Charge Migration due to Electron Correlation in Molecules: Development of a Non-Dyson-method

Holger Hennig

Theoretical Chemistry

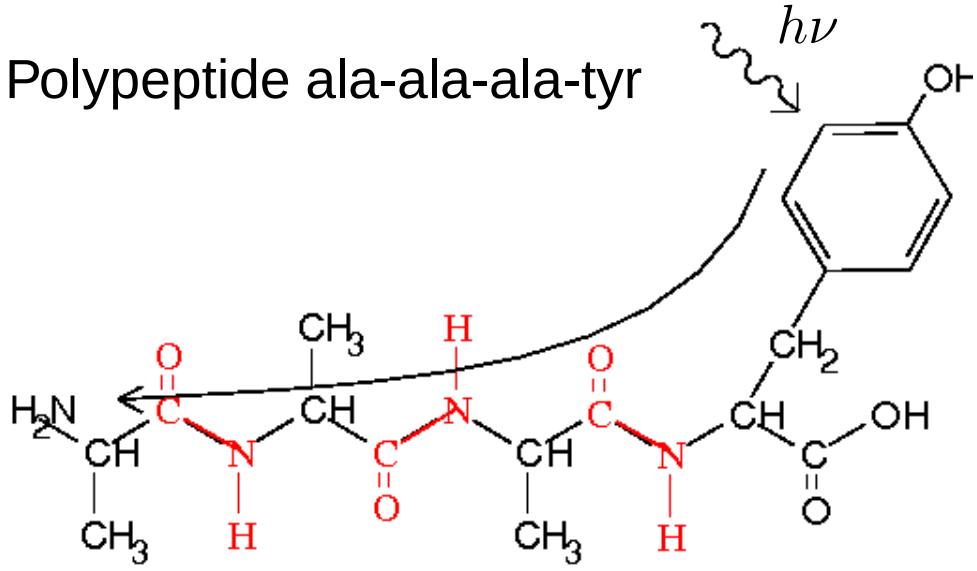
University of Heidelberg

Overview

- Experimental Motivation - What is Charge Migration?
- Dyson/CTA Method: Theory and Mechanisms of Charge Migration
- Development of the non-Dyson/CTA Method
- Illustrative Tests and Results of the non-Dyson/CTA

Experimental Motivation

Polypeptide ala-ala-ala-tyr

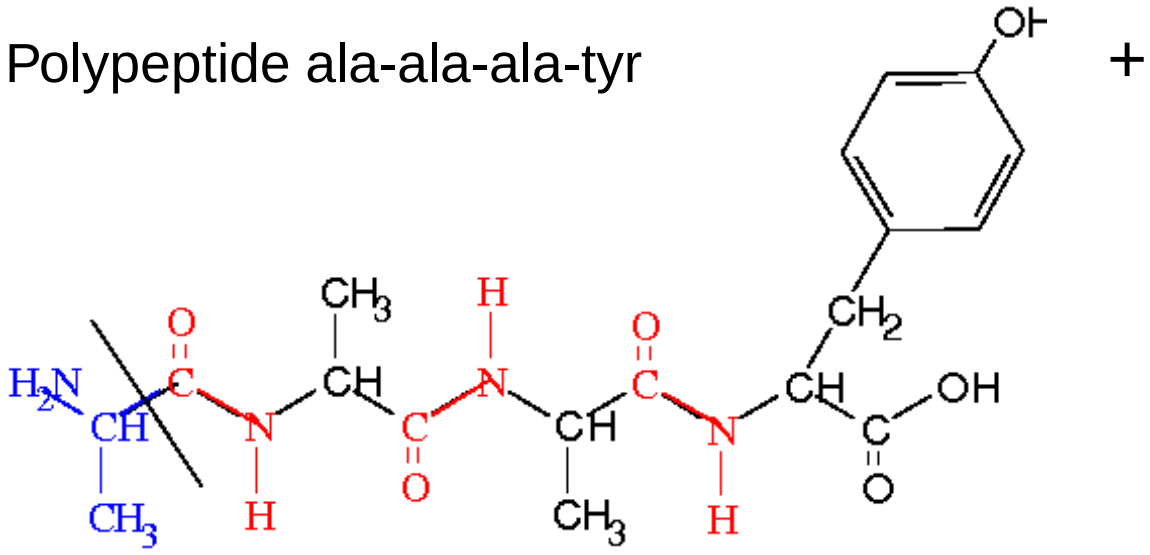


alanin | alanin | alanin | tyrosin

Ionization by UV laser pulse (≈ 14 eV).
Initial hole localized at the benzene ring of amino acid tyrosin.

Experimental Motivation

Polypeptide ala-ala-ala-tyr



Bond near the N-terminal of the protein "on the left" breaks.

What is Charge Migration?

