TDDFT beyond the linear regime

Time-Dependent Electron Localization Function
(TD-ELF)

GOAL

Time-resolved visualization of the breaking and formation of chemical bonds.

How can one give a rigorous mathematical meaning to chemical concepts such as

- **Single, double, triple bonds**
- **Lone pairs**

Note:

- Density $\rho_\sigma(\mathbf{r})$ is not useful!
- Orbitals are ambiguous (w.r.t. unitary transformations)

$$D_{\sigma}\left(\vec{r},\vec{r}'\right)=\sum_{\sigma_3\sigma_4\ldots\sigma_N}\int d^3r_3\ldots\int d^3r_N\left|\Psi\left(\vec{r}\sigma,\vec{r}'\sigma,\vec{r}_3\sigma_3\ldots,\vec{r}_N\sigma_N\right)\right|^2$$

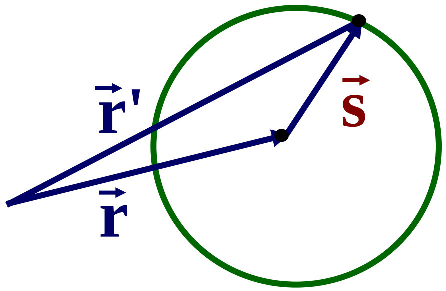
= diagonal of two-body density matrix

= probability of finding an electron with spin $\boldsymbol{\sigma}$ at $\vec{\mathbf{r}}$ and another electron with the same spin at $\vec{\mathbf{r}}'$.

$$P_{\sigma}\left(\vec{r},\vec{r}'\right):=\frac{D_{\sigma\sigma}\left(\vec{r},\vec{r}'\right)}{\rho_{\sigma}\left(\vec{r}\right)}$$

= conditional probability of finding an electron with spin $\boldsymbol{\sigma}$ at $\vec{\mathbf{r}}'$ if we know with certainty that there is an electron with the <u>same</u> spin at $\vec{\mathbf{r}}$.

Coordinate transformation



If we know there is an electron with spin σ at $\vec{\mathbf{r}}$, then $P_\sigma(\vec{\mathbf{r}},\vec{\mathbf{r}}+\vec{\mathbf{s}})$ is the (conditional) probability of finding another electron at $\vec{\mathbf{s}}$, where $\vec{\mathbf{s}}$ is measured from the reference point $\vec{\mathbf{r}}$.

Spherical average

$$p_\sigma\left(\vec{r},|\vec{s}|\right)=\frac{1}{4\pi}\int_0^{\pi}\sin\theta\, d\theta\int_0^{2\pi}d\varphi\, P_\sigma\left(\vec{r},|\vec{s}|,\theta,\varphi\right)$$

If we know there is an electron with spin σ at $\vec{\mathbf{r}}$, then $p_\sigma(\vec{\mathbf{r}},\mathbf{s})$ is the conditional probability of finding another electron at the distance **s** from $\vec{\mathbf{r}}$.

Expand in a Taylor series:

$$p_\sigma\left(\vec{r},s\right)=\underbrace{p_\sigma\left(\vec{r},0\right)}_{0}+\underbrace{\left.\frac{dp_\sigma\left(\vec{r},s\right)}{ds}\right|_{s=0}}_{0}\cdot s+\frac{1}{3}C_\sigma\left(\vec{r}\right)s^2$$

The first two terms vanish.

$C_\sigma(\vec{r})$ is a measure of electron localization.

Why? $C_\sigma(\vec{r})$, being the s^2-coefficient, gives the probability of finding a second like-spin electron very near the reference electron. If this probability very near the reference electron is low then this reference electron must be very localized.

$C_\sigma(\vec{r})$ small means strong localization at $\vec{r}$

$\mathbf{C}_\sigma$ is always ≥ 0 (because $\mathbf{p}_\sigma$ is a probability) and $\mathbf{C}_\sigma(\vec{\mathbf{r}})$ is not bounded from above.

