necessary (dynamic correlation)
- Lasers can create complex initial states (static correlation)

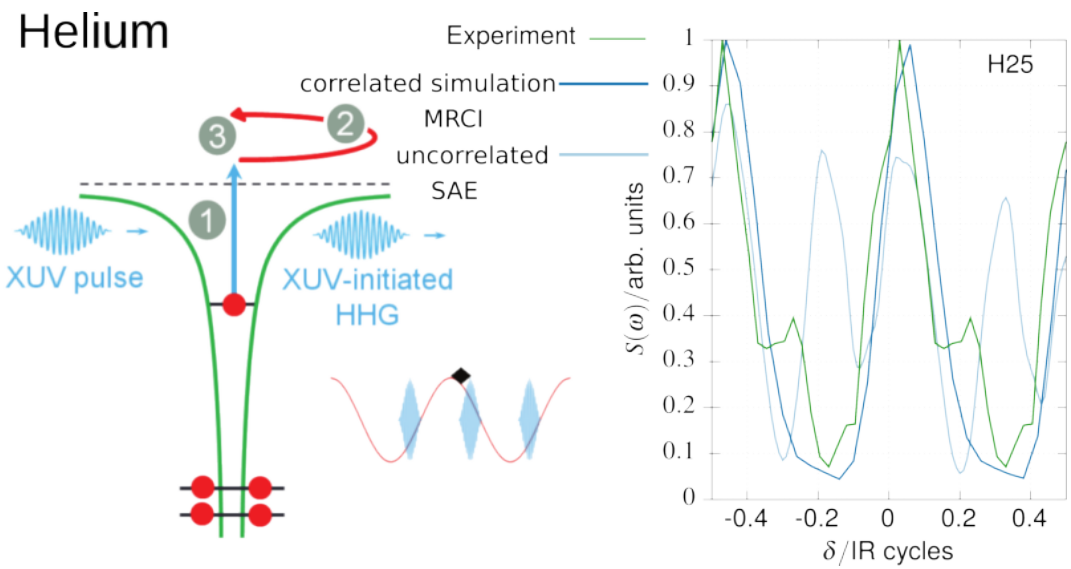


[1] L. S. Cederbaum and J. Zobeley, *Chem. Phys. Lett.*, 1999, **307**, 205–210.

El. correlation is important for ionization dynamics[1]



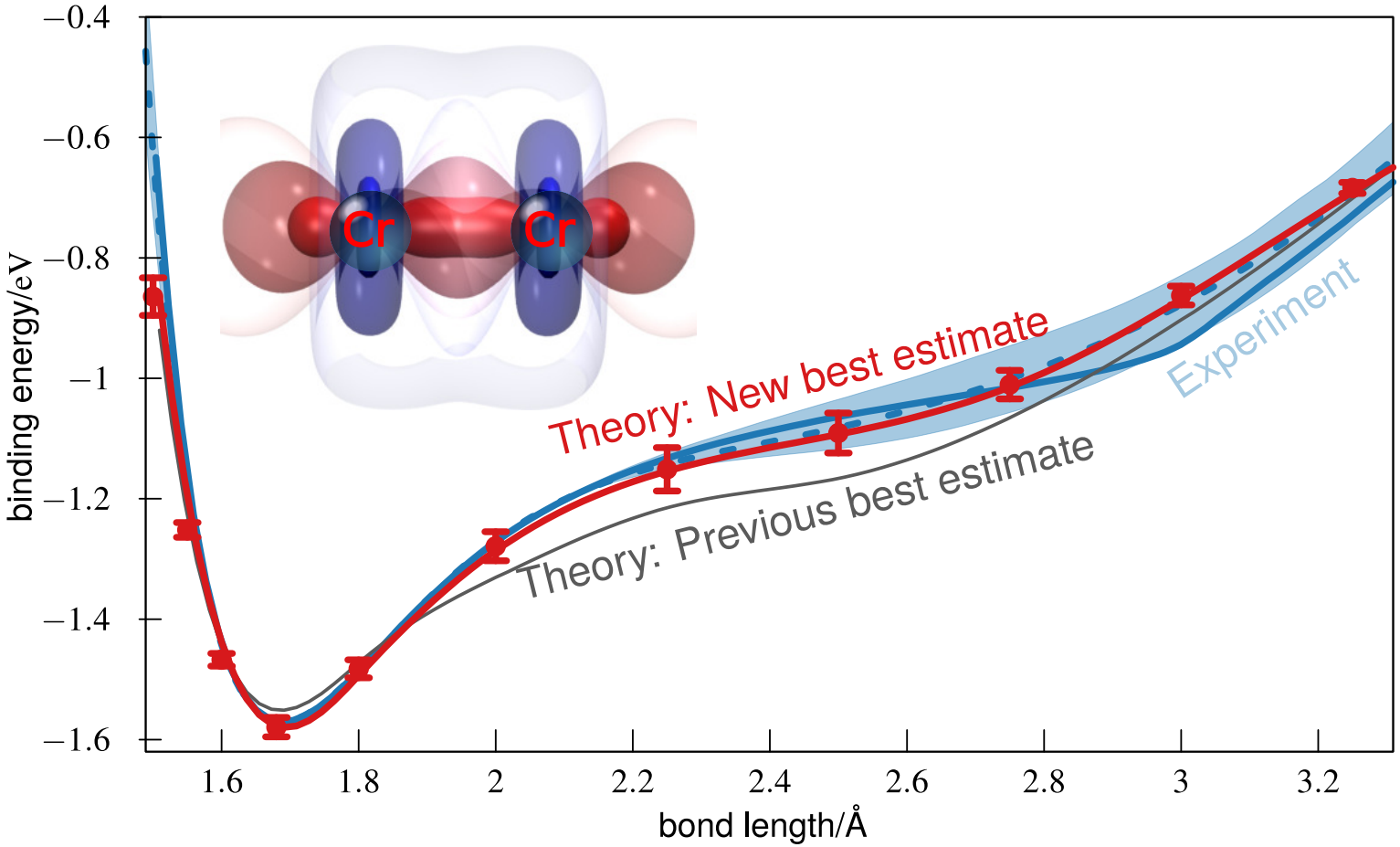
(40 eV, 3fs pulse; correlation leads to shake-up processes)



[1] H. R. Larsson et al., *Phys. Rev. A*, 2016, **93**, 013426; D. Azoury, M. Krüger, G. Orenstein, H. R. Larsson, S. Bauch, B. Bruner and N. Dudovich, *Nature Commun.*, 2017, **8**, 1453.

DMRG can answer long-standing chemistry problems

- Density matrix renormalization group (DMRG)
- 5-decade-old problem of computing the Cr_2 potential energy curve
- Solved here using DMRG variants[1]



[1] H. R. Larsson, H. Zhai, C. J. Umrigar and G. K.-L. Chan, *J. Am. Chem. Soc.*, 2022, **144**, 15932–15937.

DMRG in a nutshell[1]

- Full configuration interaction with 4 spin orbitals:

$$|\Psi\rangle = C_{1100}|1100\rangle + C_{1010}|1010\rangle + \cdots = \sum_{\{\sigma\}} C_{\sigma_1\sigma_2\sigma_3\sigma_4}|\sigma_1\sigma_2\sigma_3\sigma_4\rangle$$

- Matrix product state (MPS) approximation using matrices $\mathbf{M}^{\sigma_i}$:

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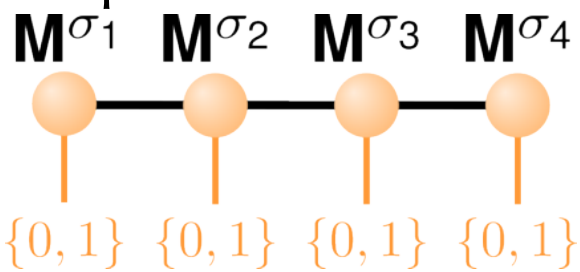
- Graphical notation



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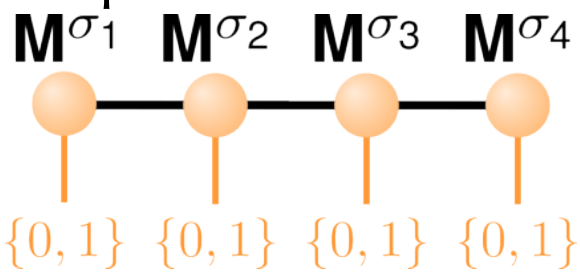

- DMRG: Variational ground state search: Optimize $\mathbf{M}^{\sigma_i}$ one by one

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TD-DMRG in a nutshell

1. Apply time-dependent variational principle (TDVP) to MPS ansatz[1]

$$\left\langle \frac{\partial \Psi}{\partial \mathbf{M}^{\sigma_i}} \middle| \hat{H} - \mathrm{i}\frac{\partial}{\partial t} \middle| \Psi \right\rangle = 0 \quad \text{for all } \mathbf{M}^{\sigma_i}$$

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[2] H. R. Larsson, *Mol. Phys.*, 2024, **122**, e2306881.

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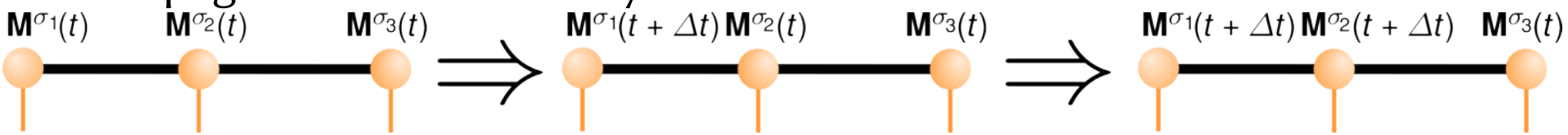
2. Apply Lie-Trotter splitting to propagator in MPS form
3. Propagate each $\mathbf{M}^{\sigma_i}$ one by one



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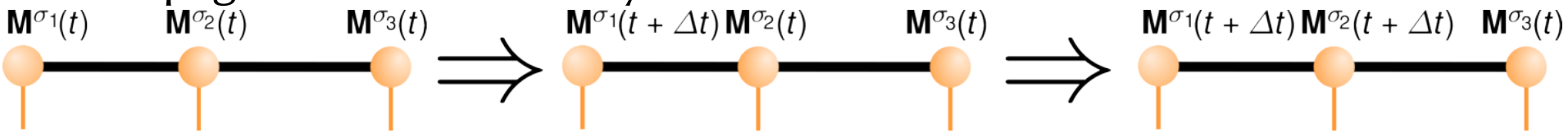

- Quasi-identical to multilayer multi-configuration time-dependent Hartree (ML-MCTDH) method[2]

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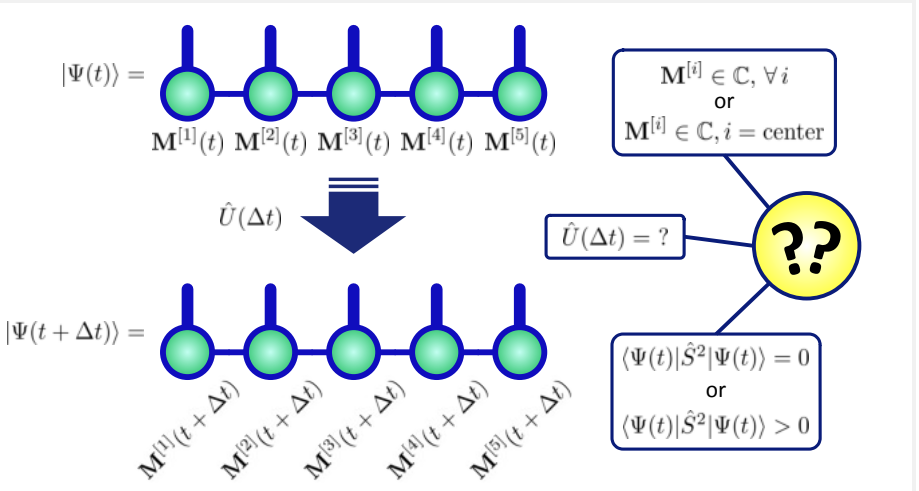
TD-DMRG in practice

Typical questions

- Which DMRG code?
- All $\mathbf{M}^{\sigma_i}$ complex-valued or just one?
- Use faster approximations of TDVP?
- How to deal with doublet states?
- How to select orbitals?
- How to choose orbital shape?



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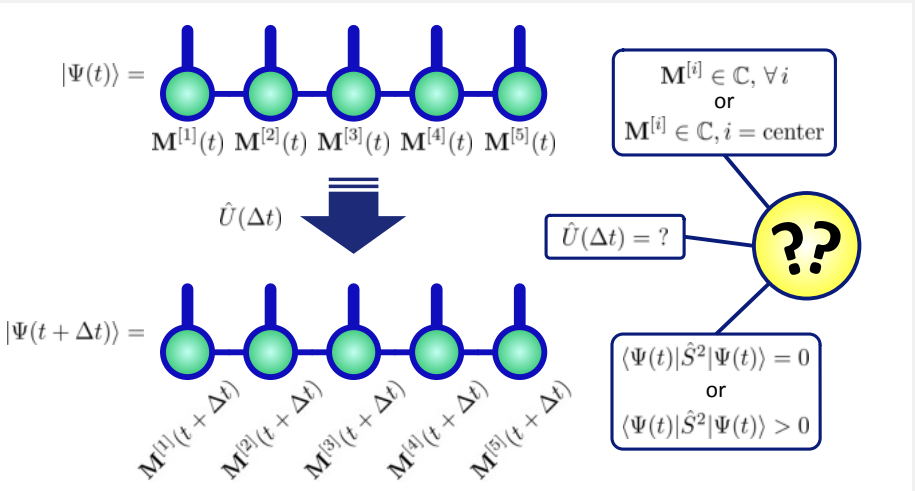

Our answers

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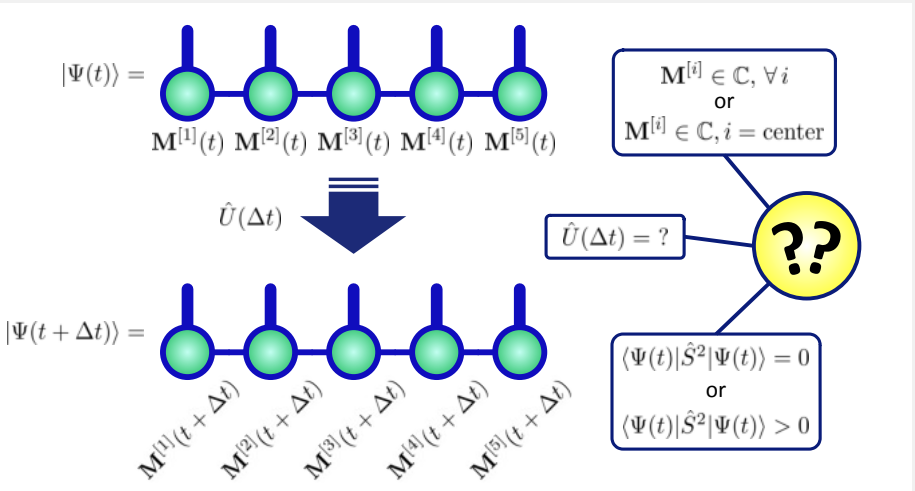

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- Fast code optimized for molecular electronic structure[1]
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- Wisdom from ground-state DMRG not always transferable to TD-DMRG

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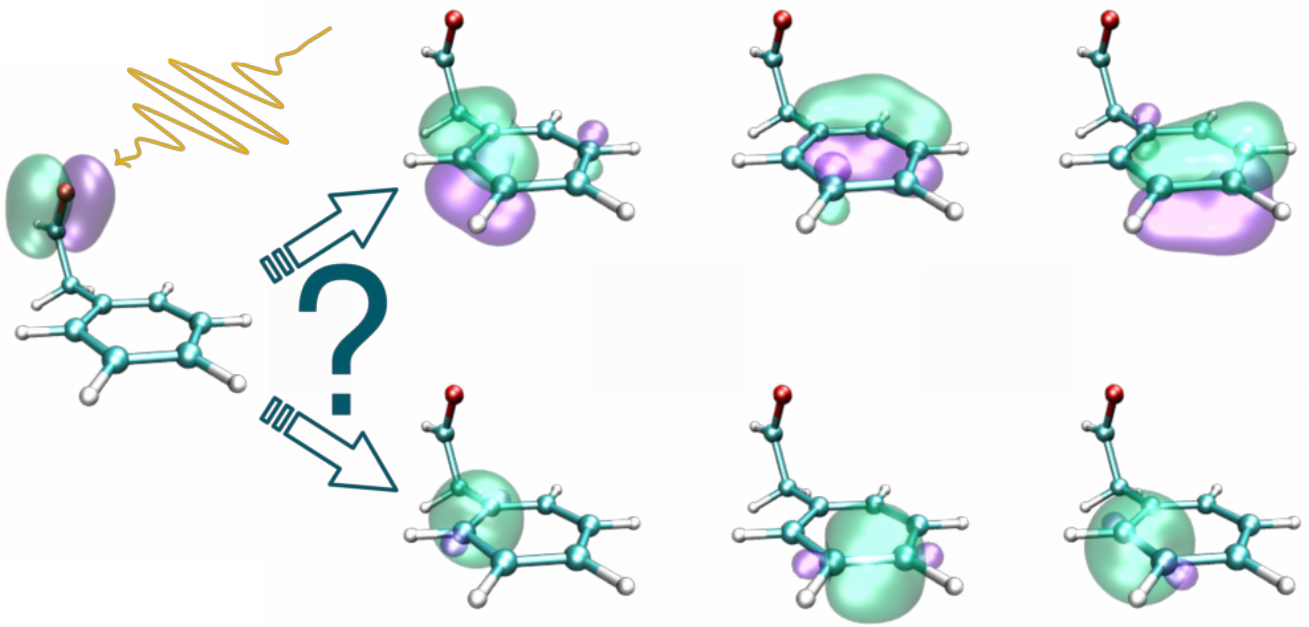
How will the hole migrate into the ring?