Charge migration =
Charge transfer solely driven by electron correlation

- Geometry of nuclei fixed (Born-Oppenheimer approximation)
- relevant timescale: few fs

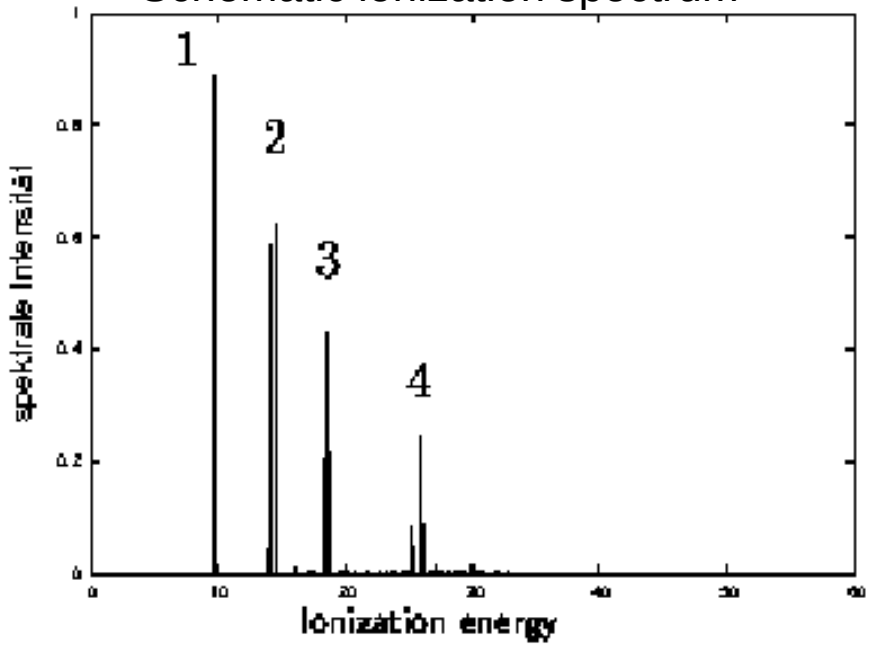
Charge Transfer Analysis (CTA) developed in this group showed that efficient and ultrafast charge migration is, in fact, possible!

Dyson/CTA Method

The Dyson/CTA method consists of

- 1. Dyson-ADC(3) scheme
  in order to gain
  the ionization spectrum

Schematic ionization spectrum



- 2. Subsequent Charge Transfer Analysis (CTA)

Dyson/CTA Method

1. What is Algebraic Diagrammatic Construction (ADC(3))?

- Approximation of the many-particle Green's function via diagrammatic perturbation theory in 3rd order (Feynman graphs)
- Terms of an algebraic expansion of a series are identified with terms resulting from Feynman graphs
- Dyson-ADC: Green's function determined via the Dyson equation

Why do we use ADC?

- Size consistency
- Compactness
- Experience with ADC, existence of programs

Dyson/CTA Method

2. Charge transfer Analysis (CTA)

- Ionization of neutral molecule in "exact" ground state $|\Psi_0\rangle$ (sudden approximation).

=> hole density

$$Q(\vec{r},t) := \underbrace{\langle\Psi_0|\rho(\vec{r},t)|\Psi_0\rangle}_{\rho_0(\vec{r})} - \underbrace{\langle\Phi_i|\rho(\vec{r},t)|\Phi_i\rangle}_{\rho_i(\vec{r},t)},$$

where

- ρ: charge density-operator
- $|\Phi_i\rangle$: cationic initial state

Dyson/CTA Method

Charge density of cationic state:

$$\begin{aligned}\rho_i(\vec{r},t) &= \sum_{I,J}\langle\Phi_i|I\rangle\langle I|e^{iHt}\rho(\vec{r},0)e^{-iHt}|J\rangle\langle J|\Phi_i\rangle \\ &= \sum_{pq}\varphi_p^*(\vec{r})\varphi_q(\vec{r})\underbrace{\sum_{I,J}x_I\underbrace{\langle I|a_p^\dagger a_q|J\rangle}_{\text{perturb. exp.}}x_J\,cos((E_I-E_J)t)}_{N_{pq}(t)}\end{aligned}$$

where

- $\{|I\rangle\}$ basis of eigenstates of the ionized molecule
- $x_I = \langle\Phi_i|I\rangle$ transition amplitudes
- $\{\varphi_p\}$ one-particle HF-orbital basis, $\rho(\vec{r},0) = \sum_{pq}\varphi_p^*(\vec{r})\varphi_q(\vec{r})a_p^\dagger a_q$

Dyson/CTA Method

Calculate $\langle I|a_p^\dagger a_q|J\rangle$ via perturbation theory. Ansatz:

$$|I\rangle = \sum_j c_j^{(I)} a_j|\Phi_0\rangle + \sum_{a,k<l} c_{akl}^{(I)} a_a^\dagger a_k a_l|\Phi_0\rangle + \ldots$$

$\Rightarrow$ Hole density

$$Q(\vec{r},t) = \sum_{p,q} \varphi_p^*(\vec{r})\varphi_q(\vec{r})N_{pq}(t) = \sum_p |\tilde{\varphi}_p(\vec{r},t)|^2 \tilde{n}_p(t)$$