Define as a useful visualization of localization
(A.D. Becke, K.E. Edgecombe, JCP 92, 5397 (1990))

$$\boxed{\mathrm{ELF} = \frac{1}{1+\left(\frac{C_\sigma(\vec{r})}{C_\sigma^{\mathrm{uni}}(\vec{r})}\right)^2}}$$

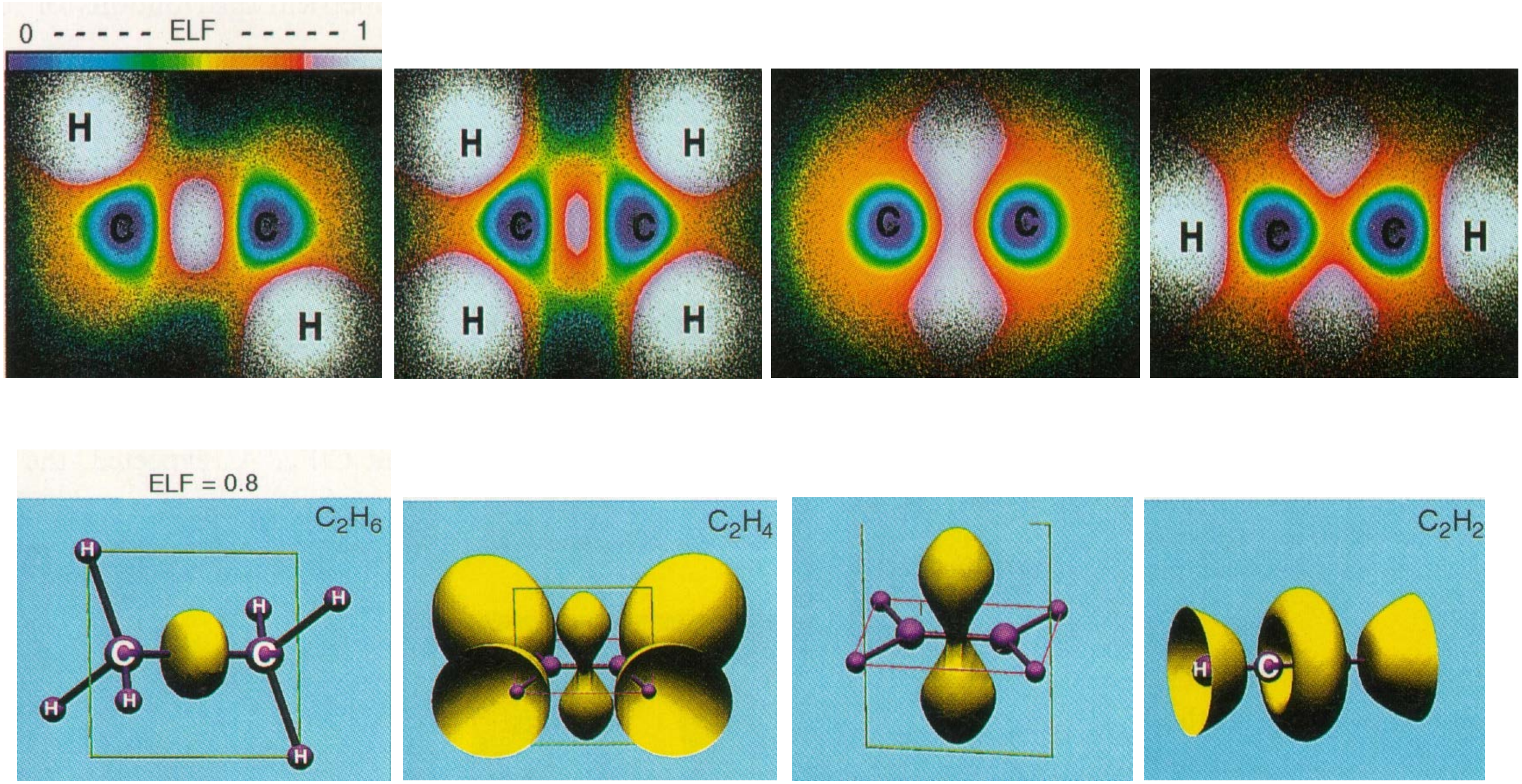
where

$$C_\sigma^{\mathrm{uni}}(\vec{r}) = \frac{3}{5}\left(6\pi^2\right)^{2/3}\rho_\sigma^{5/3}(\vec{r}) = \tau_\sigma^{\mathrm{uni}}(\vec{r})$$

is the kinetic energy density of the uniform gas.