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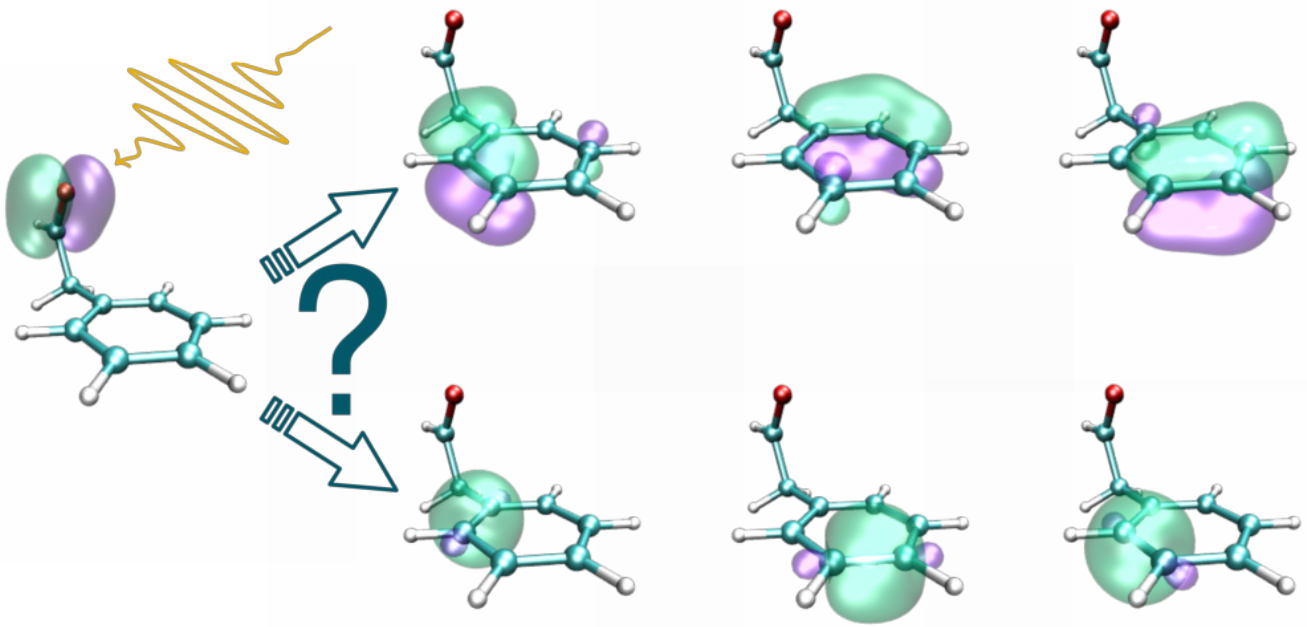


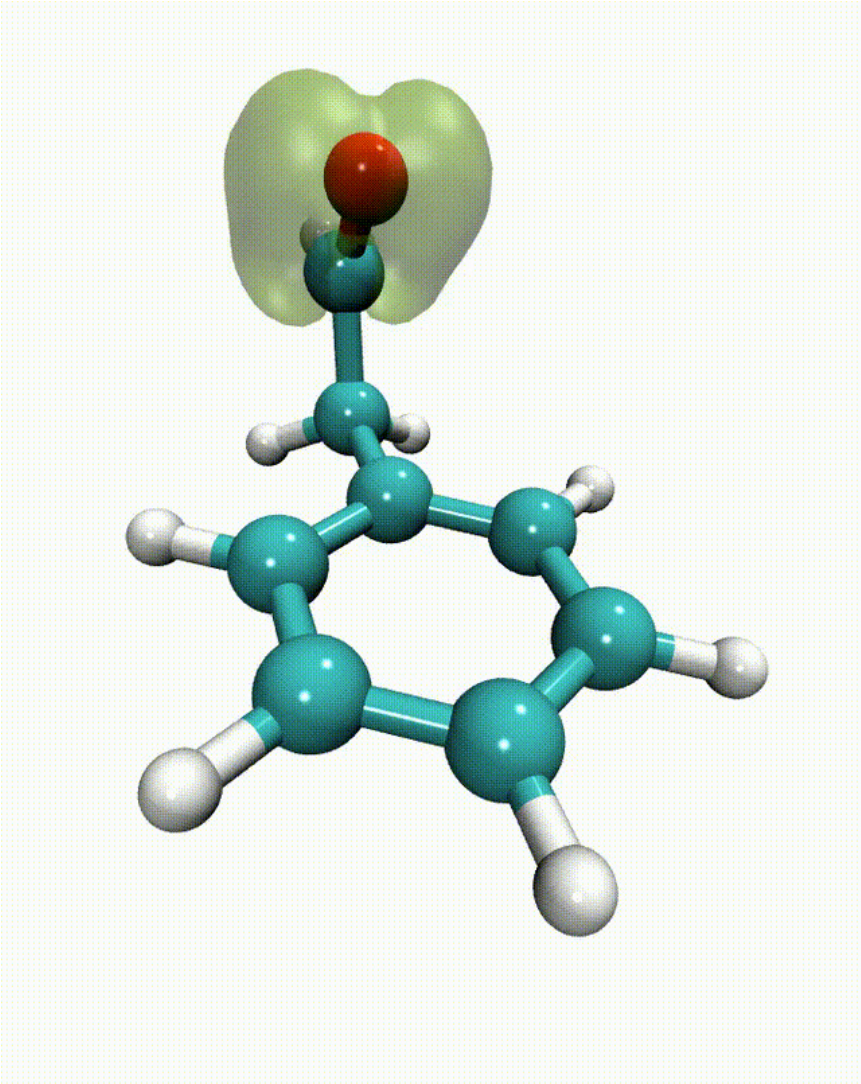
- phenyl π ring:

- phenyl σ ring:

- both:

Simulating electron dynamics using the DMRG[1]

2 fs real-time DMRG dynamics after sudden ionization with
45 fully correlated electrons and 50 spatial orbitals (complete active space)



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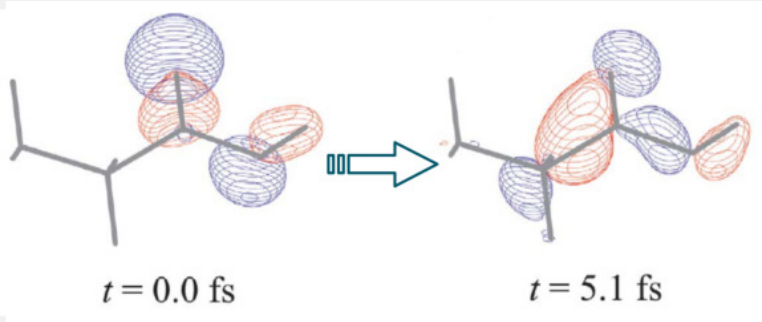
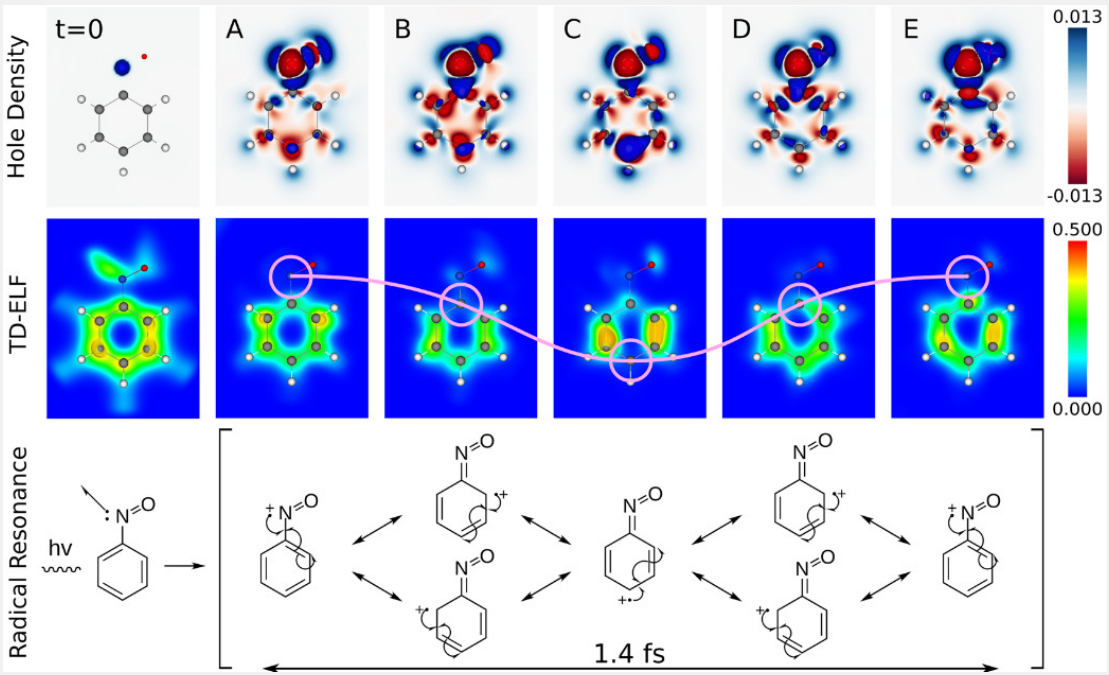
How can we understand charge migration dynamics?

Natural charge orbitals: Diagonalize hole density[1]



- Many time-dependent orbitals
- Complex shape
- Complex-valued

Electron localization function[2]



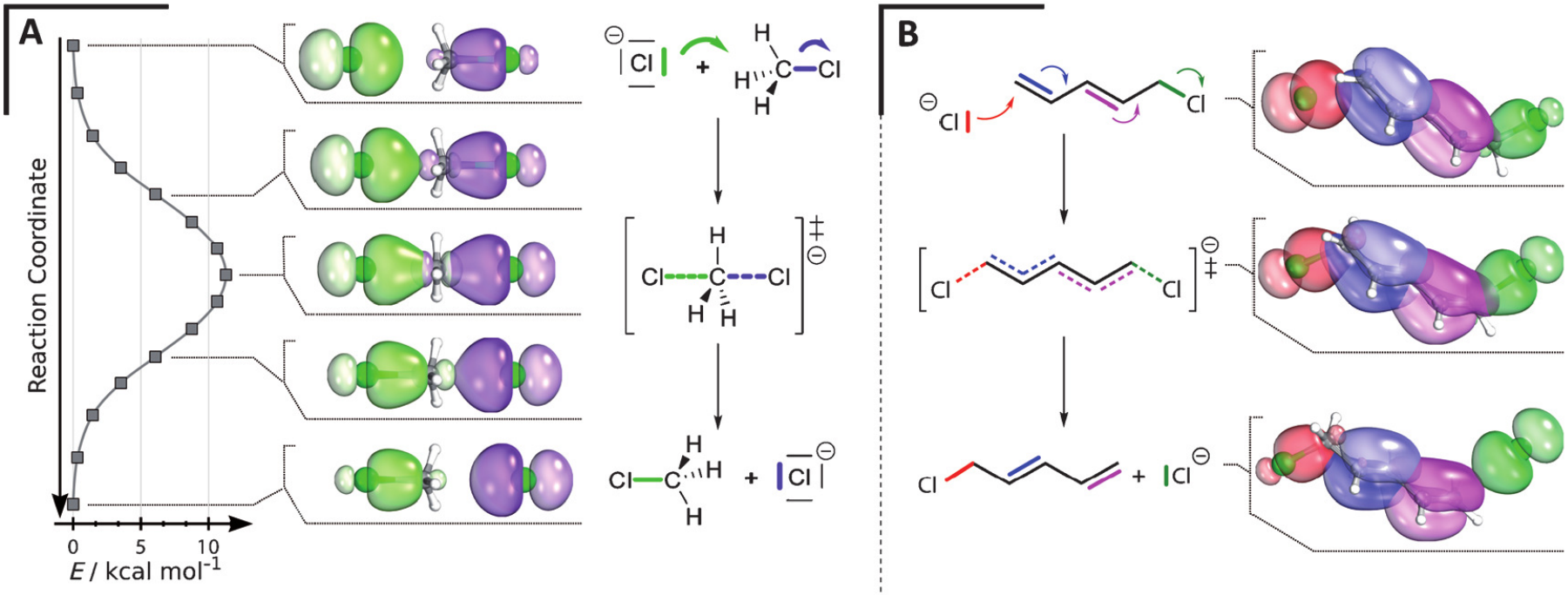
- Based on local kinetic energy density
- No insights from orbitals
- Not easy to analyze superpositions

[1] A. I. Kuleff et al., *J. Chem. Phys.*, 2005, **123**, 044111

[2] A. Bruner et al., *J. Phys. Chem. Lett.*, 2017, **8**, 3991–3996

Localized orbitals can describe chemistry

- Intrinsic bond orbitals (IBOs)[1]



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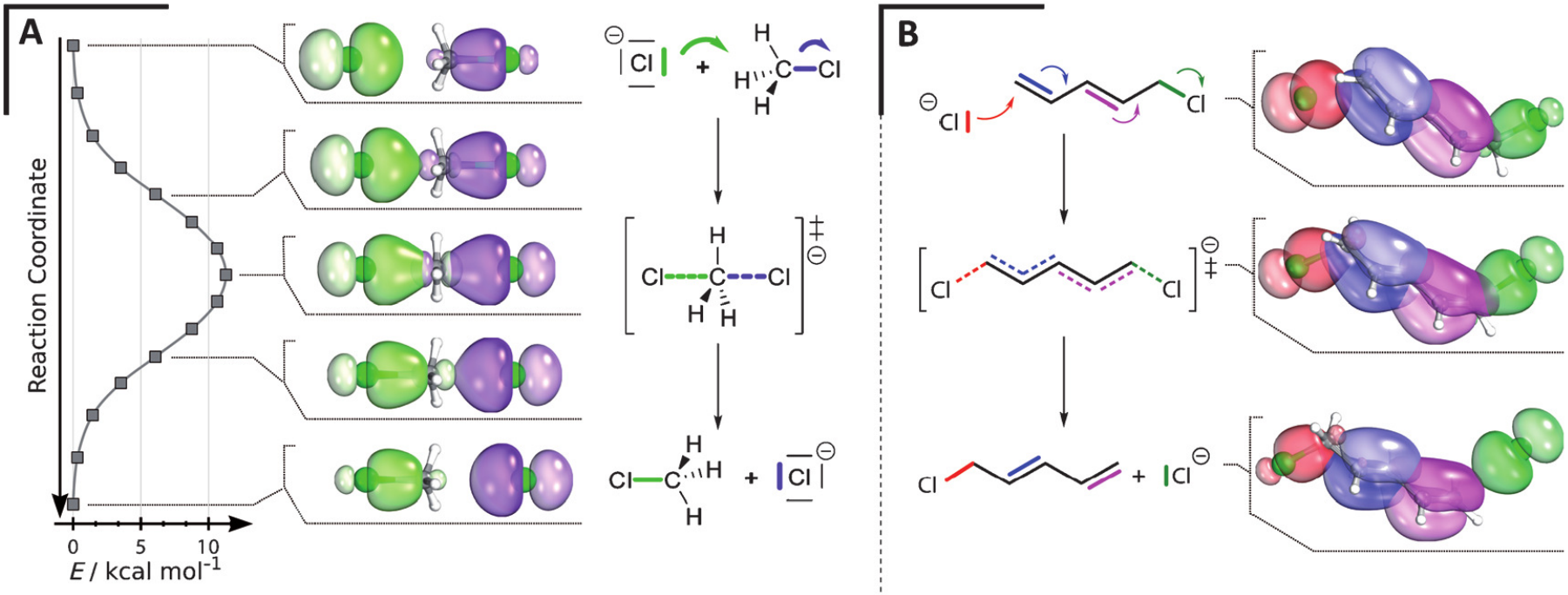

- Antibonding IBO-like orbitals needed for excited states/dynamics[2]

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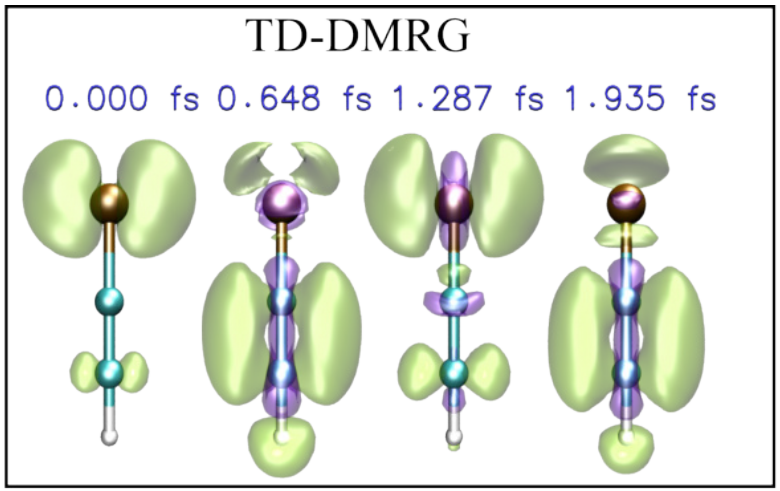
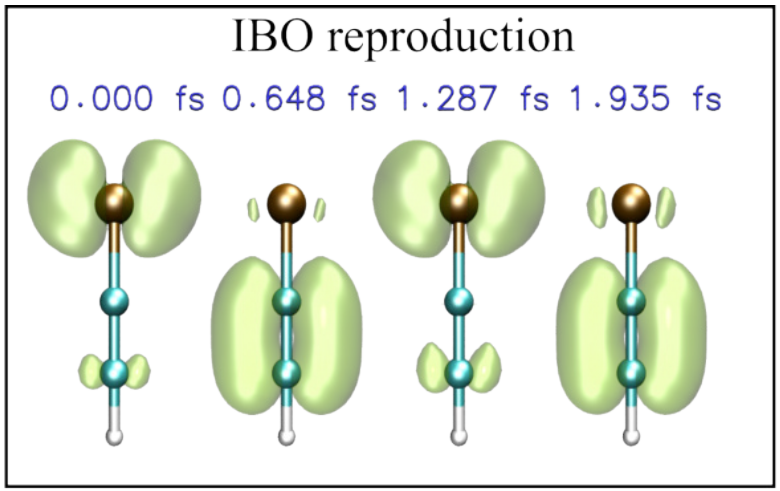
Example: Chloroacetylene