Diagonalization

Eigenfunctions $\{\tilde{\varphi}_p\}$ called *natural charge orbitals*

Eigenvalues $\{\tilde{n}_p(t)\}$ called *hole occupation numbers*

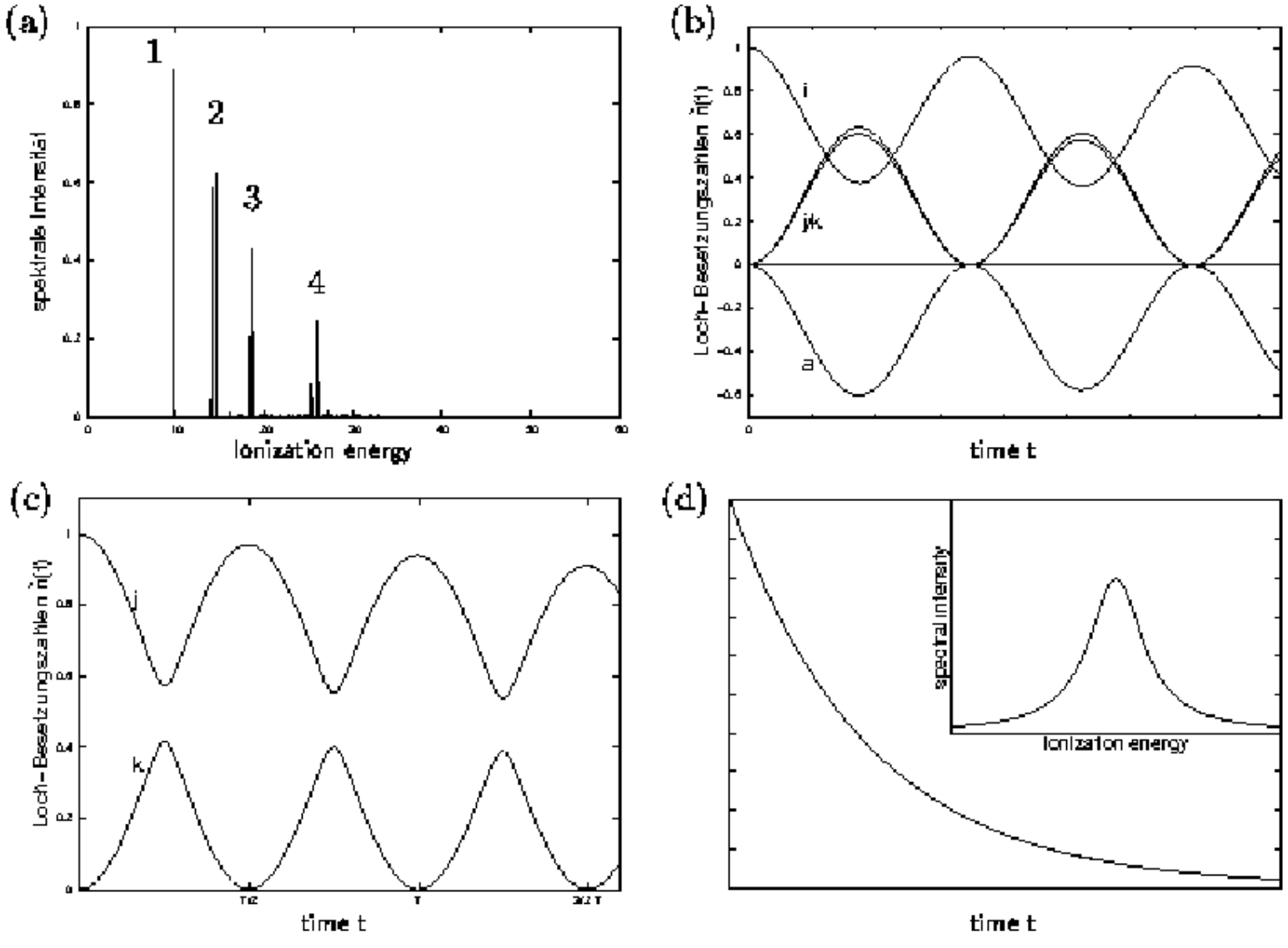
Dyson/CTA Method

Brief summary:

A numerical Dyson/CTA-calculation consists of

1. Hartree-Fock calculation
2. Dyson-ADC(3)
3. Diagonalization of the ADC-matrix
4. Charge Transfer Analysis (CTA)

Mechanisms of Charge Migration



Overview

- Experimental Motivation - What is Charge Migration?
- Dyson/CTA Method: Theory and Mechanisms of Charge Migration
- **Development of the non-Dyson/CTA Method**
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Developing a non-Dyson/CTA Method

Why developing a new method?

- Biophysical relevant systems are too large for Dyson/CTA calculations
- Bottleneck is diagonalization of ADC-matrix

Idea: Circumvent diagonalization of ADC-matrix by propagating in the basis, in which the ADC-matrix is represented.