Advantage: ELF is dimensionless and $0 \leq \mathrm{ELF} \leq 1$

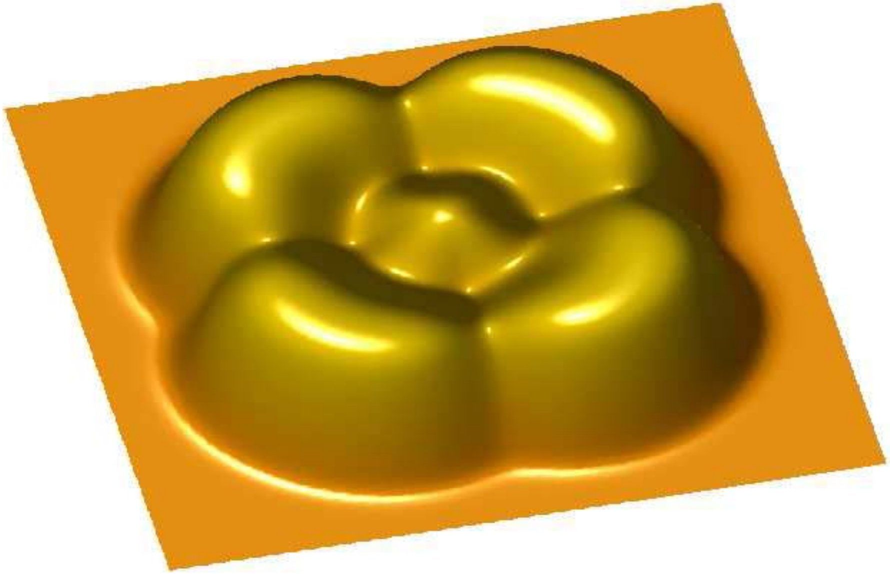
ELF



A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, Angew. Chem. Int. Ed. 36, 1808 (1997)

12-electron 2D quantum dot with four minima

Density



ELF

E. Räsänen, A. Castro and E.K.U. Gross, Phys. Rev. B 77, 115108 (2008).

For a determinantal wave function one obtains

in the static case:

$$C_\sigma^{\det}(\vec{r}) = \sum_{i=1}^{N_\sigma} \left|\nabla\varphi_{i\sigma}(\vec{r})\right|^2 - \frac{1}{4}\frac{\left(\nabla\rho_\sigma(\vec{r})\right)^2}{\rho_\sigma(\vec{r})}$$

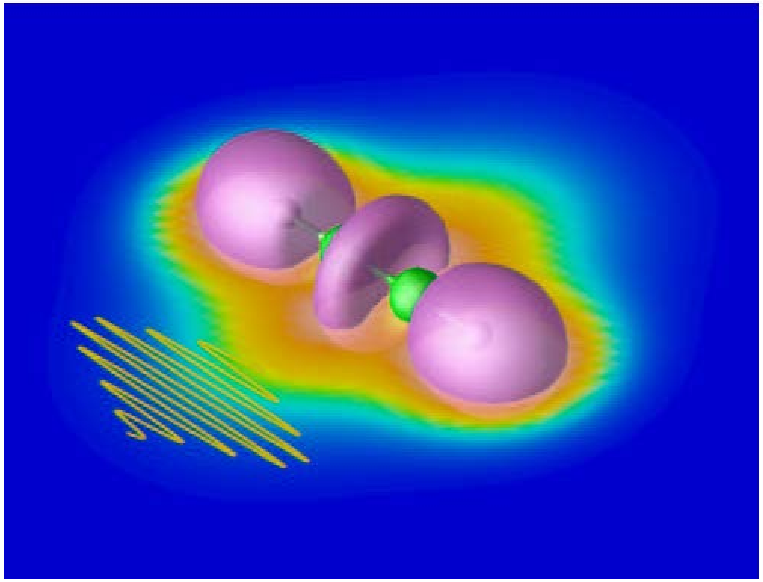
(A.D. Becke, K.E. Edgecombe, JCP 92, 5397 (1990))

in the time-dependent case:

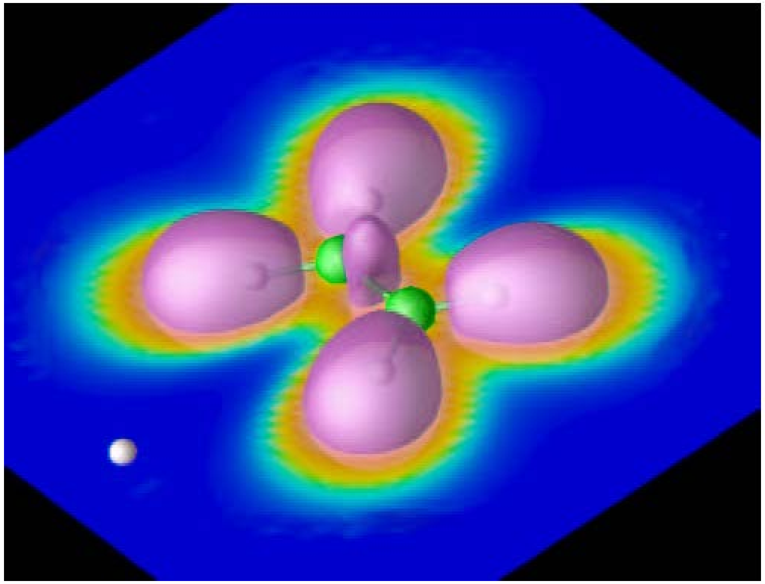
$$\boxed{C_\sigma^{\det}(\vec{r},t) = \sum_{i=1}^{N_\sigma} \left|\nabla\varphi_{i\sigma}(\vec{r},t)\right|^2 - \frac{1}{4}\frac{\left(\nabla\rho_\sigma(\vec{r},t)\right)^2}{\rho_\sigma(\vec{r},t)} - j_\sigma(\vec{r},t)^2 \big/ \rho_\sigma(\vec{r},t)}$$

(T. Burnus, M. Marques, E.K.U.G., PRA (Rapid Comm) 71, 010501 (2005))