- Project hole density $h(\mathbf{r}, t) = \rho_{\text{neutral}}(\mathbf{r}) - \rho_{\text{cation}}(\mathbf{r}, t)$ into smaller IBO space (# IBOs: convergence parameter)





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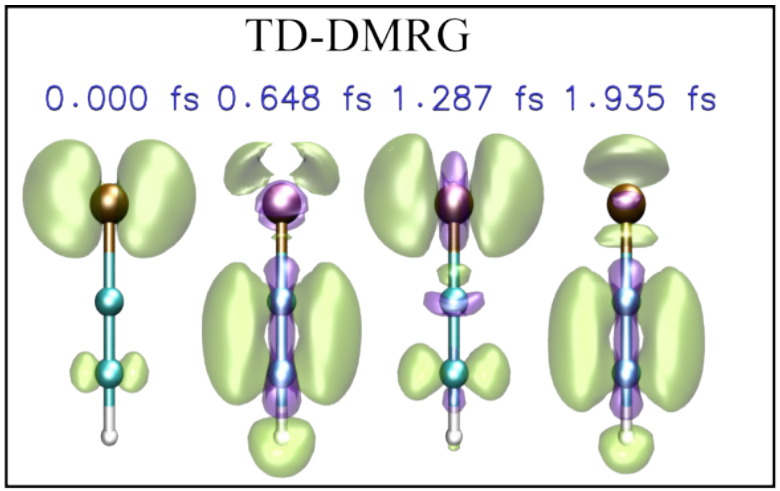
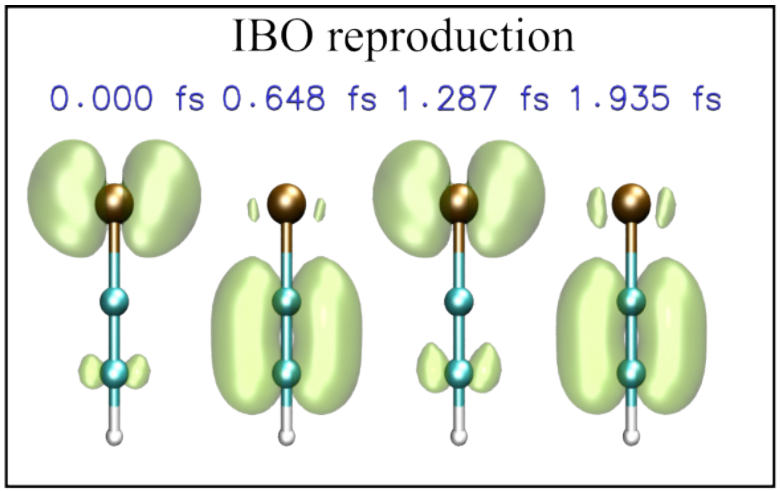
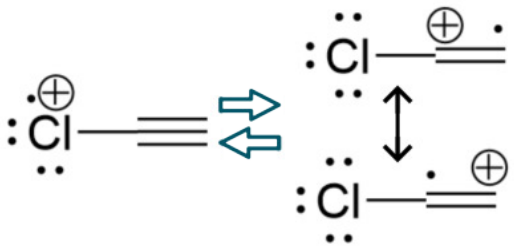
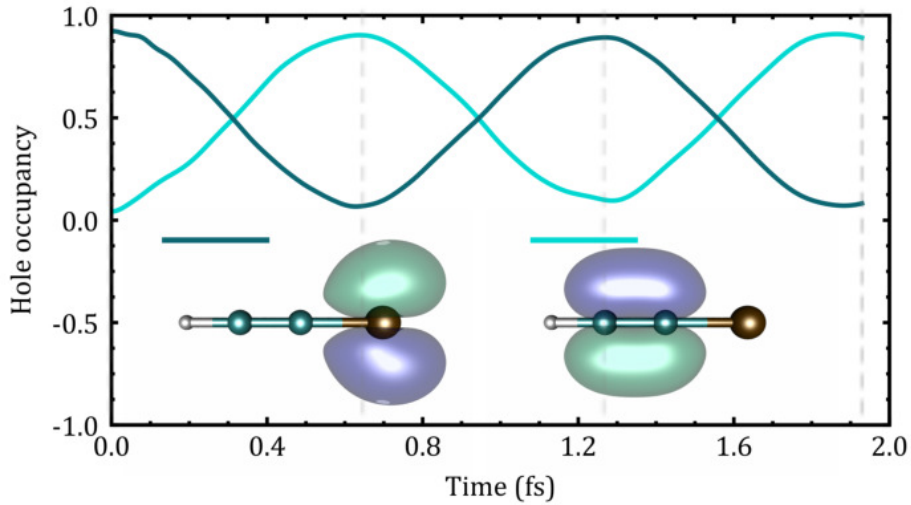




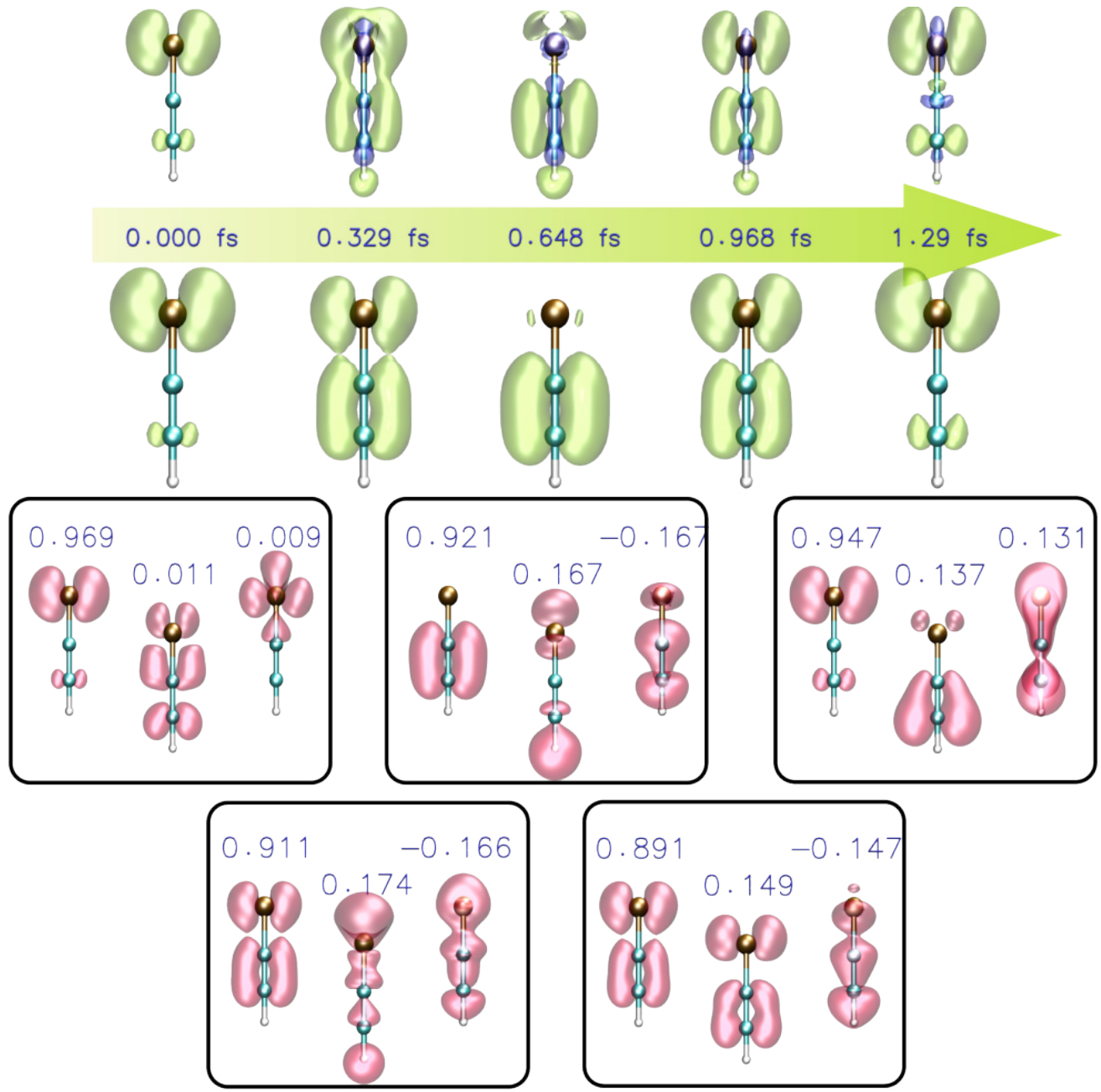
- Only use two IBOs to extract main mechanism:





- $|\Psi(t)\rangle \approx a(t)|\Psi_1\rangle + b(t)|\Psi_2\rangle$

Natural charge orbitals are not helpful here



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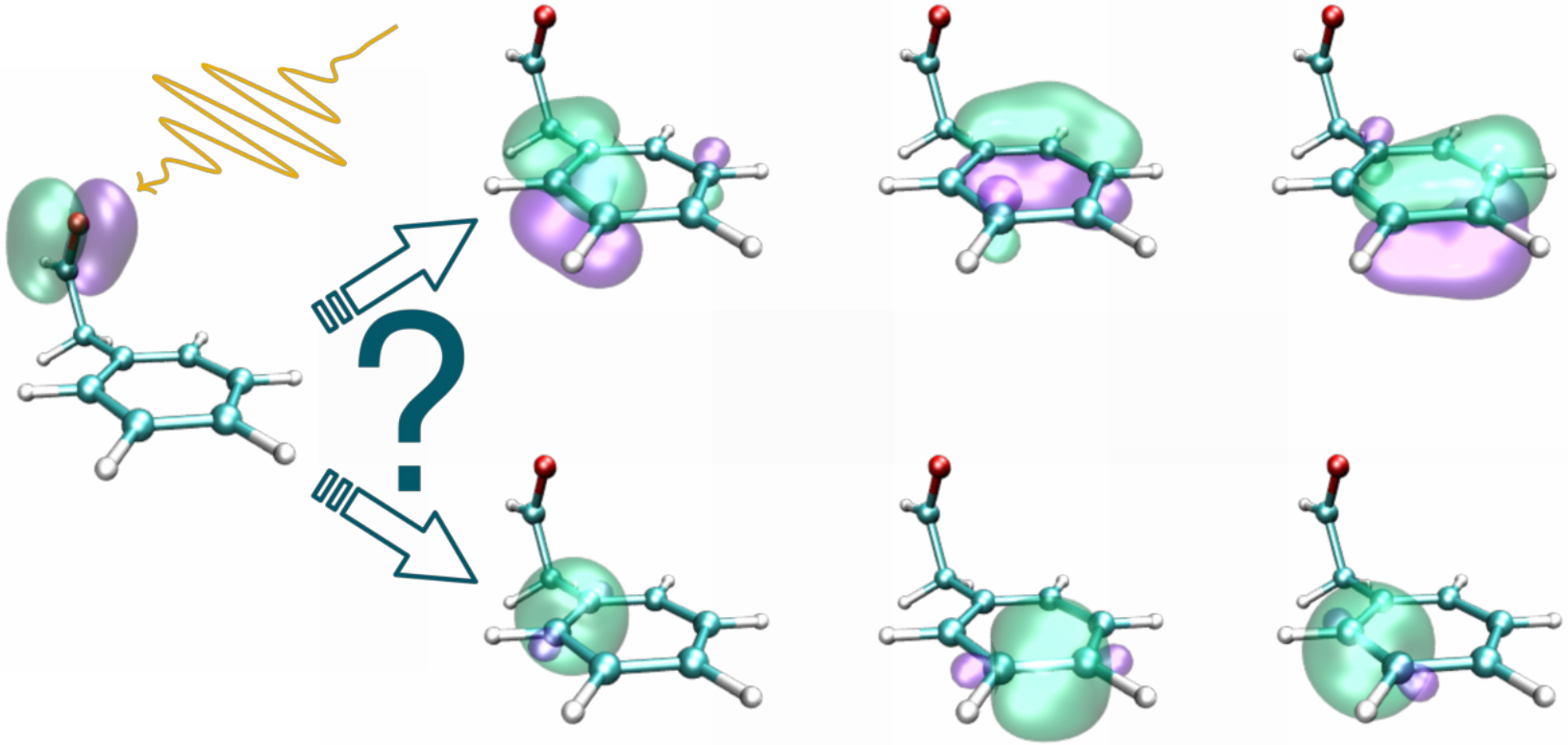
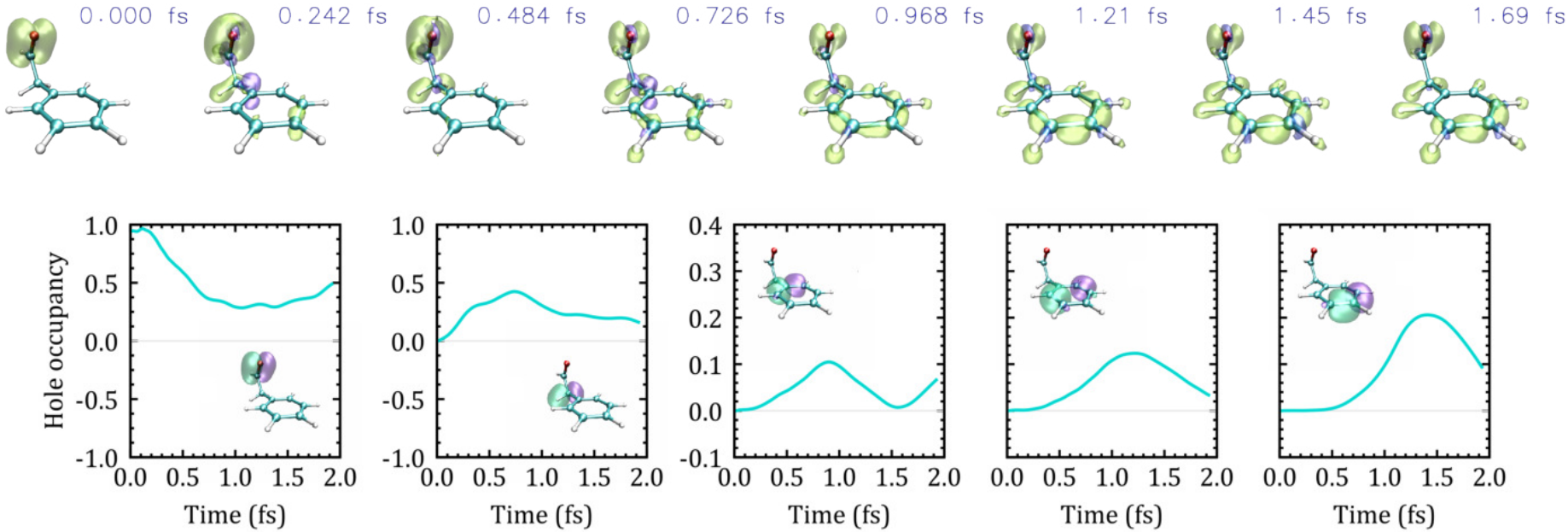