What is non-Dyson-ADC?

- Perturbation expansion directly of Green's function, not using Dyson equation $\Rightarrow$ "non-Dyson"-ADC
- Nondiagonal representation of Green's function - basis is basis of "Intermediate States" (Intermediate state representation, ISR)

Developing a non-Dyson/CTA Method

Hole density

$$Q(\vec{r},t) := \underbrace{\langle\Psi_0|\rho(\vec{r},t)|\Psi_0\rangle}_{\rho_0(\vec{r})} - \underbrace{\langle\Phi_i|\rho(\vec{r},t)|\Phi_i\rangle}_{\rho_i(\vec{r},t)},$$

ρ: charge density operator, $|\Phi_i\rangle$: cationic initial state

- Insert $1 = \sum |\tilde{\Psi}_{\mathcal{M}}\rangle\langle\tilde{\Psi}_{\mathcal{M}}|$, where $\{|\tilde{\Psi}_{\mathcal{M}}\rangle\}$: Basis of Intermediate States

$$\begin{aligned}
\rho_i(\vec{r},t) &= \sum_{\mathcal{M},\mathcal{N}} \langle\Phi_i|e^{iHt}\tilde{\Psi}_{\mathcal{M}}\rangle\langle\tilde{\Psi}_{\mathcal{M}}|\rho(\vec{r},0)|\tilde{\Psi}_{\mathcal{N}}\rangle\langle\tilde{\Psi}_{\mathcal{N}}e^{-iHt}|\Phi_i\rangle \\
&= \sum_{pq} \varphi_p^*(\vec{r})\varphi_q(\vec{r}) \underbrace{\sum_{\mathcal{M},\mathcal{N}} \langle\Phi_i(t)|\tilde{\Psi}_{\mathcal{M}}\rangle\langle\tilde{\Psi}_{\mathcal{M}}|a_p^\dagger a_q|\tilde{\Psi}_{\mathcal{N}}\rangle\langle\tilde{\Psi}_{\mathcal{N}}|\Phi_i(t)\rangle}_{\tilde{N}_{pq}(t)}
\end{aligned}$$

Developing a non-Dyson/CTA Method

$\Rightarrow$ Hole density

$$Q(\vec{r},t) = \sum_{pq} \varphi_p^* \varphi_q \tilde{N}_{pq}(t),$$

$$\tilde{N}_{pq}(t) := \delta_{pq} n_p - \sum_{\mathcal{M},\mathcal{N}} \langle \Phi_i(t) | \tilde{\Psi}_\mathcal{M} \rangle \underbrace{\langle \tilde{\Psi}_\mathcal{M} | a_p^\dagger a_q | \tilde{\Psi}_\mathcal{N} \rangle}_{\text{perturb. expansion}} \langle \tilde{\Psi}_\mathcal{N} | \Phi_i(t) \rangle$$

Main tasks

- Perturbation expansion of $\langle \tilde{\Psi}_\mathcal{M} | a_p^\dagger a_q | \tilde{\Psi}_\mathcal{N} \rangle$ in 2nd order
  ... and its "spinfree" formulation necessary for subsequent implementation
- Implementing a propagation $e^{-iHt} | \Phi_i \rangle = | \Phi_i(t) \rangle$

Analytical Comparison of the Methods

In which way do the two methods differ analytically?

The newly developed non-Dyson/CTA and the so far used Dyson/CTA

- build up on non-Dyson-ADC resp. Dyson-ADC $\Rightarrow$ ionization spectra are slightly different
- are identical in terms of zeroth order

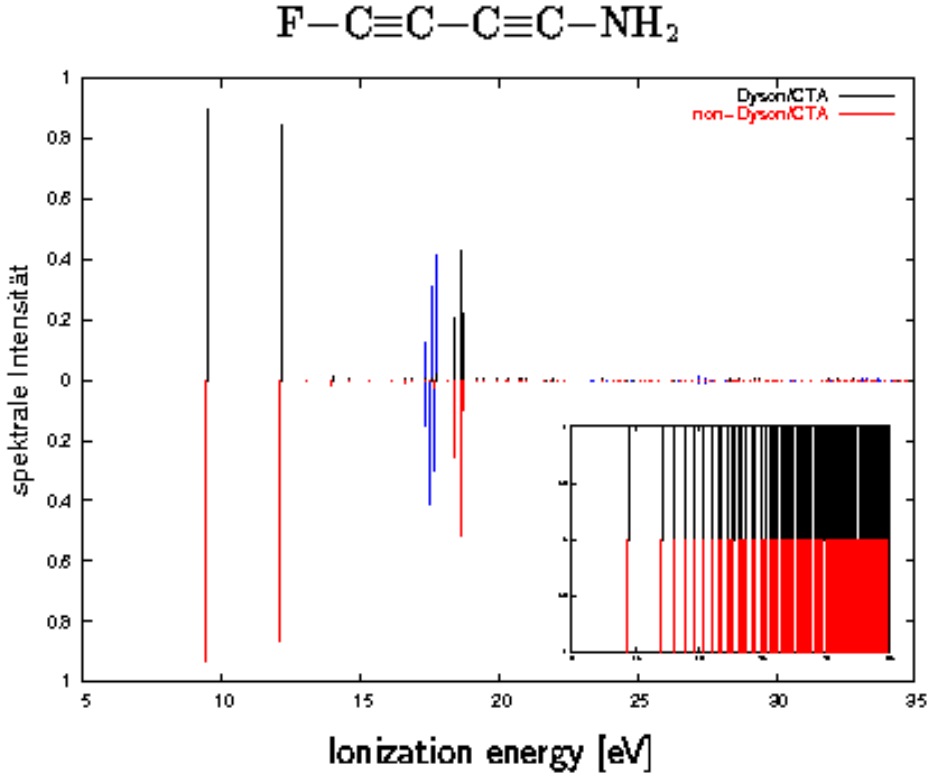
Do the numerical results of the two methods show conformity?