Acetylene in laser field
(ħω = 17.15 eV, I = 1.2×10^{14} W/cm$^{2)}$

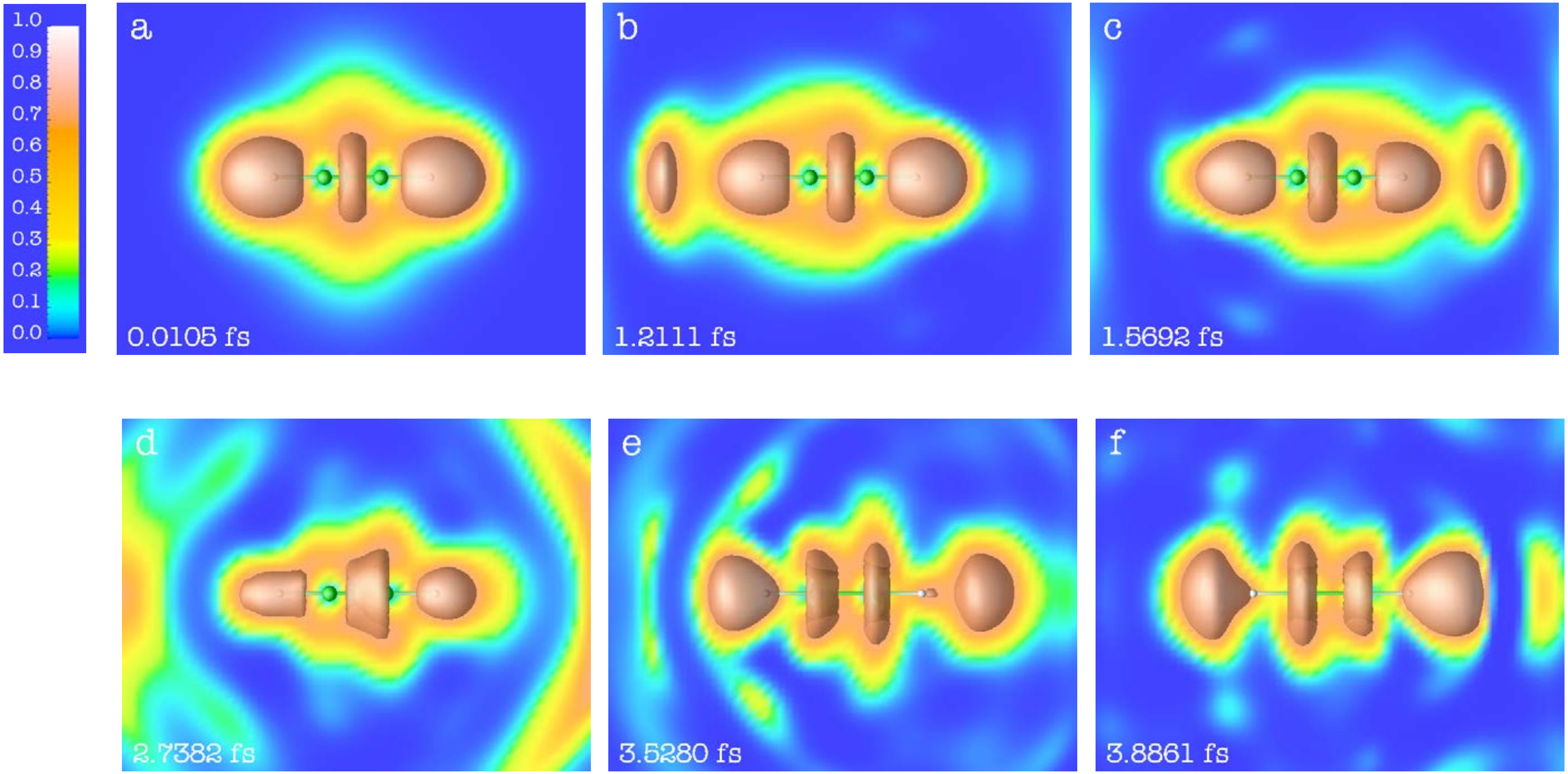


Scattering of a proton from ethylene
(E_{kin}(proton) = 2 keV)



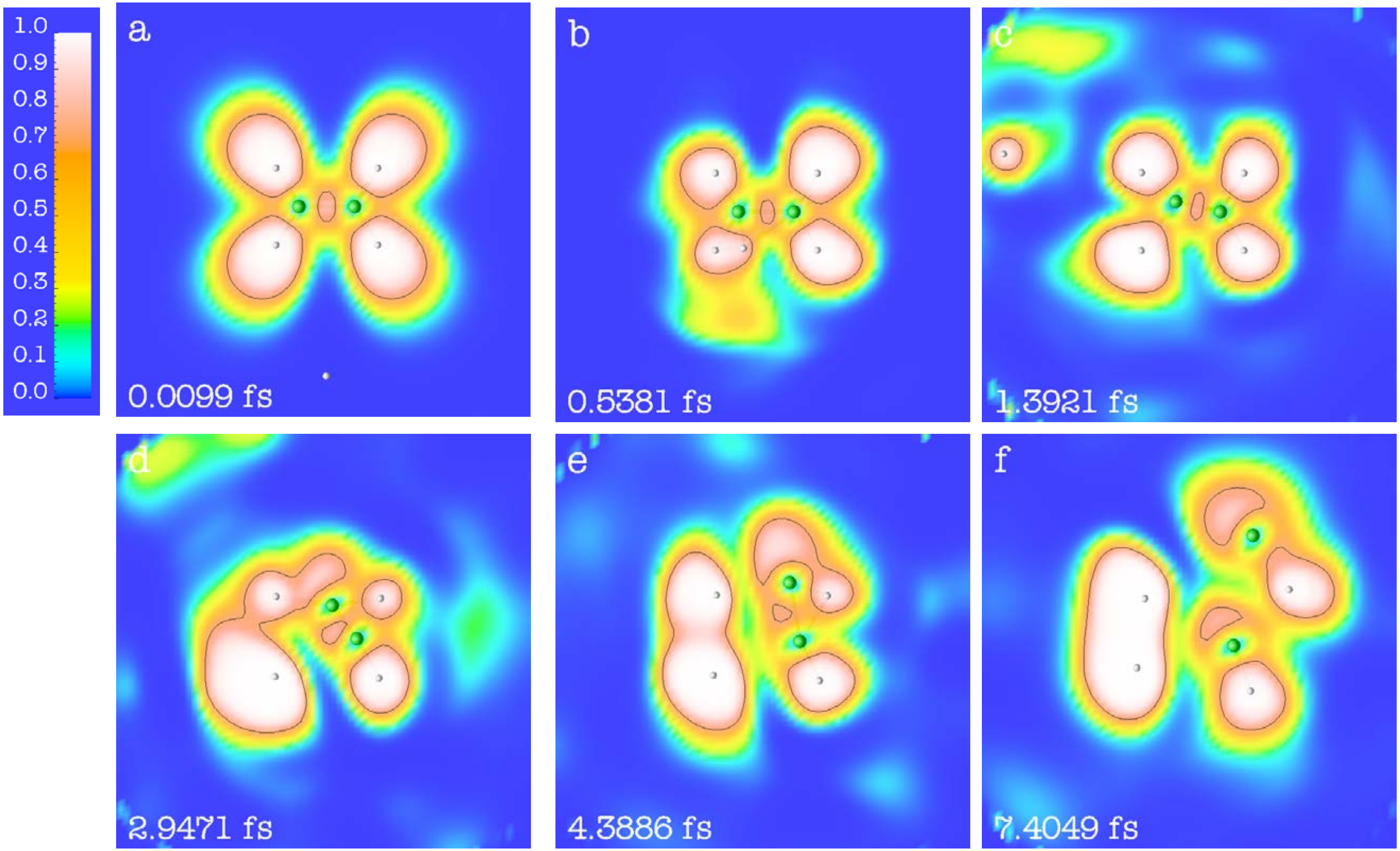
TDELF for acetylene in strong laser field