Initial C=O π hole in phenylacetaldehyde



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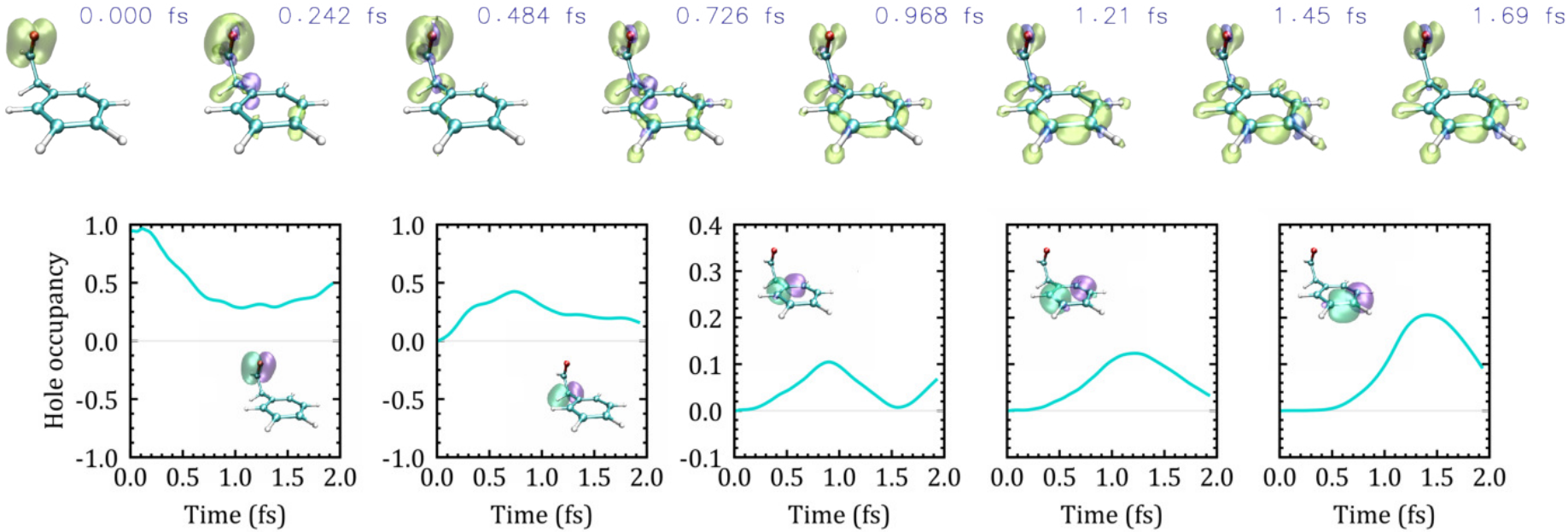
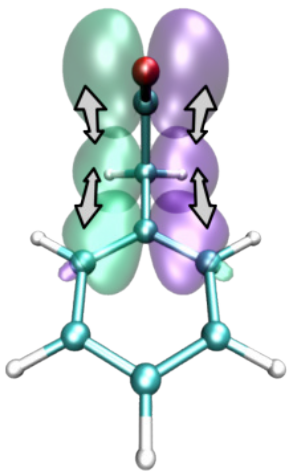
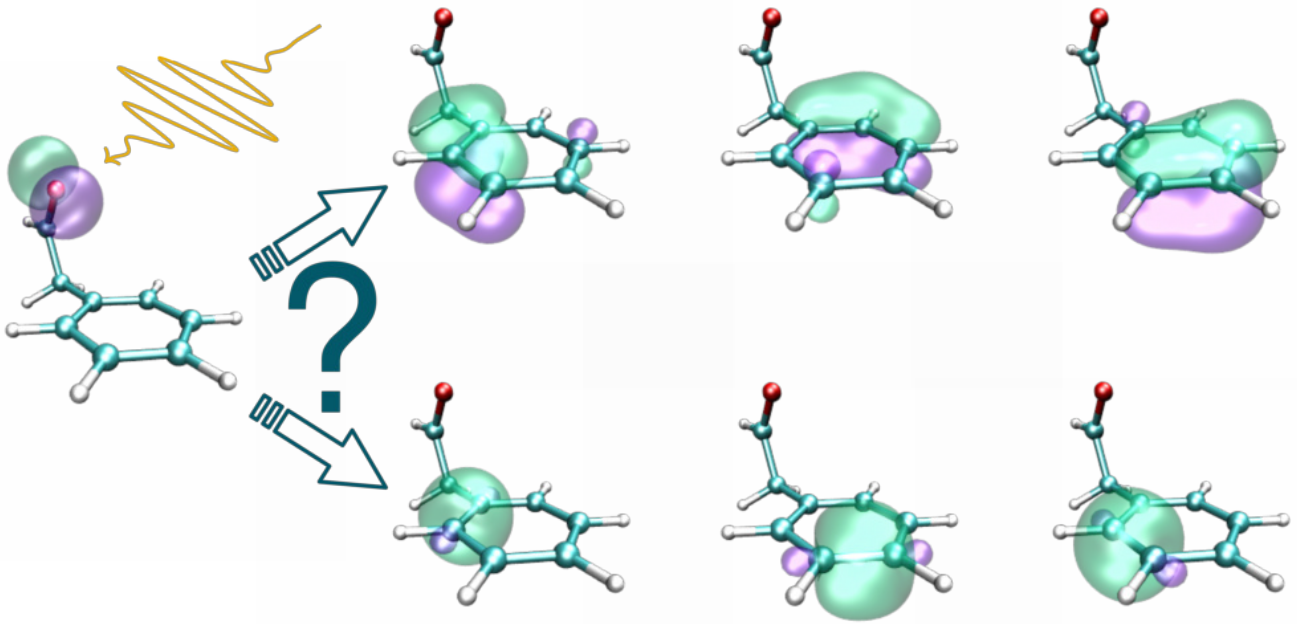


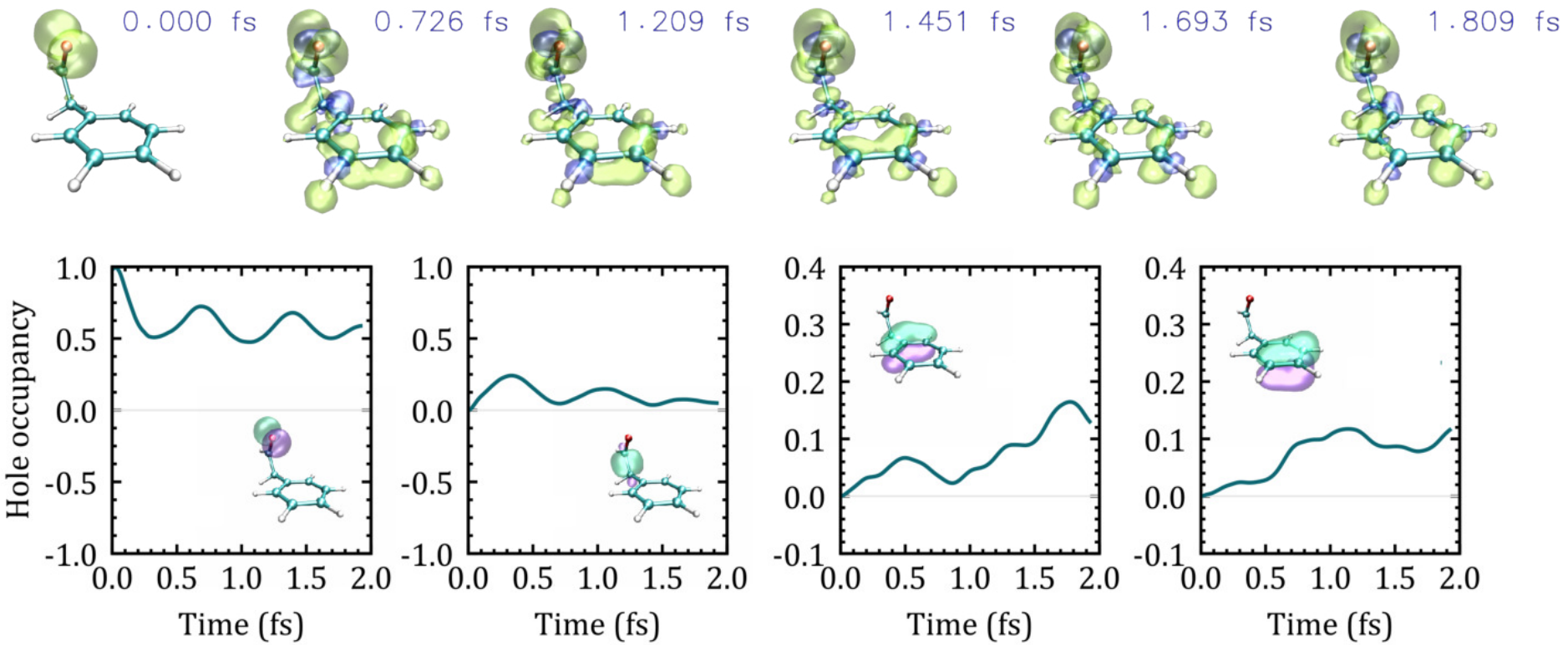
Hyperconjugation/through-space interactions



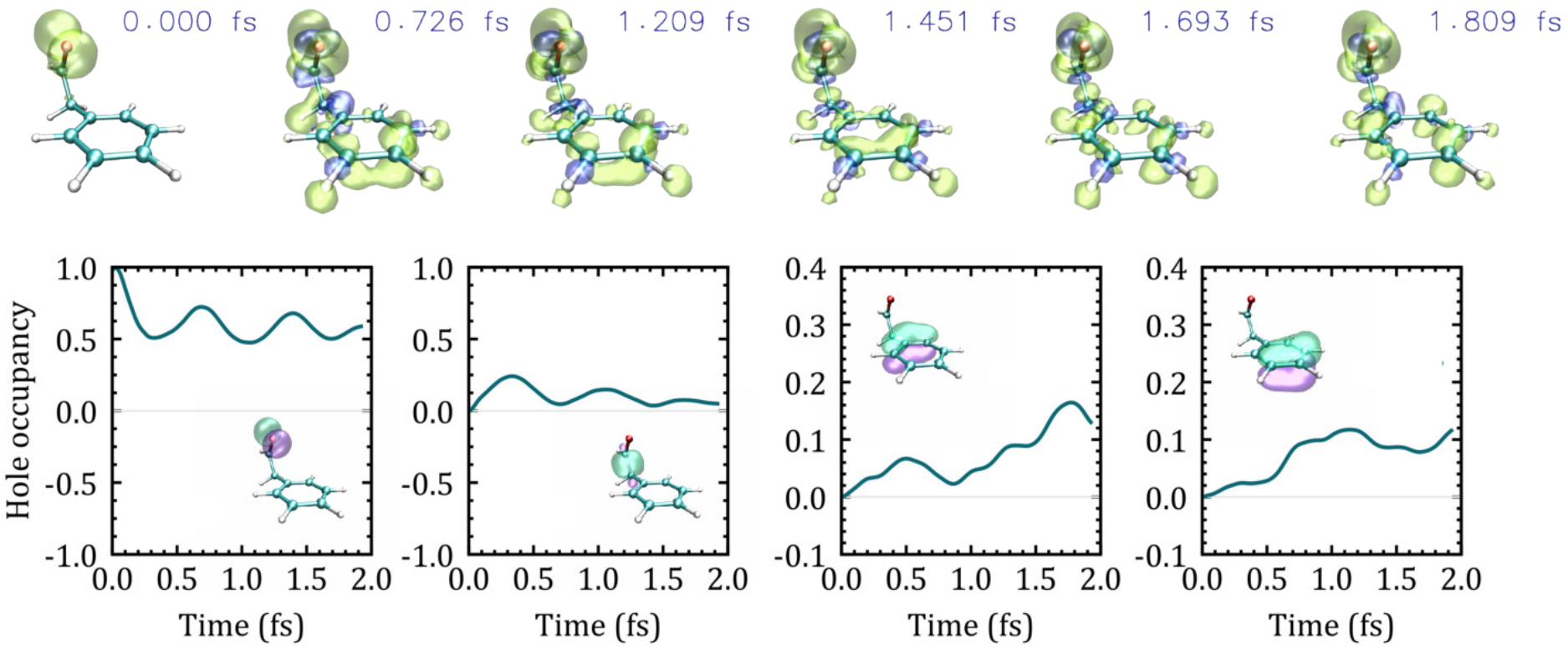
How will the hole migrate into the ring?



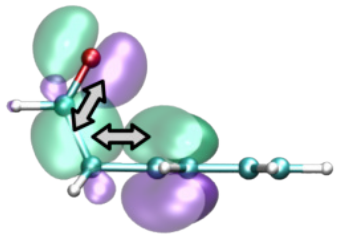
Initial C=O *p* hole in phenylacetaldehyde



Initial C=O *p* hole in phenylacetaldehyde



main mechanism (next to others): through-space interactions



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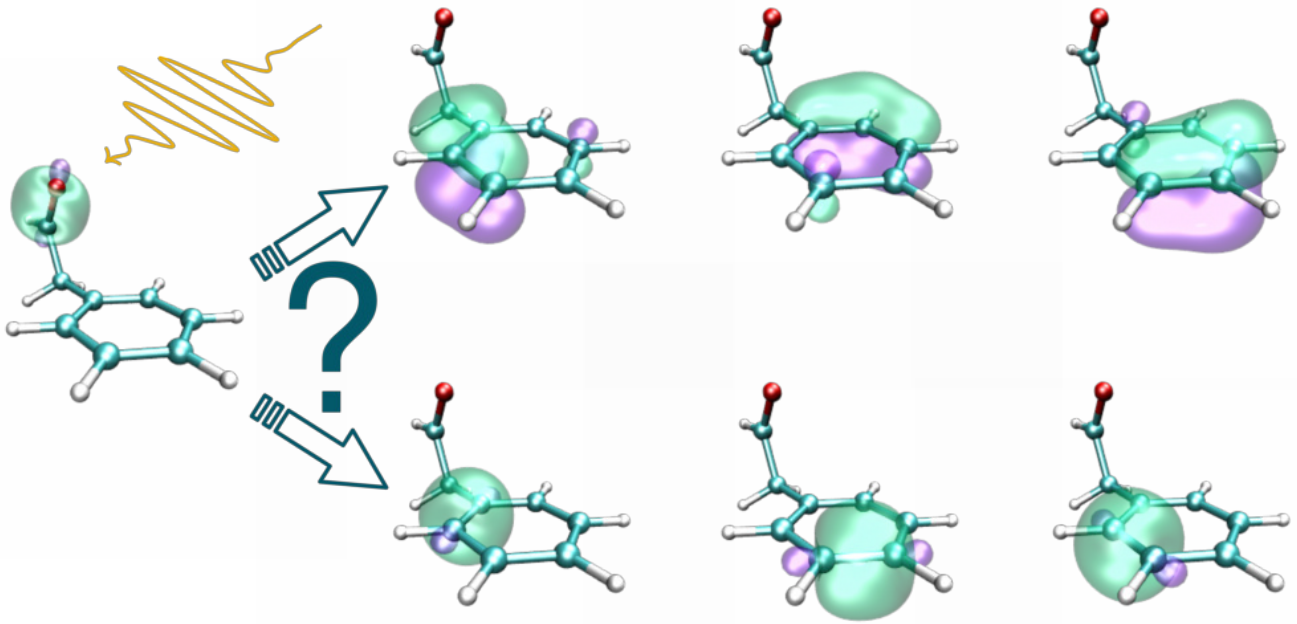
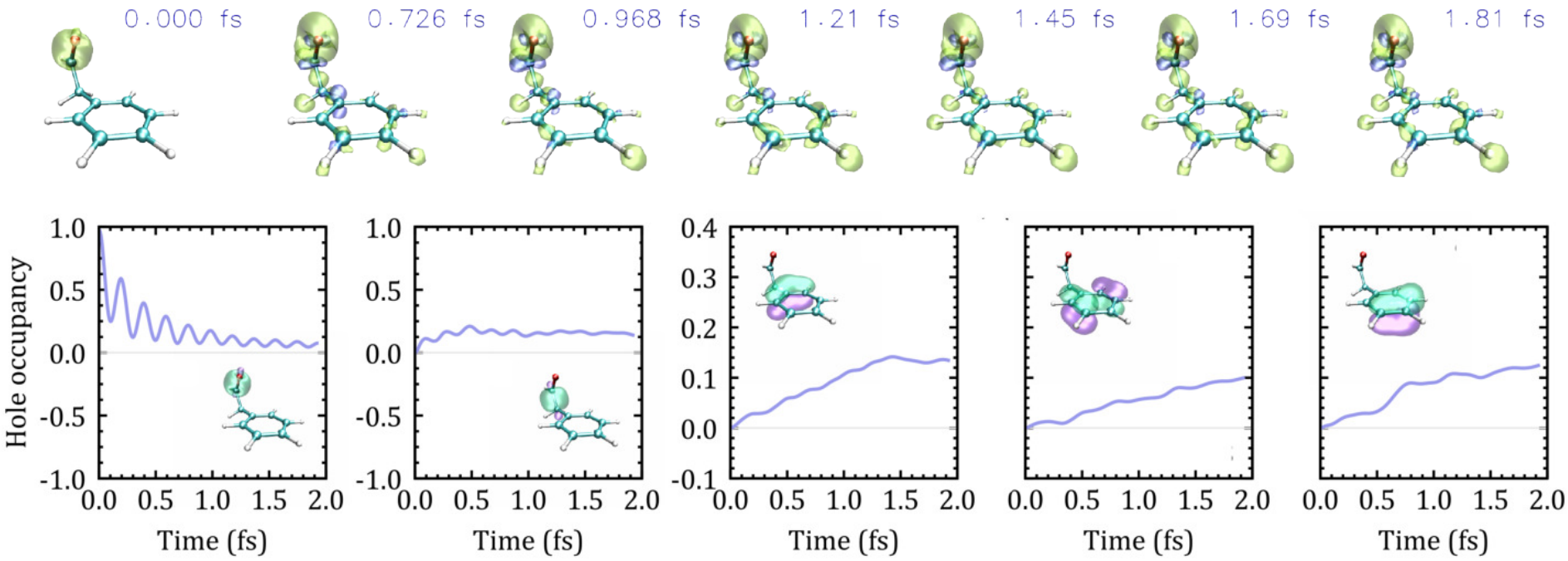
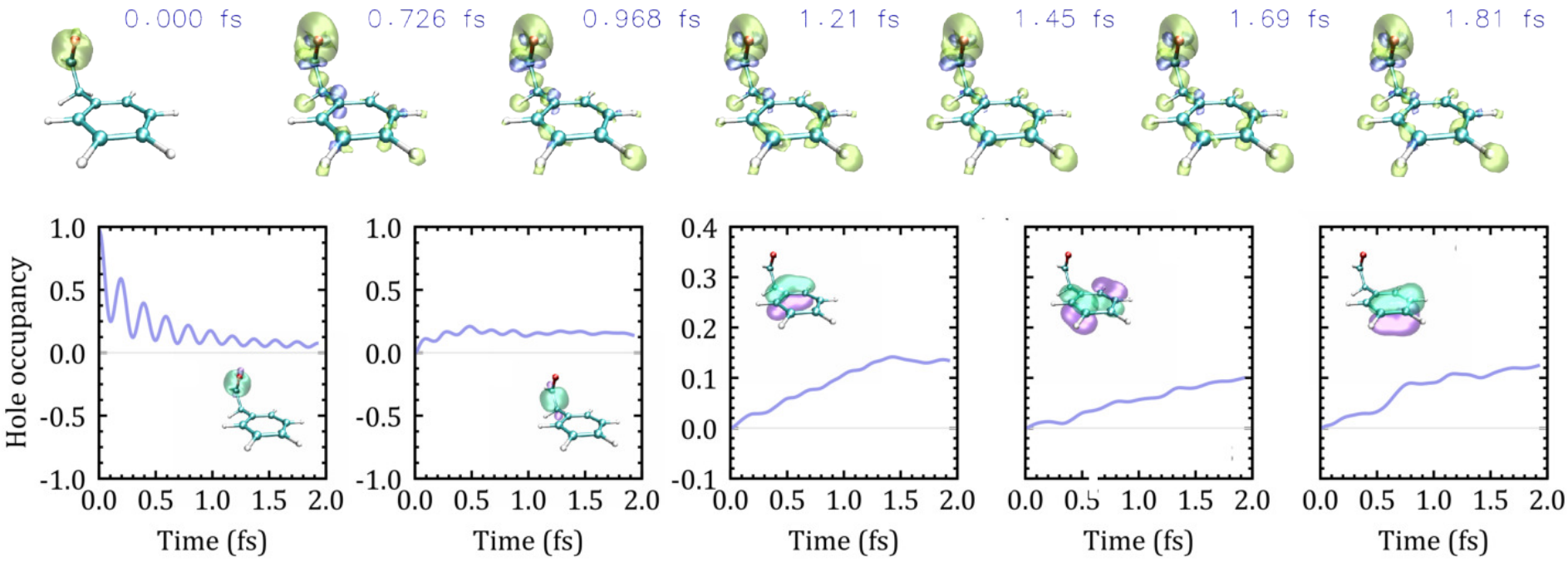