$\Rightarrow$ Propagate while using the "complete" eigenvalue spectrum (resulting from a full diagonalization of the non-Dyson-ADC matrix) and compare with corresponding Dyson/CTA results

Testing non-Dyson/CTA

Comparison of ionization spectra

- Molecule: FC_4NH_2
- Basis: DZP
  (double zeta basis with
  add. polarisation functions)
- Full diagonalization
  of both matrices
- Black: Dyson/CTA
  red: non-Dyson/CTA

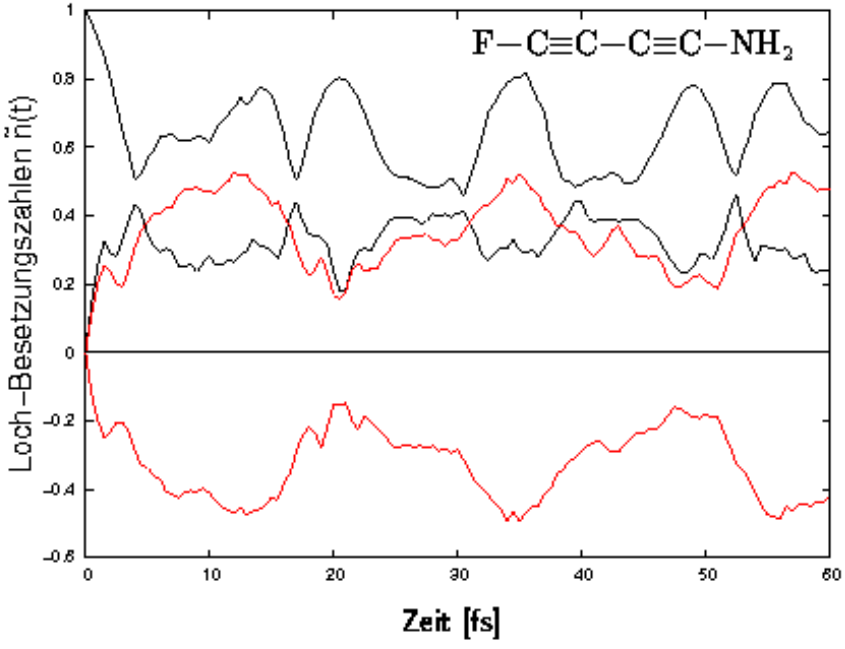


Good agreement.