($\hbar\omega$ = 17.15 eV, I = 1.2×10^{14} W/cm^2)



TDELF for scattering process

2 keV proton colliding with ethylene



INFORMATION ACCESSIBLE THROUGH TDELF

- **How long does it take to break a bond in a laser field?**
- **Which bond breaks first, which second, etc, in a collision process?**
- **Are there intermediary (short-lived) bonds formed during a collision, which are not present any more in the collision products ?**

TDELF movies produced from TD Kohn-Sham equations

$$i\hbar\frac{\partial}{\partial t}\varphi_j(rt)=\left(-\frac{\hbar^2\nabla^2}{2m}+v_{KS}[\rho](rt)\right)\varphi_j(rt)$$

$$v_{KS}[\rho(r't')](rt)=v(rt)+\int d^3r'\frac{\rho(r't)}{|r-r'|}+v_{xc}[\rho\ (r't')](r\ t)$$

propagated numerically on real-space grid using **`octopus`** code

***octopus: a tool for the application of time-dependent density functional theory,* A. Castro, M.A.L. Marques, H. Appel, M. Oliveira, C.A. Rozzi, X. Andrade, F. Lorenzen, E.K.U.G., A. Rubio, Physica Status Solidi 243, 2465 (2006).**

Most commonly used approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Approximation

$$v_{xc}^{adiab}(\vec{r}\ t) := v_{xc,stat}^{approx}[n]\Big|_{n=\rho(\vec{r}\ t)}$$

$$\text{e.g. } v_{xc}^{ALDA}(\vec{r}\ t) := v_{xc,stat}^{hom}\left(\rho(\vec{r}\ t)\right)$$

$v_{xc,stat}^{hom}$ **= xc potential of static homogeneous e-gas**

How restrictive is the adiabatic approximation,
i.e. the neglect of memory in the functional $v_{xc}[\rho(r',t')](r,t)$?
Can we assess the quality of the exact adiabatic approximation?

1D MODEL

- Restrict motion of electrons and nuclei to 1D (along polarization axis of laser)

- Replace in Hamiltonian all 3D Coulomb interactions by soft 1D interactions (Eberly et al)

$$\frac{1}{\sqrt{x^2+y^2+z^2}} \longrightarrow \frac{1}{\sqrt{\alpha^2+z^2}}$$

$\alpha =$ constant

- Use exact numerical solution of 1D-TDSE as exact reference to test approximate xc functionals of time-dependent density functional theory

Assess the quality of the adiabatic approximation by the following steps:

- **Solve 1D model for He atom in strong laser fields (numerically) exactly. This yields exact TD density $\rho(r,t)$.**

- **Inversion of one-particle TDSE yields exact TDKS potential. Then, subtracting the laser field and the TD-Hartree term, yields the exact TD xc potential .**