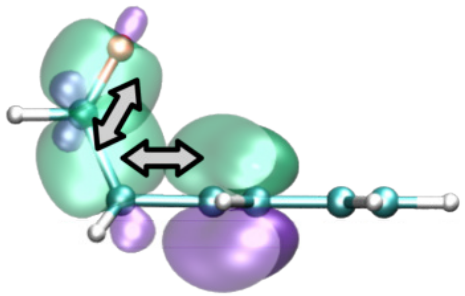
Initial C=O σ hole in phenylacetaldehyde I



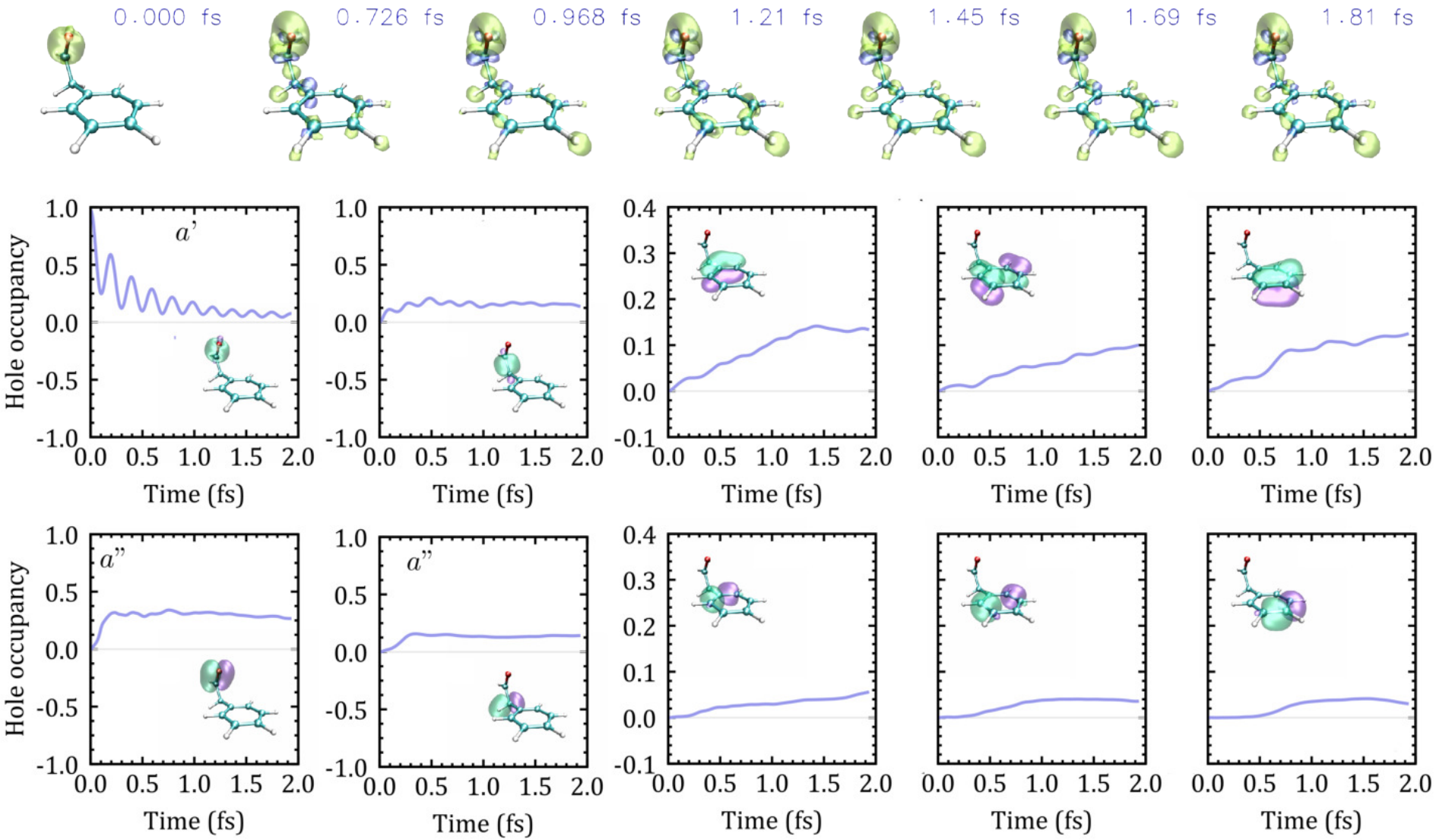
Initial C=O σ hole in phenylacetaldehyde I



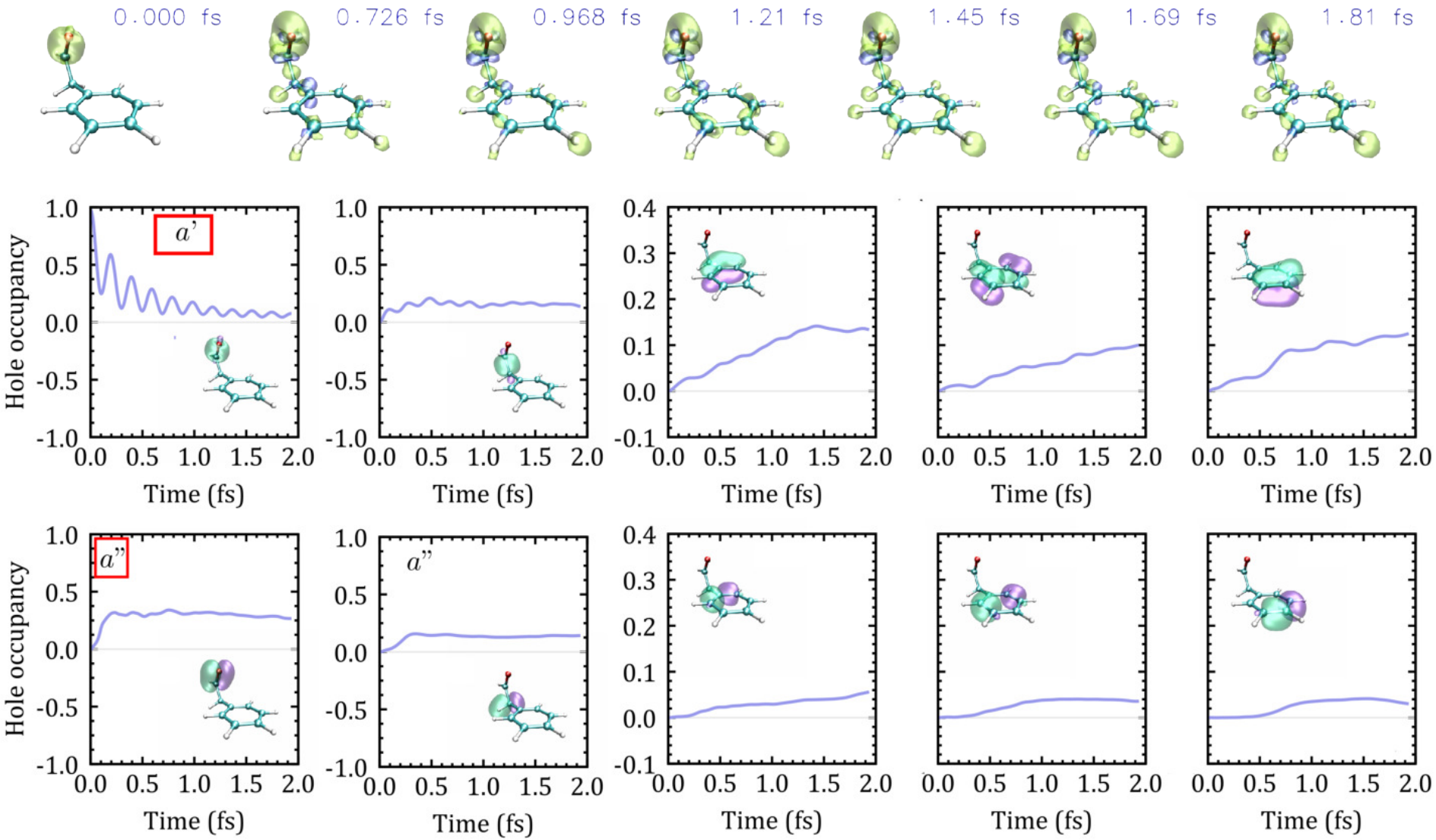
first mechanism: through-space interactions



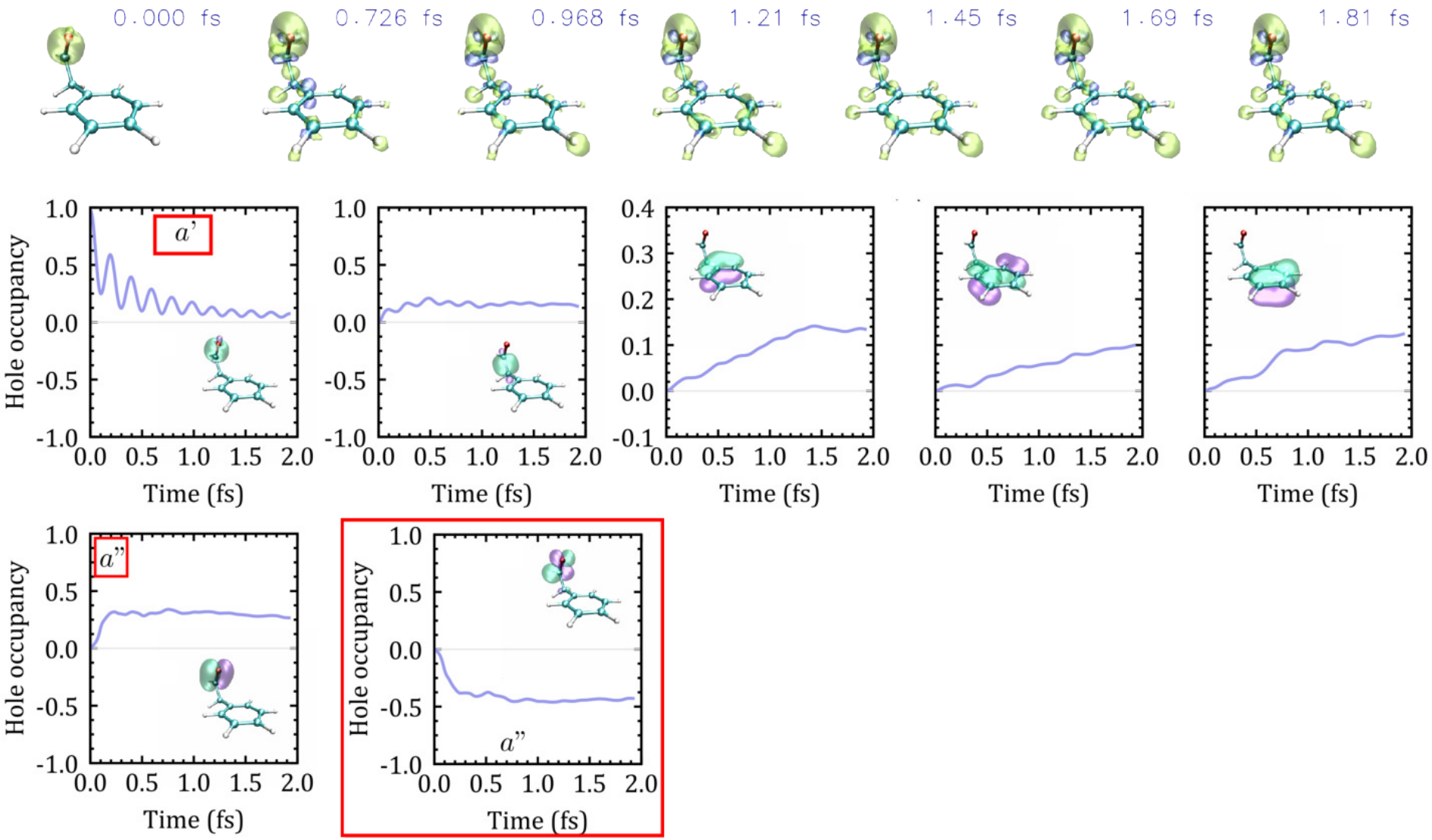
Initial C=O σ hole in phenylacetaldehyde II



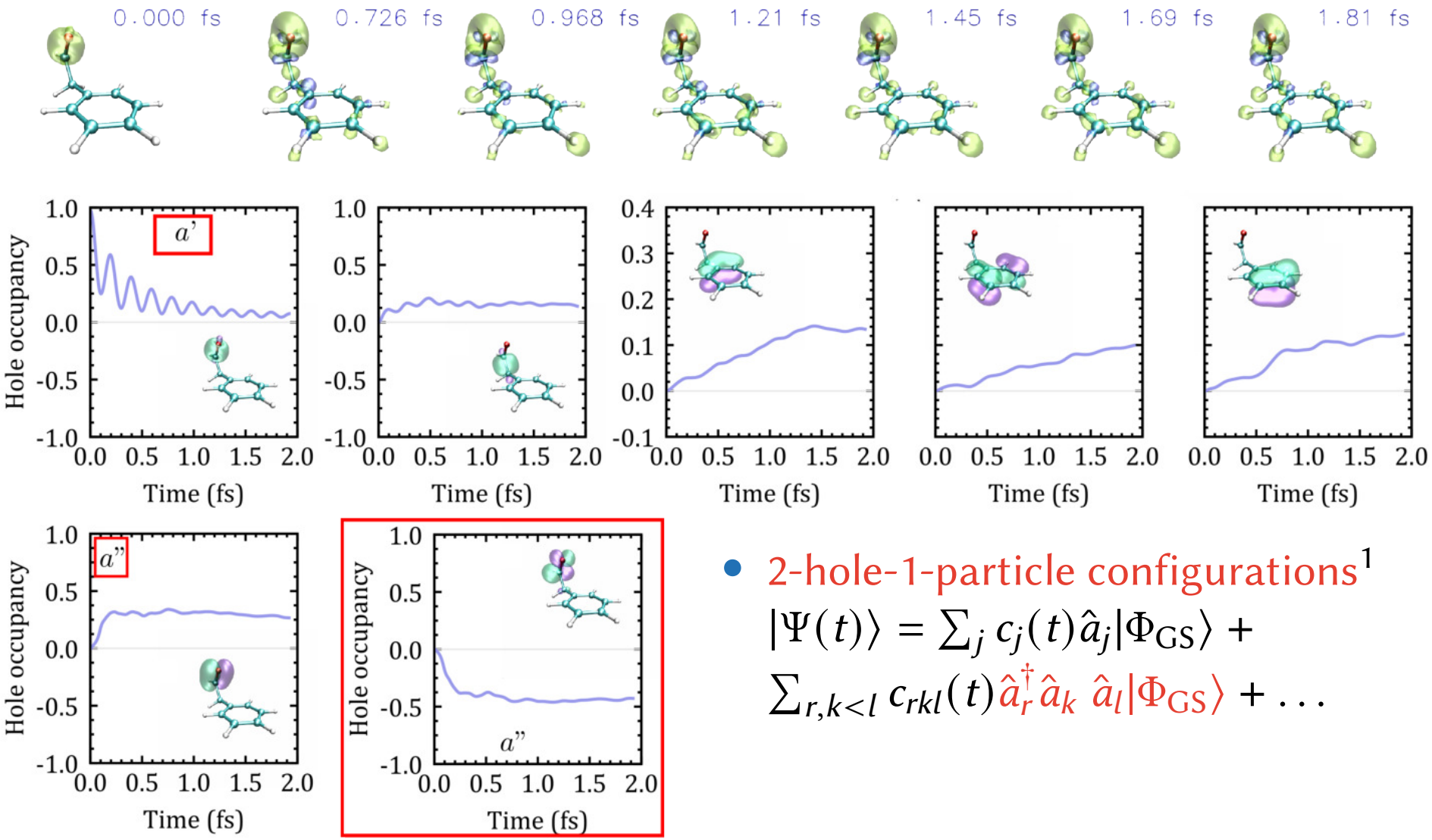
Initial C=O σ hole in phenylacetaldehyde II