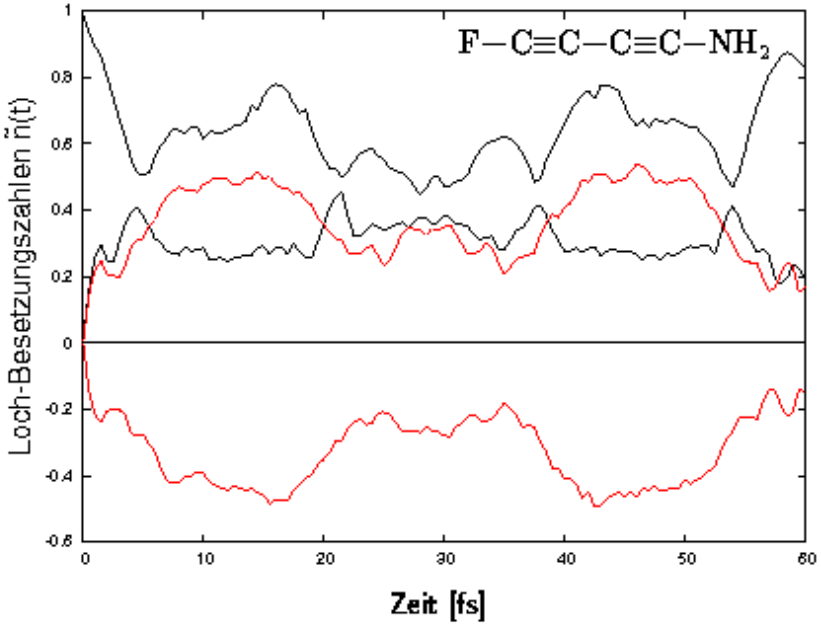
Testing non-Dyson/CTA

Comparison of time-dependent hole occupation numbers

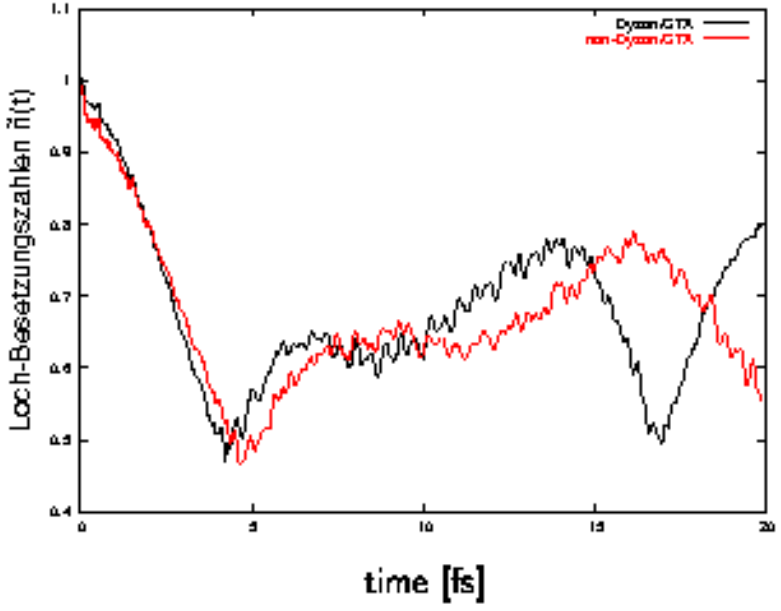
Dyson/CTA



non-Dyson/CTA