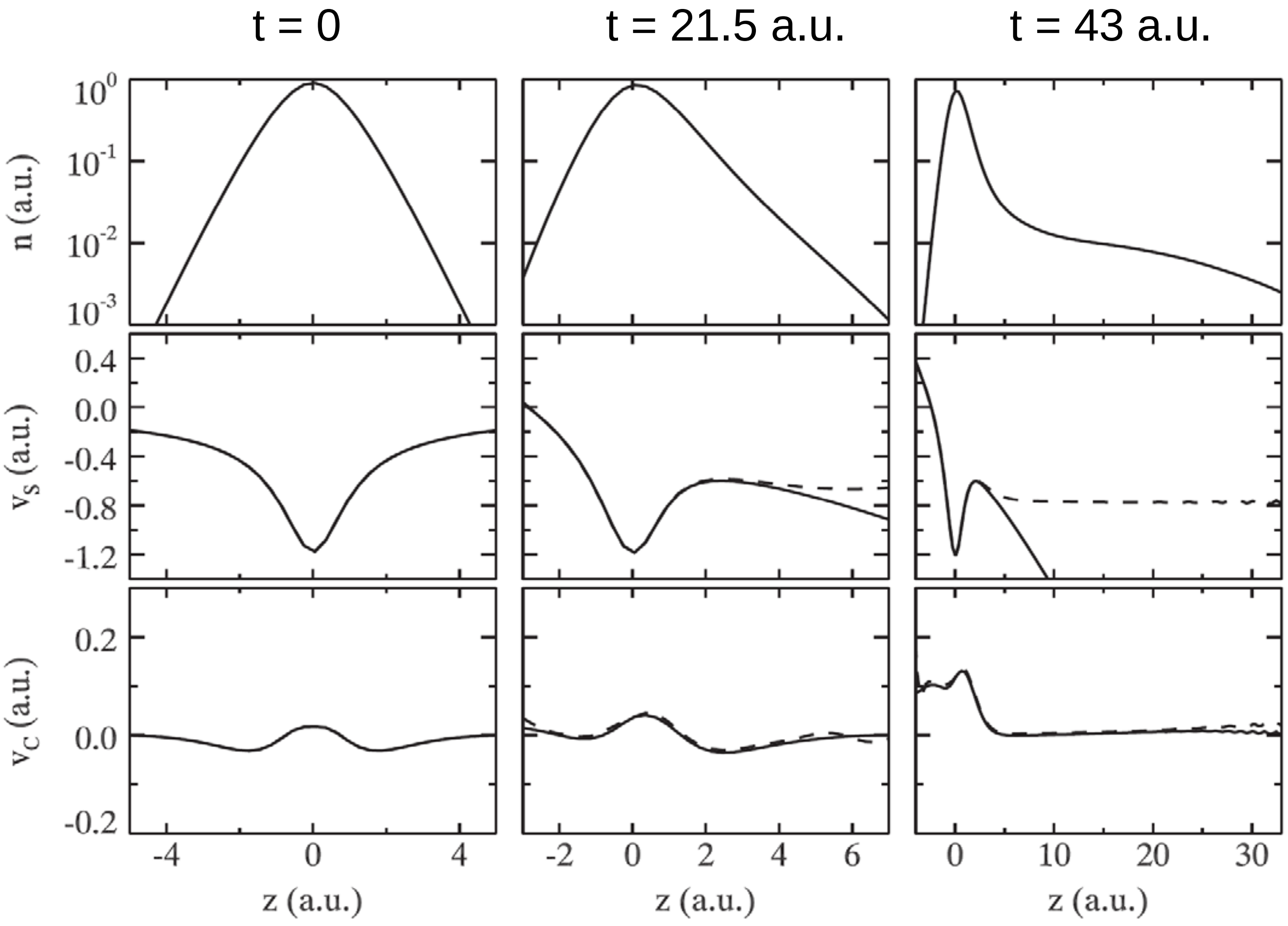
- **Inversion of one-particle ground-state SE yields the exact static KS potential, $v_{\text{KS-static}}[\rho(t)]$, that gives (for each separate t) $\rho(r,t)$ as ground-state density.**

- **Inversion of the many-particle ground-state SE yields the static external potential, $v_{\text{ext-static}}[\rho(t)]$, that gives (for each separate t) $\rho(r,t)$ as interacting ground-state density .**

- **Compare the exact TD xc potential of step 1 with the exact adiabatic approximation which is obtained by subtraction :**

$$v_{\text{xc-exact-adiab}}(t) = v_{\text{KS-static}}[\rho(t)] - v_H[\rho(t)] - v_{\text{ext-static}}[\rho(t)]$$

E(t) ramped over 27 a.u. (0.65 fs) to the value E=0.14 a.u. and then kept constant