Initial C=O σ hole in phenylacetaldehyde II



Initial C=O σ hole in phenylacetaldehyde II

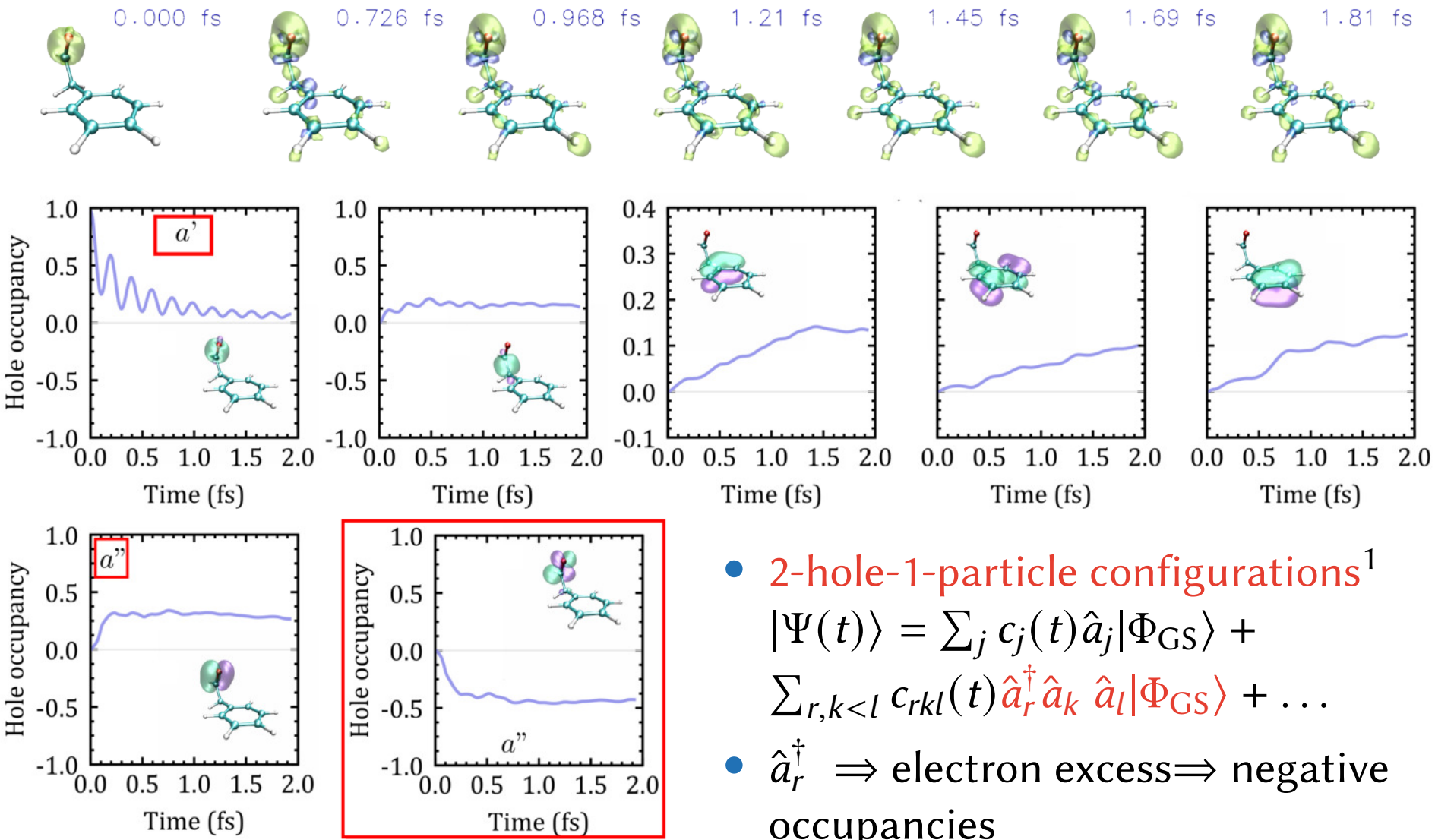


- 2-hole-1-particle configurations[1]

$$|\Psi(t)\rangle = \sum_j c_j(t)\hat{a}_j|\Phi_{GS}\rangle + \sum_{r,k<l} c_{rkl}(t)\hat{a}_r^\dagger \hat{a}_k\, \hat{a}_l|\Phi_{GS}\rangle + \ldots$$

[1] J. Breidbach and L. S. Cederbaum, *J. Chem. Phys.*, 2003, **118**, 3983–3996.

Initial C=O σ hole in phenylacetaldehyde II



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- $\hat{a}_r^\dagger \implies$ electron excess$\implies$ negative occupancies

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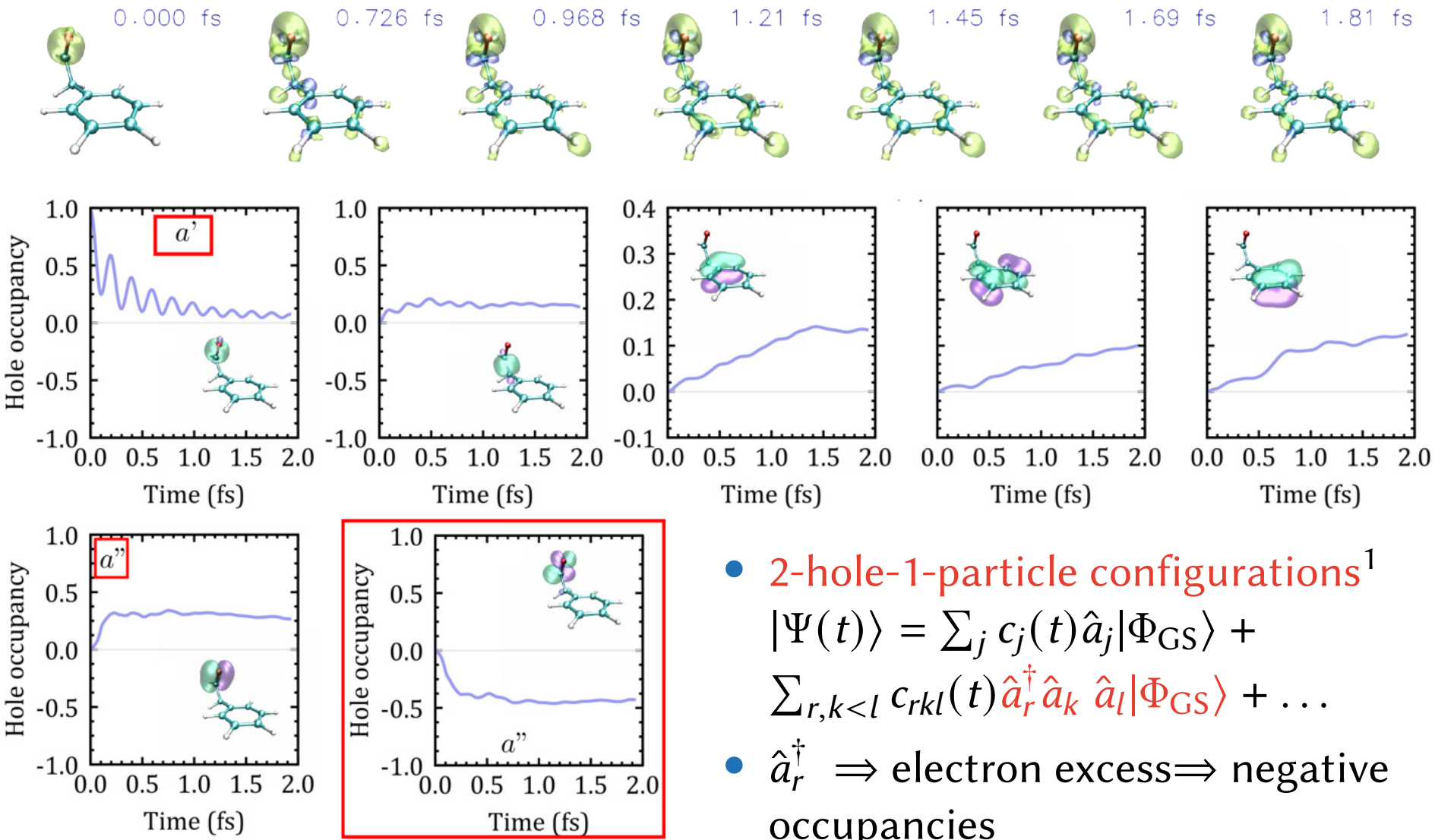

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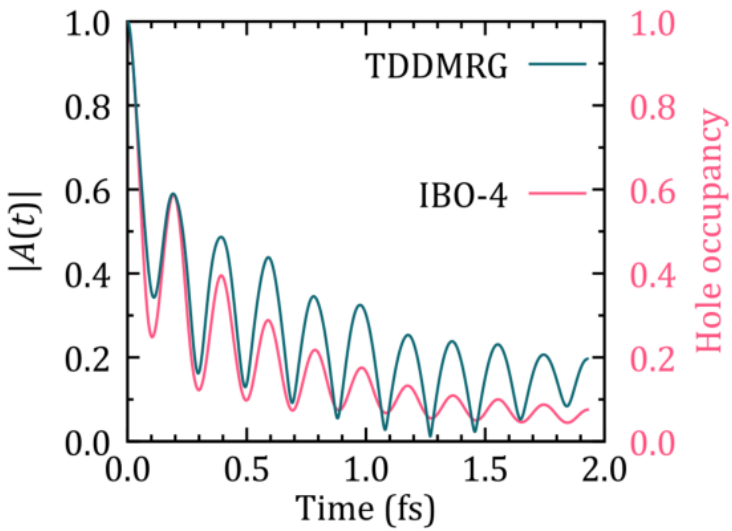
$\implies$ Different orbitals/irreps appear

[1] J. Breidbach and L. S. Cederbaum, *J. Chem. Phys.*, 2003, **118**, 3983–3996.

C=O σ hole leads to breakdown of the MO picture

- Quasi-exponential decay of autocorrelation $\langle \Psi(t=0) | \Psi(t) \rangle$



[1] H. Zhai, H. R. Larsson et al., *J. Chem. Phys.*, 2023, **159**, 234801; E. Ronca et al., *J. Chem. Theory Comput.*, 2017, **13**, 5560–5571

[2] J. Breidbach and L. S. Cederbaum, *J. Chem. Phys.*, 2003, **118**, 3983–3996

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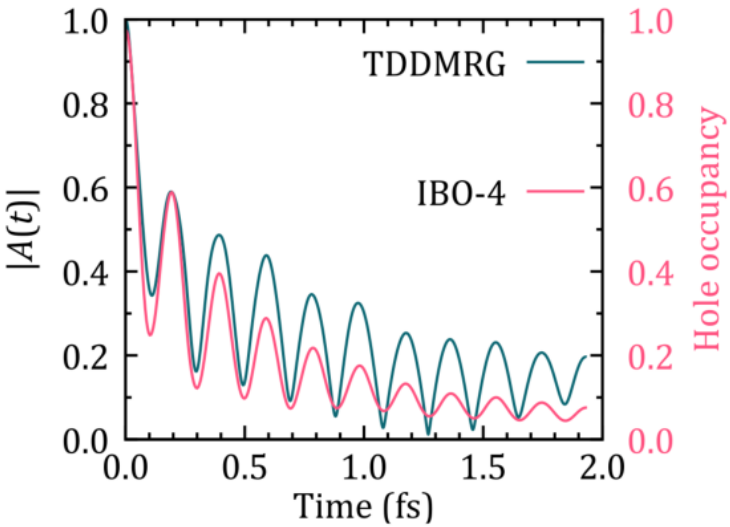
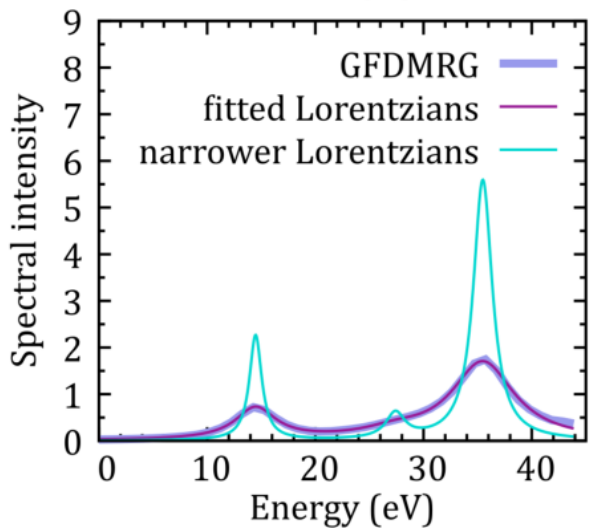
- Green's-function DMRG for ionization spectrum[1]
- Quasi-continuum $\Rightarrow$ many 2h1p configs





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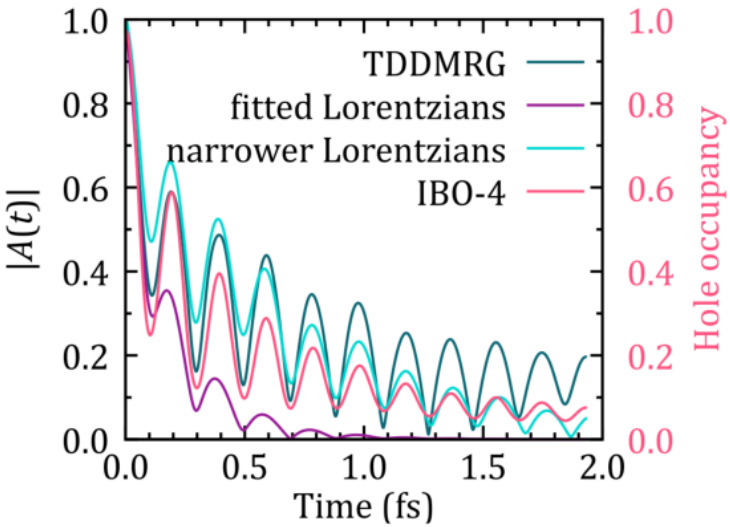

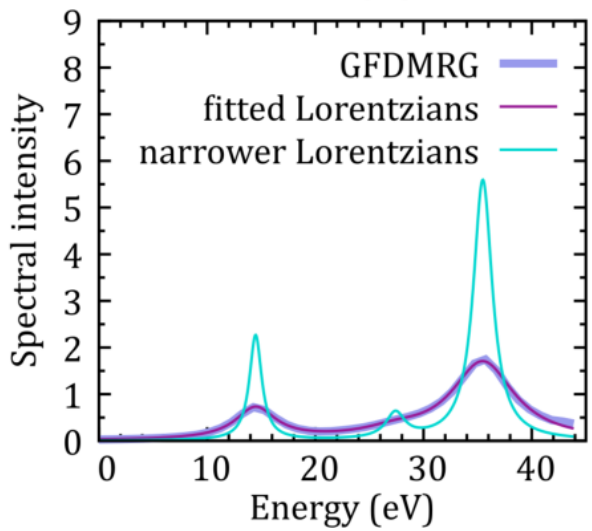

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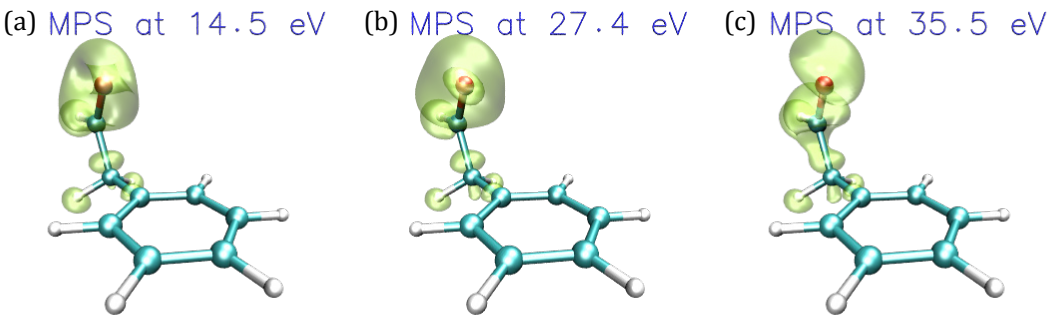