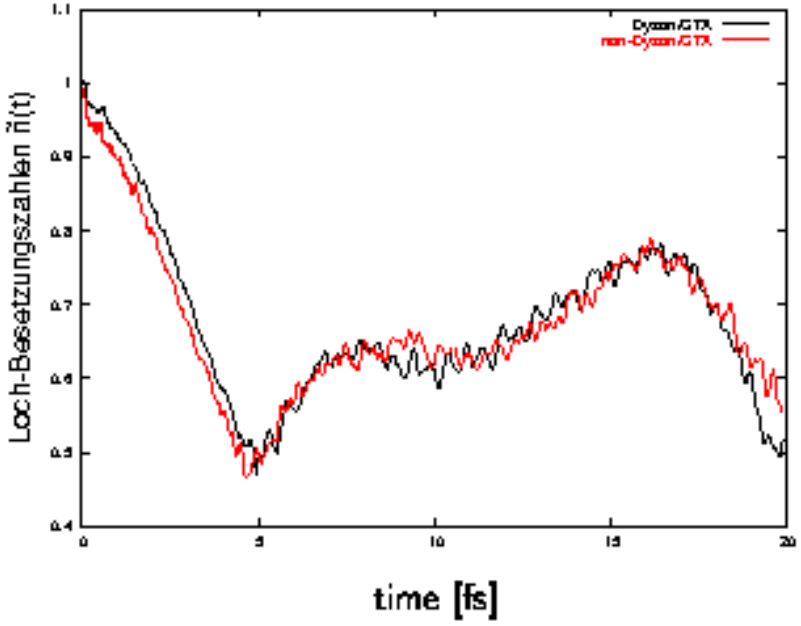


Testing non-Dyson/CTA



comparison Dyson/CTA

with non-Dyson/CTA



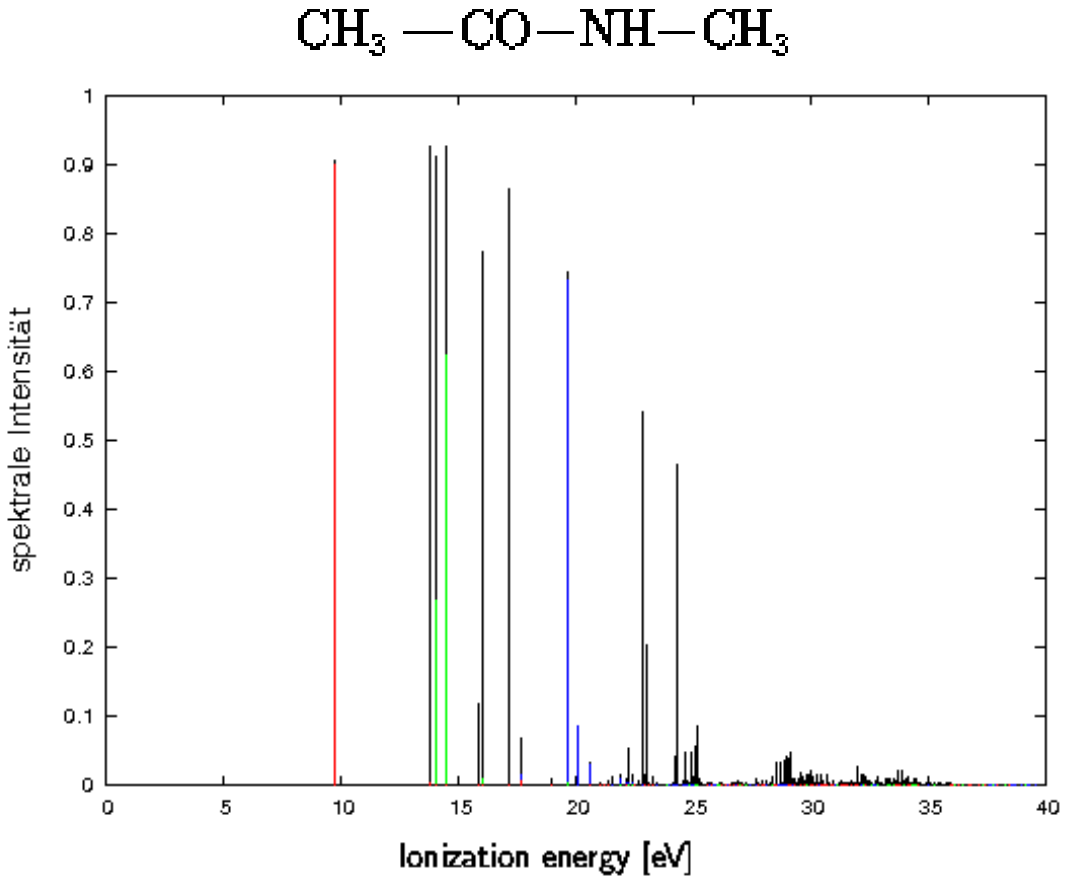
...with correction due to

different spectra

Surprisingly good agreement!