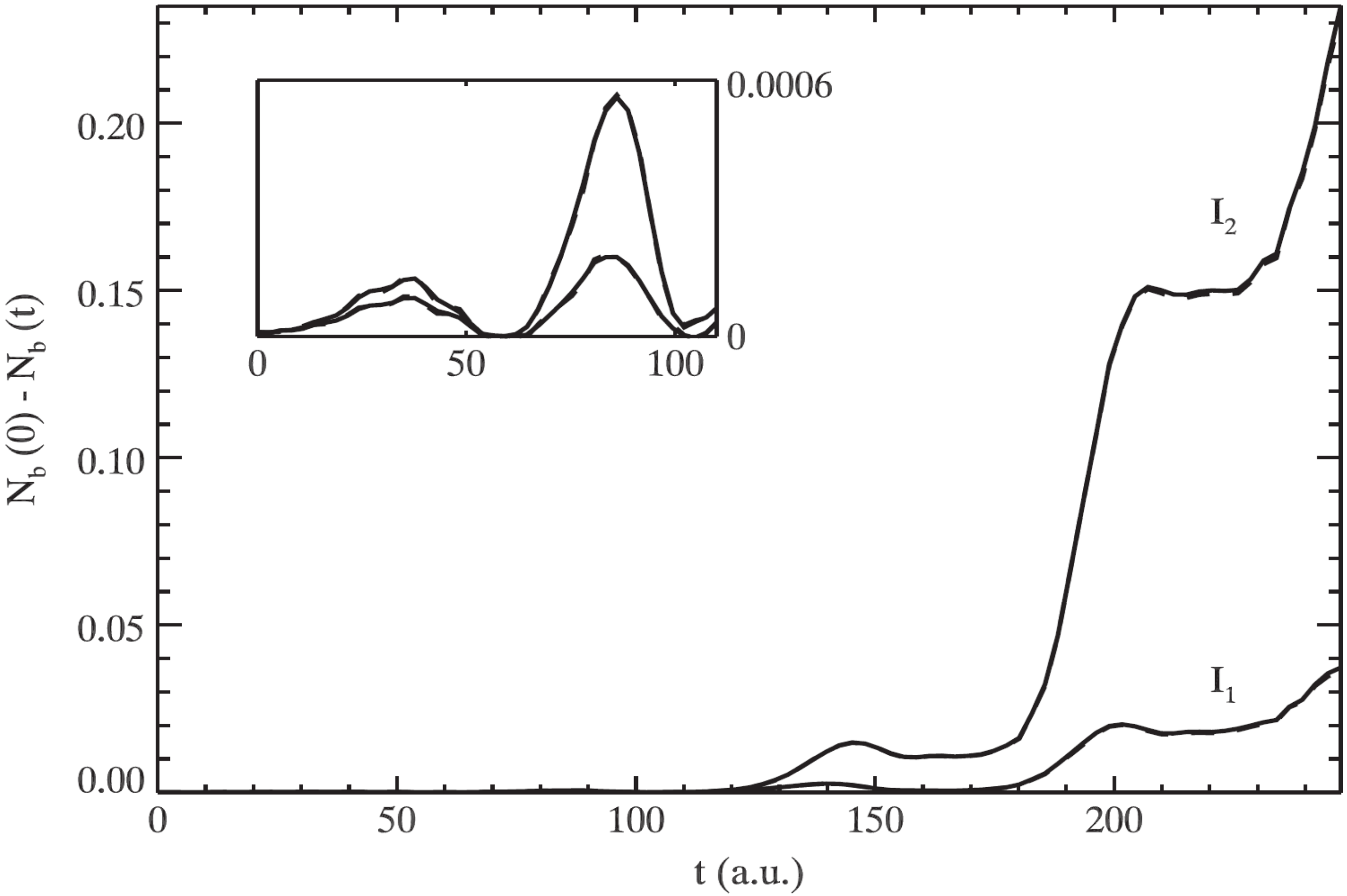


Solid line: exact

Dashed line:
exact adiabatic

M. Thiele, E.K.U.G., S. Kuemmel, Phys. Rev. Lett. **100,** 153004 (2008)

4-cycle pulse with λ = 780 nm, I_1= 4x10^{14}W/cm^2, I_2=7x10^{14}W/cm^2



Solid line: exact

Dashed line:
exact adiabatic

M. Thiele, E.K.U.G., S. Kuemmel, Phys. Rev. Lett. **100,** 153004 (2008)

Thanks !