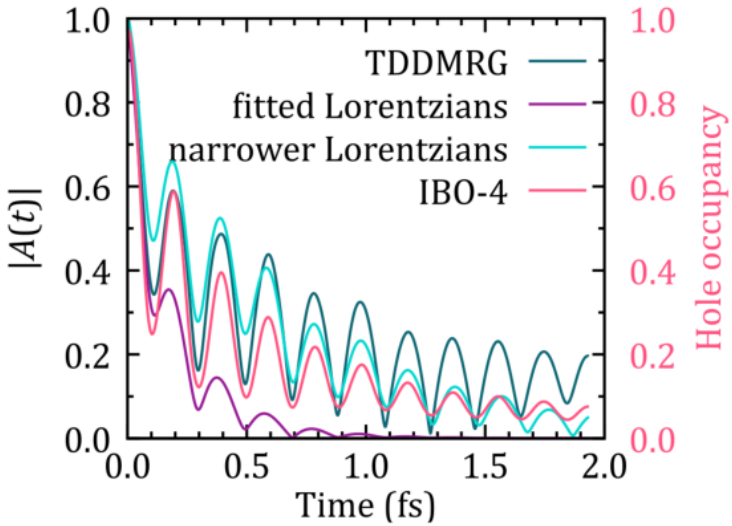

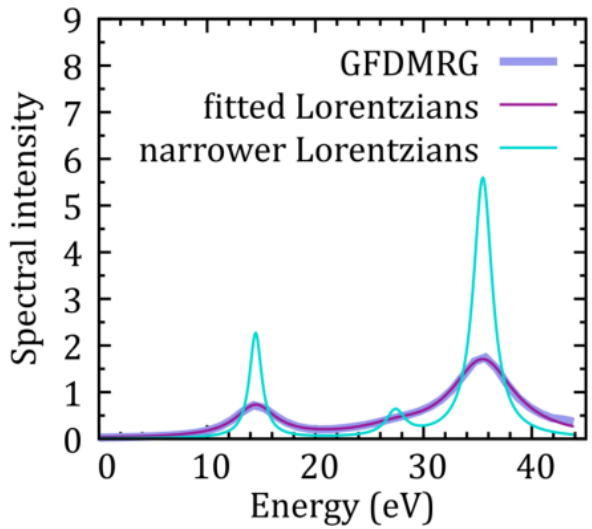

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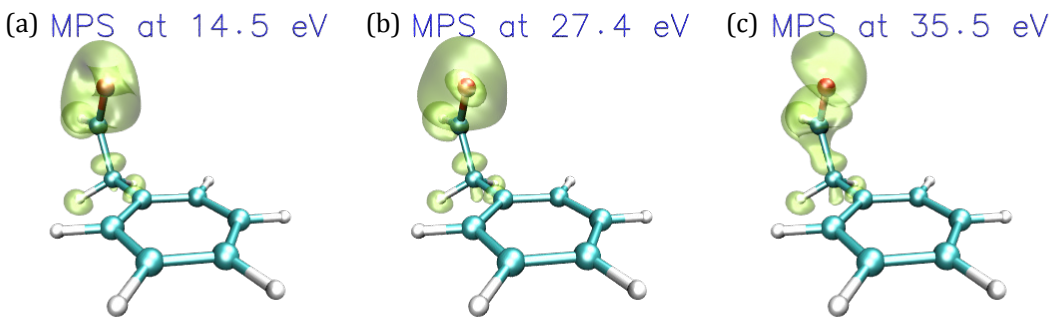
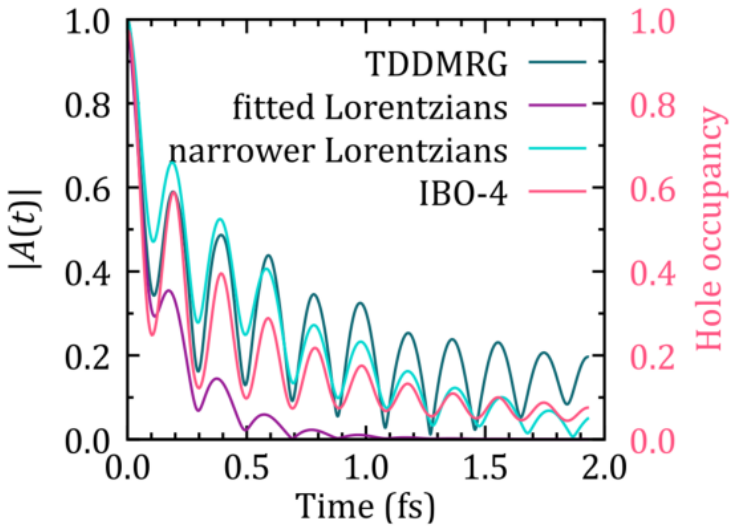
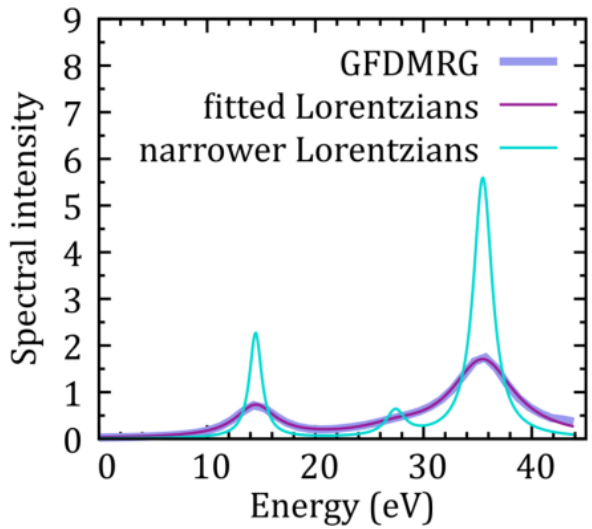
- Green's-function DMRG for ionization spectrum[1]
- Quasi-continuum $\Rightarrow$ many 2h1p configs
- inner-valence ionization: "breakdown of the MO picture"[2]
- IBO analysis still possible







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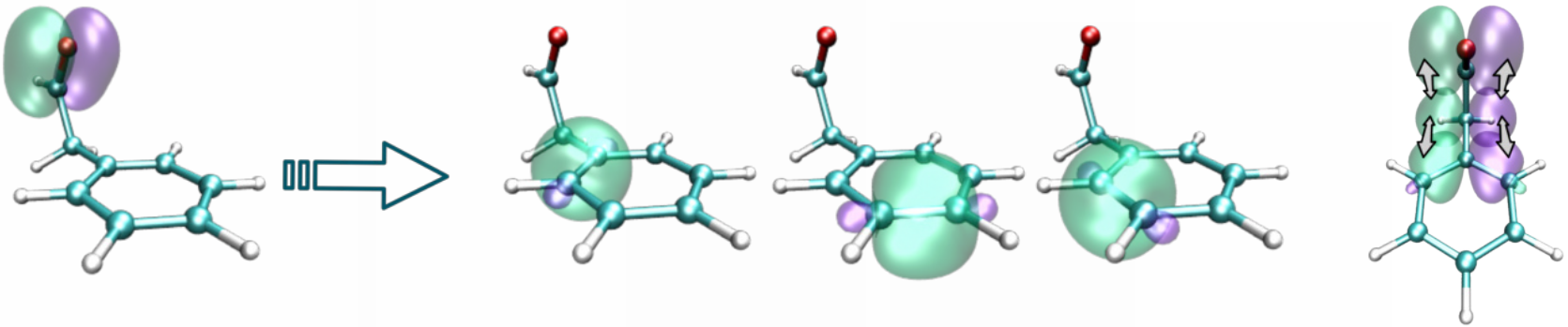
Phenylacetaldehyde: Summary



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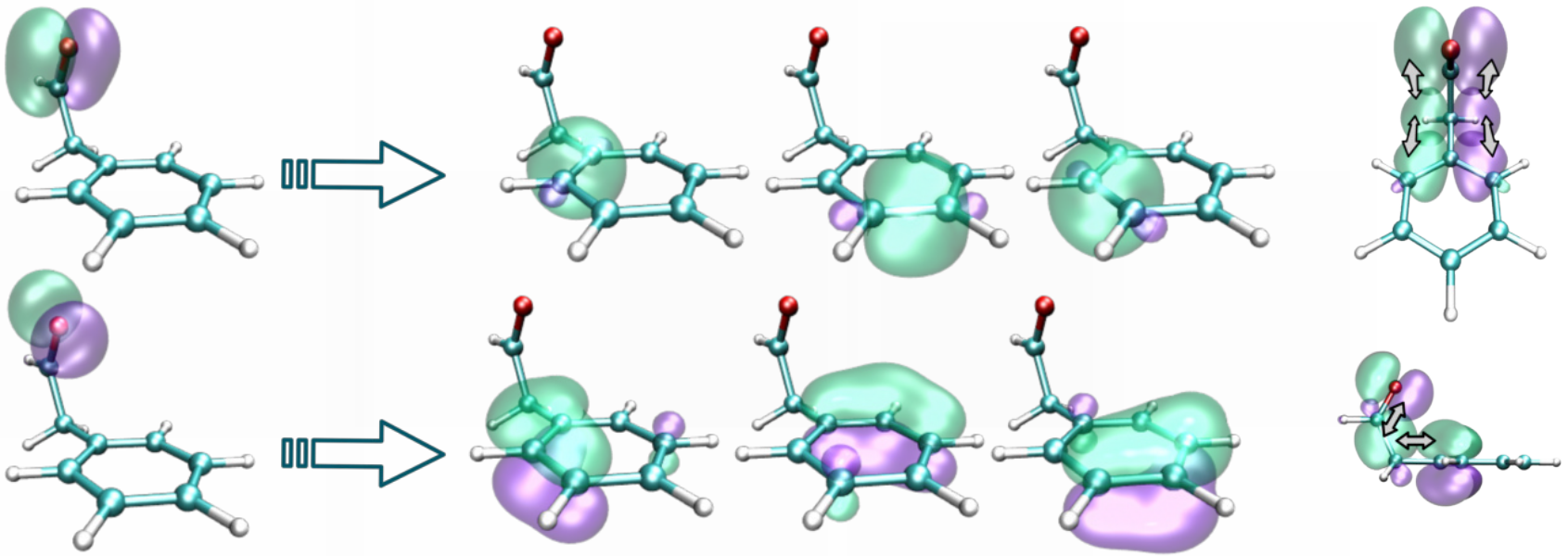
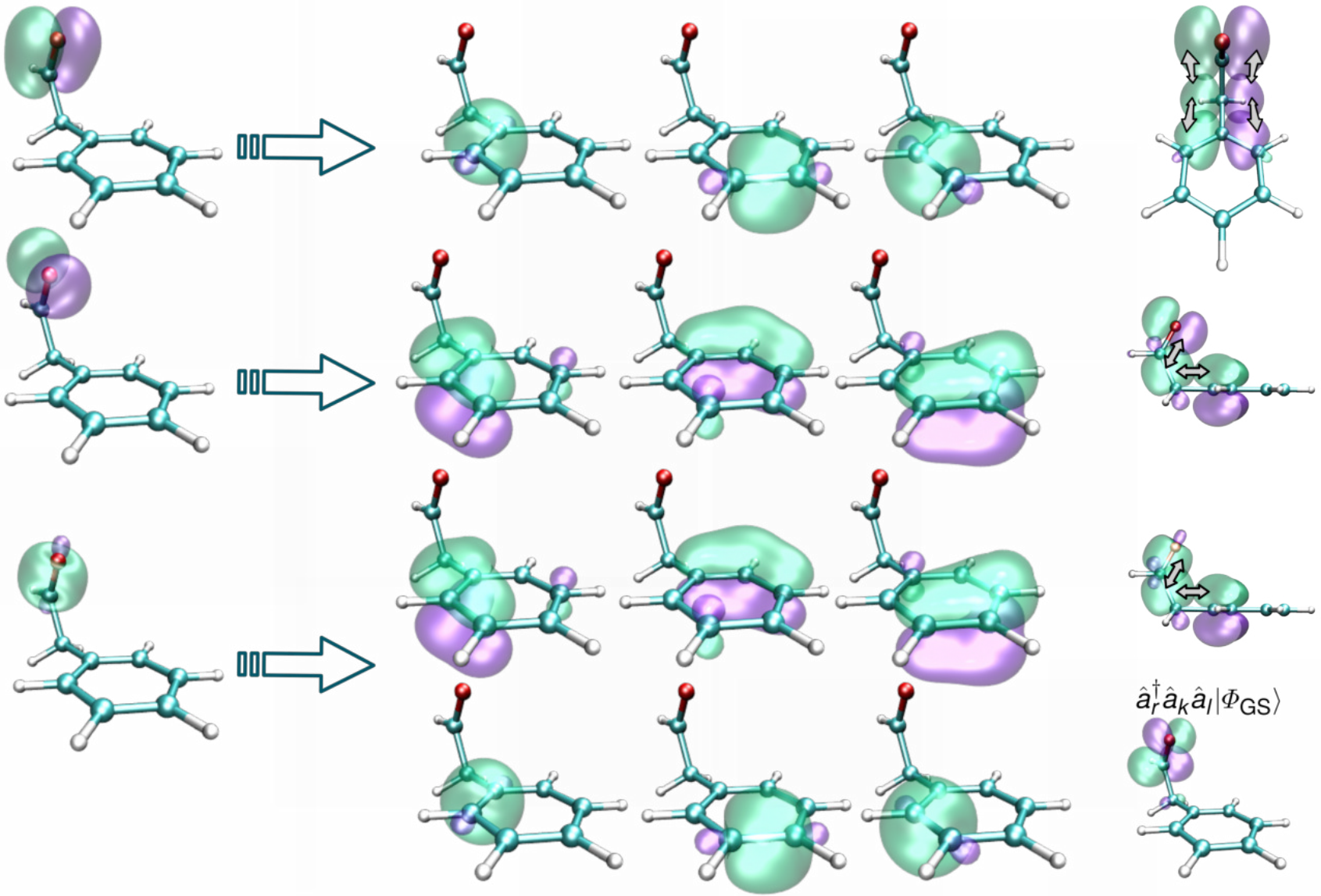
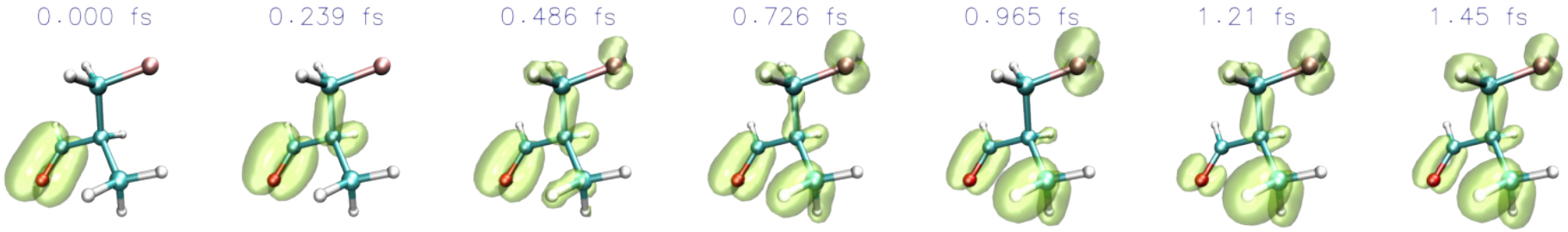


Phenylacetaldehyde: Summary

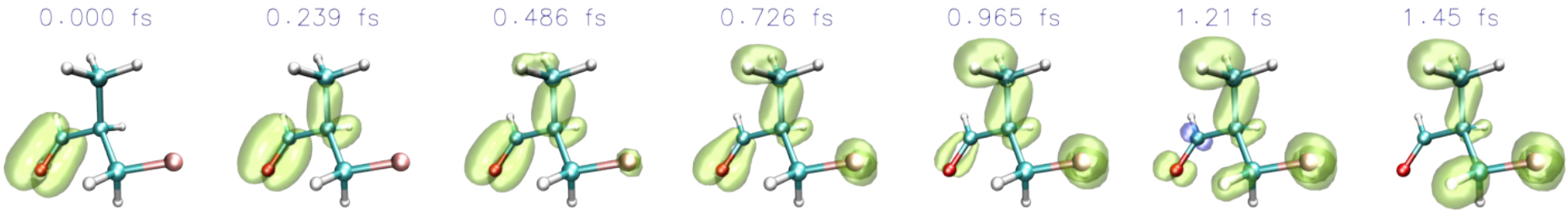


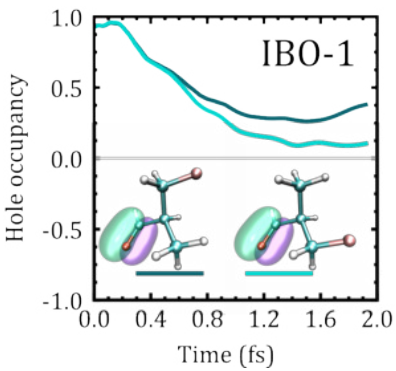
Conformers of sc-3-fluoro-2-methylpropanal

sc-3-fluoro-2-methylpropanal



sp-3-fluoro-2-methylpropanal





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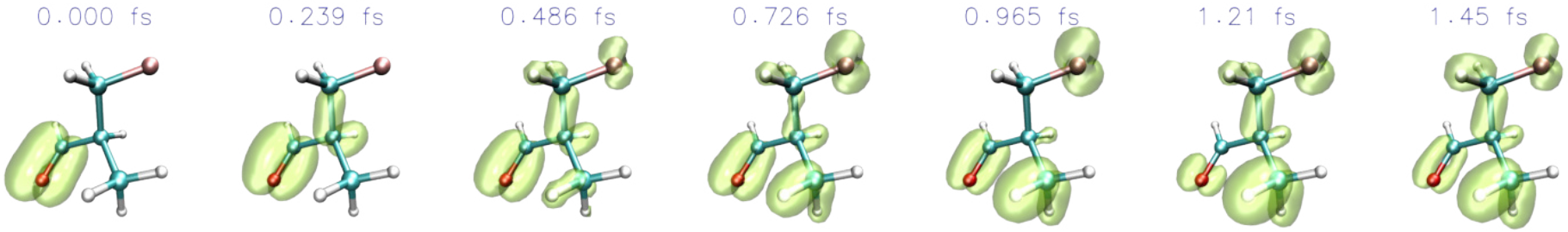