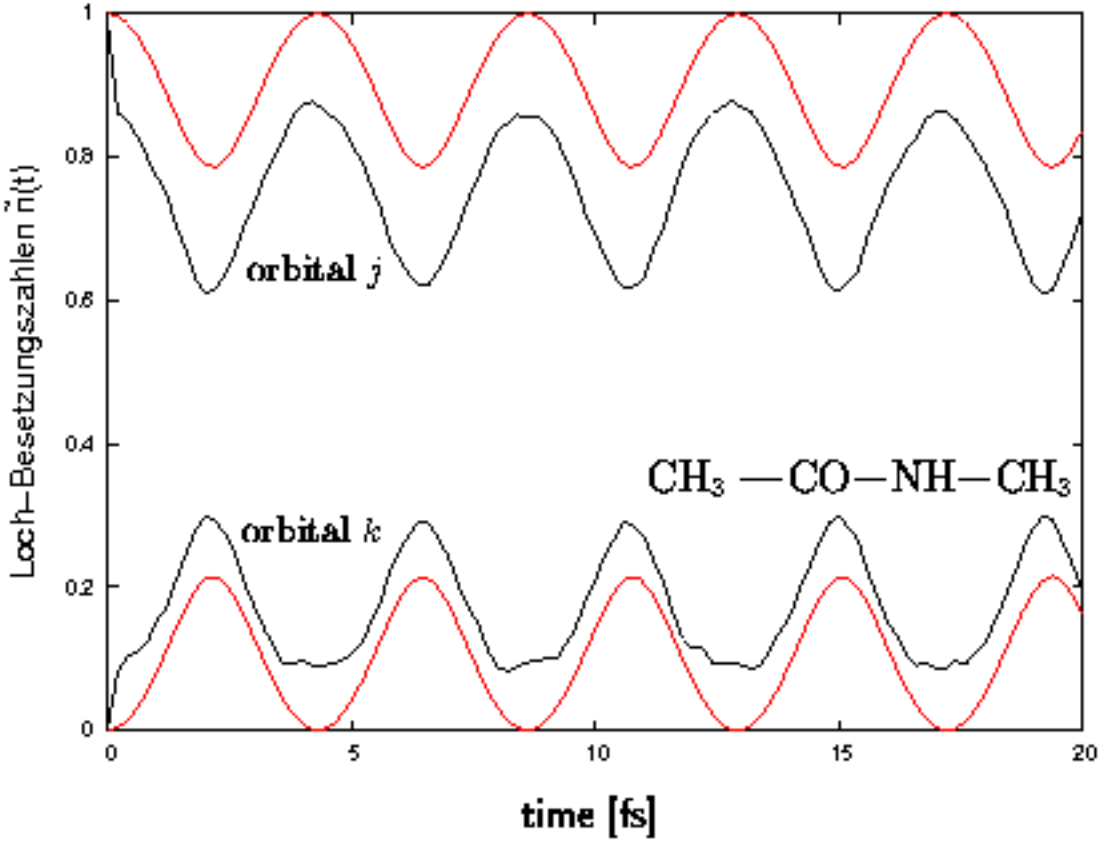
Results of the non-Dyson/CTA

- Molecule:
  N-methyl-acetamide
- Basis: DZP



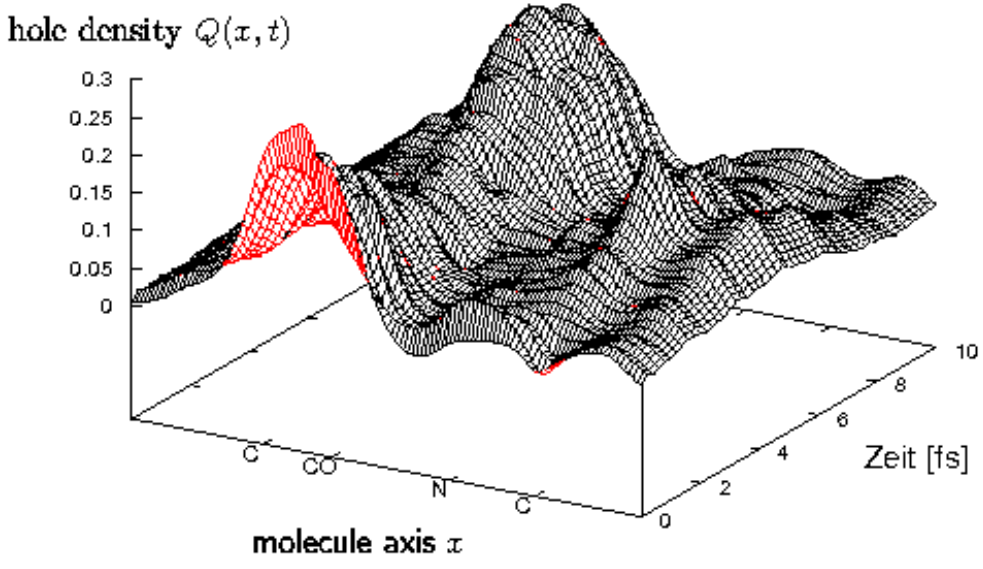
Consider ionization out of orbital 13a’ (lines marked green)

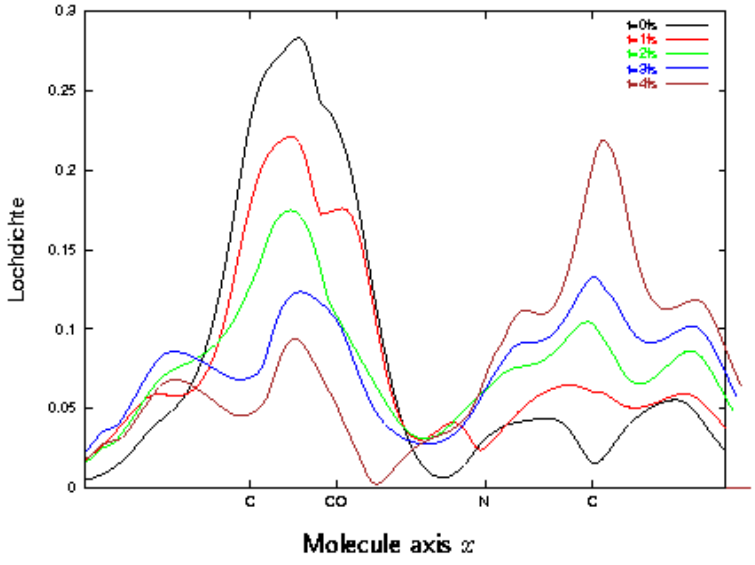
Results of the non-Dyson/CTA



red curve: $\tilde{n}(t)_{j,k} = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - 4(ab)^2 \sin^2(\omega t)}$

Results of the non-Dyson/CTA





Very efficient mechanism of charge migration over a peptid bond.

Dinstinct ultrafast charge migration due to electron correlation.

Brief Summary

- An ab initio method called Dyson/CTA to investigate charge migration was presented. Problem: calculating larger systems
- A new non-Dyson/CTA was developed for a charge migration analysis towards investigating biophysical relevant systems
- Analytical comparison of the formulas of the so far used Dyson/CTA with the newly developed non-Dyson/CTA method
- Comparison of the numerical results of the new non-Dyson/CTA with Dyson/CTA and presentation of results of the non-Dyson/CTA – **using full diagonalization of non-Dyson-ADC matrix**

Outlook

- Potential of non-Dyson/CTA method: Circumvent diagonalization of non-Dyson-ADC matrix
  (propagation routine implemented, tested with random matrices)
- Implementation of non-Dyson/CTA method represents a first step towards the analysis of charge migration in biologically relevant systems.

Further projects...

- Apply a complex absorbing potential (CAP) - prepared
- Sudden approximation vs. shape of laser pulse

Acknowledgements

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Thank you for your attention!