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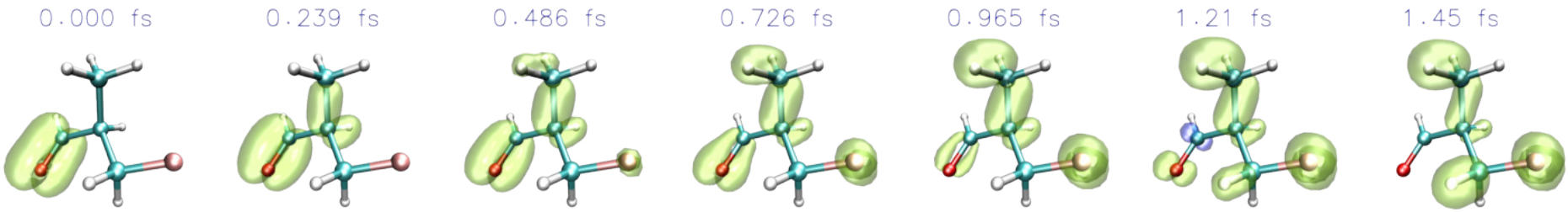

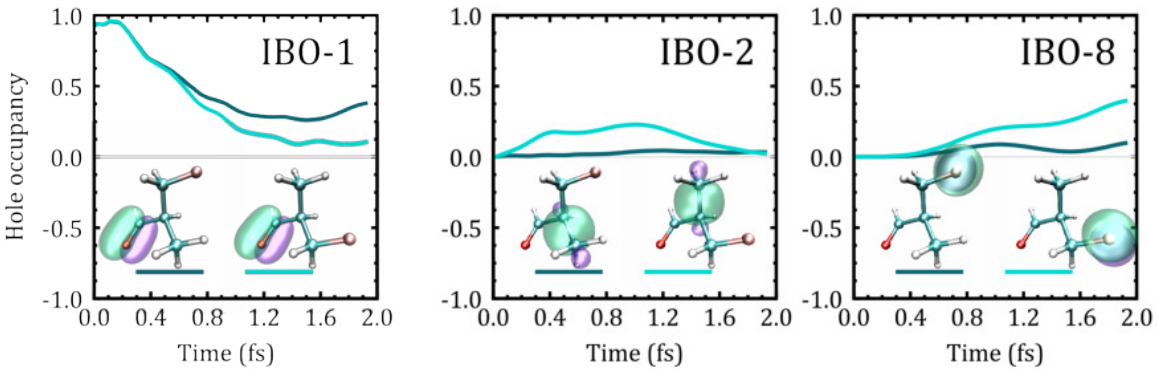

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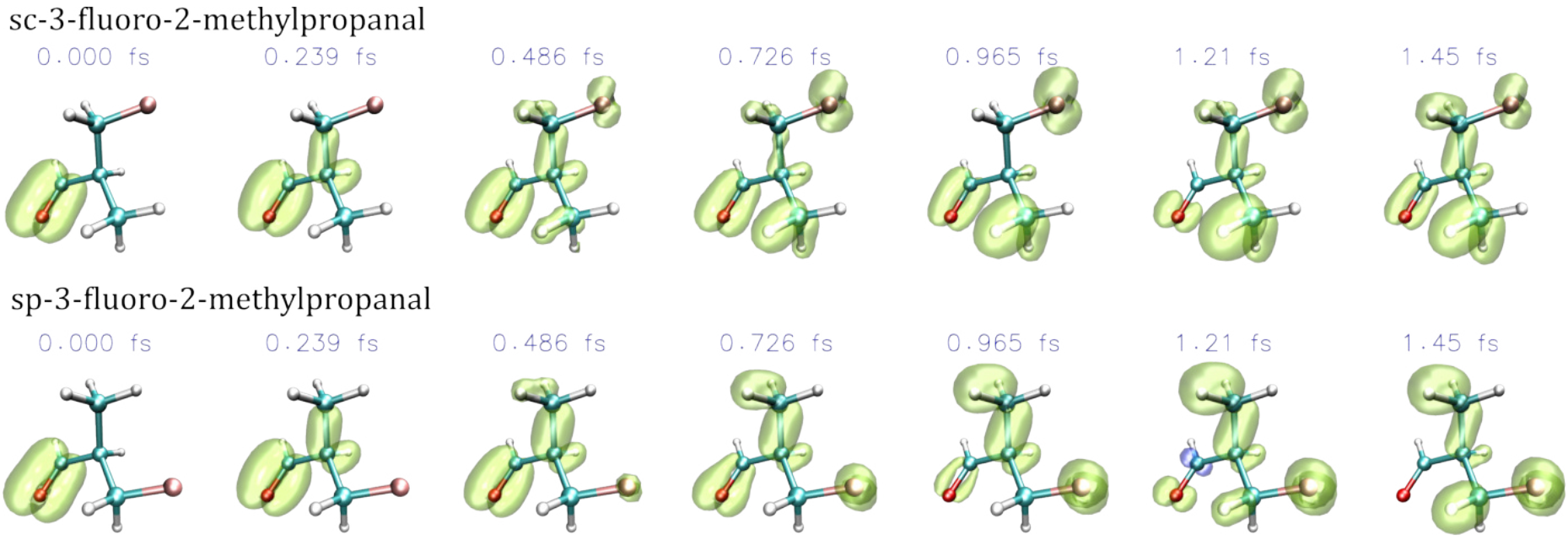
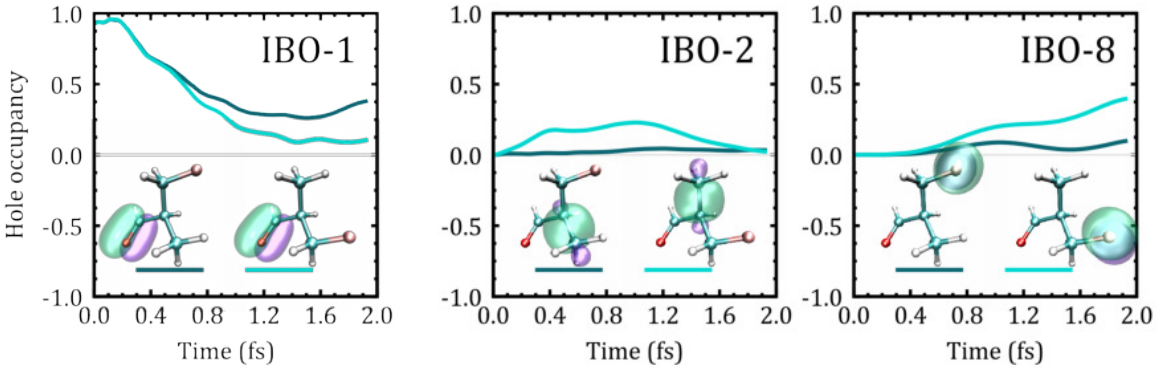
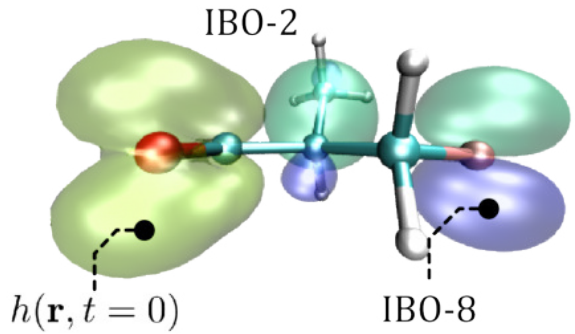


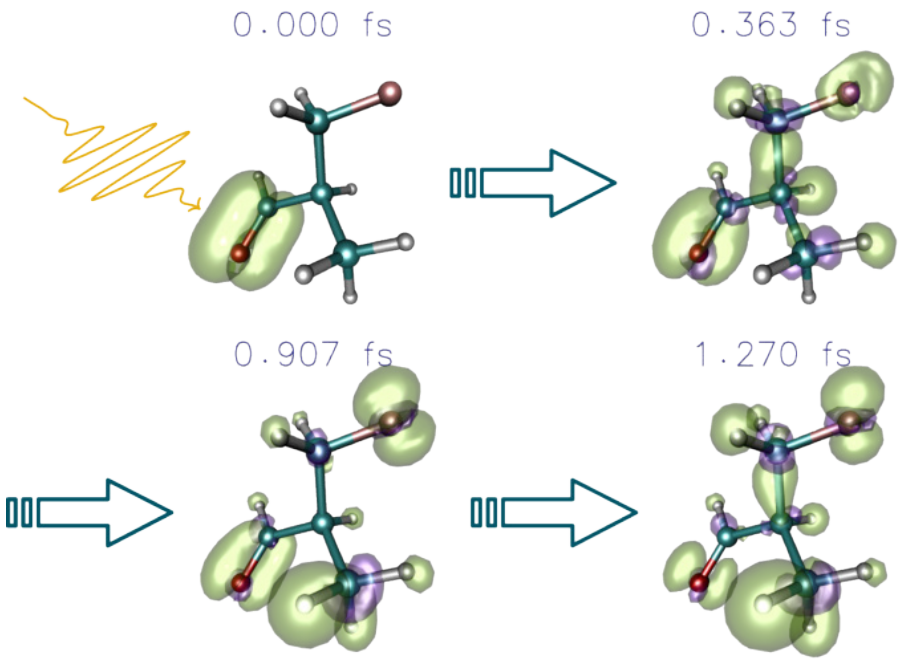




Hyperconjugation interactions: $\pi \Leftrightarrow \sigma \Leftrightarrow p$ lone pair

Summary

- *Ab initio* real-time correlated electron dynamics using time-dependent density matrix renormalization group



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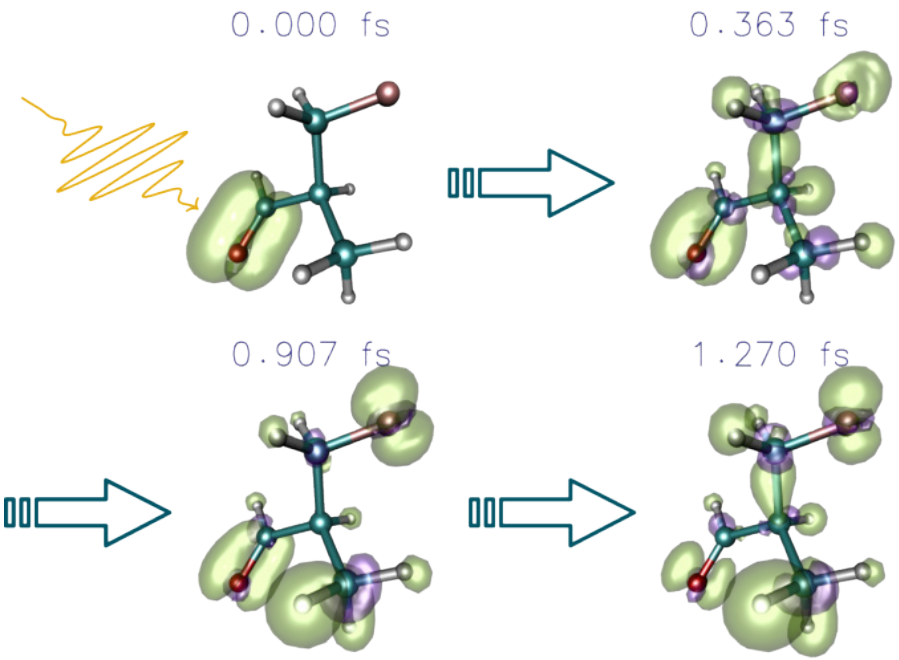
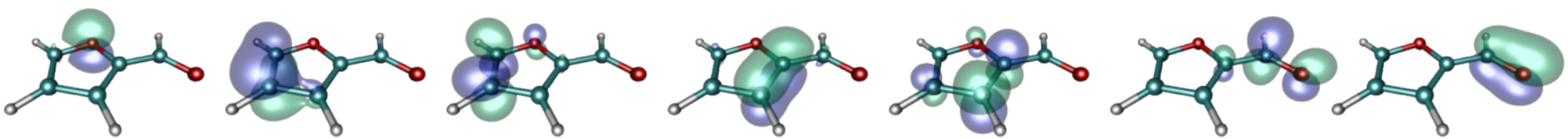
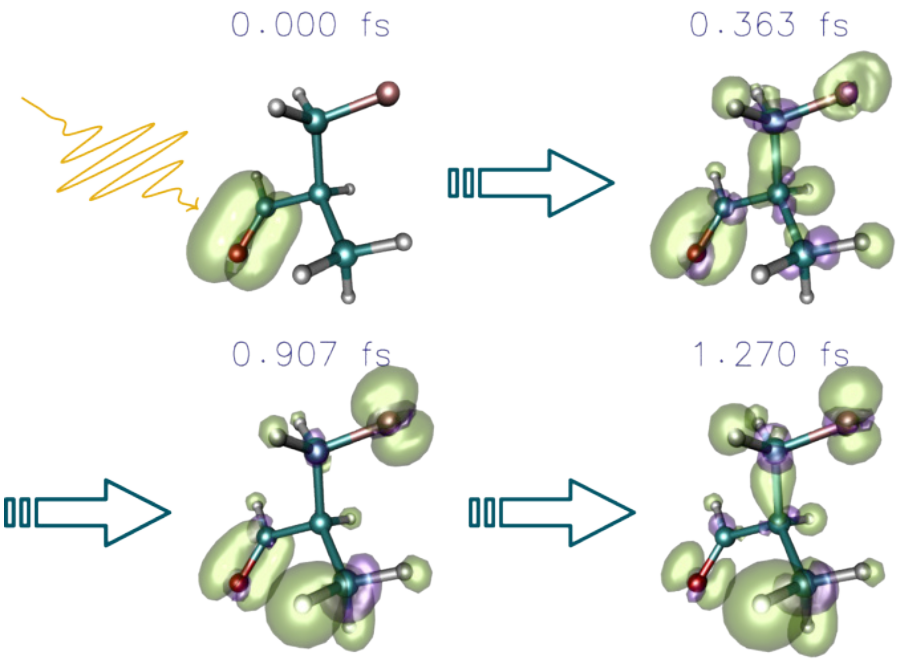
- *Ab initio* real-time correlated electron dynamics using time-dependent density matrix renormalization group
- Use localized orbitals to decode complex charge migration

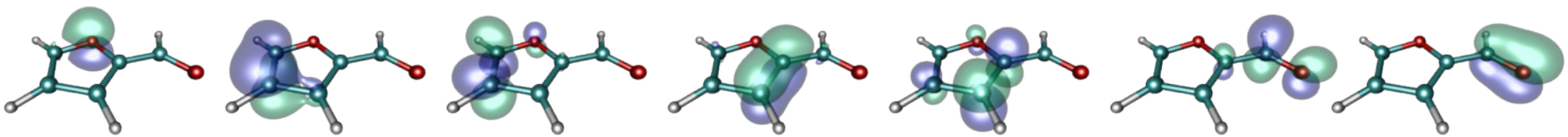




Summary

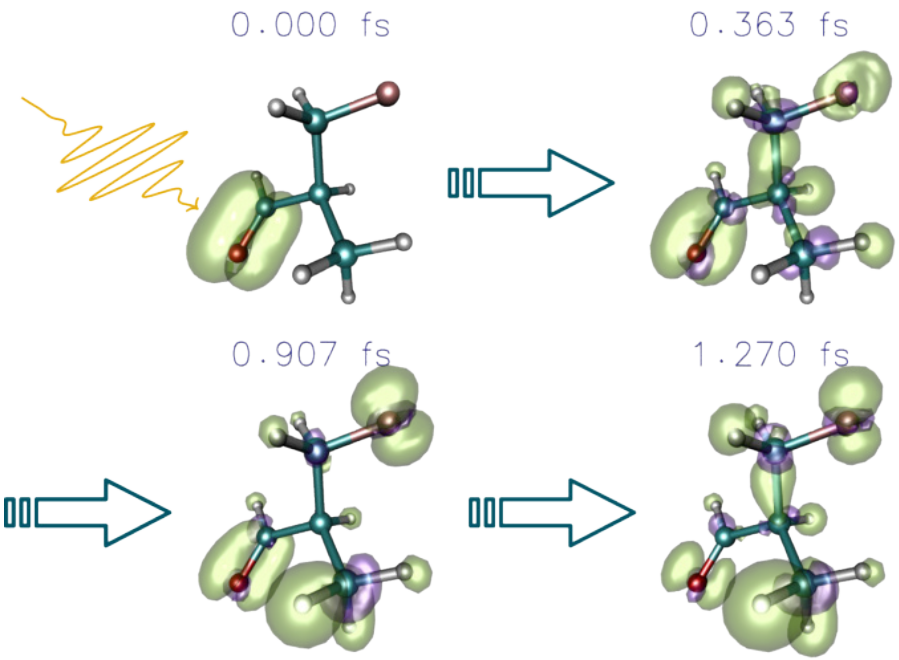
- *Ab initio* real-time correlated electron dynamics using time-dependent density matrix renormalization group
- Use localized orbitals to decode complex charge migration
- Importance of through-space/bond orbital interactions

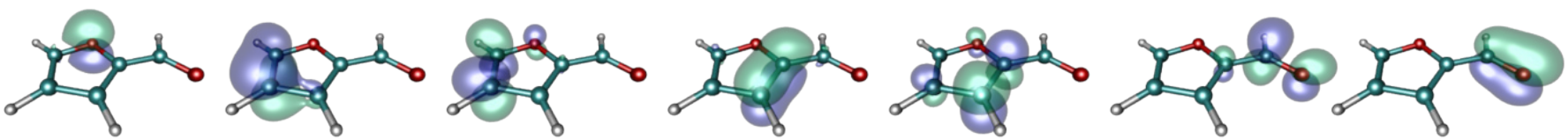




Summary

- *Ab initio* real-time correlated electron dynamics using time-dependent density matrix renormalization group
- Use localized orbitals to decode complex charge migration
- Importance of through-space/bond orbital interactions
- Not restricted to DMRG





Thank You For Your Attention!

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