Analysis and Optimal Control of Electron Dynamics

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OUTLINE

- **TD Electron Localization Function (TD-ELF)**

- **Optimal control of static and time-dependent targets**

THANKS

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Marko Erdmann
Volker Engel

Jan Werschnik
Ioana Serban

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)

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

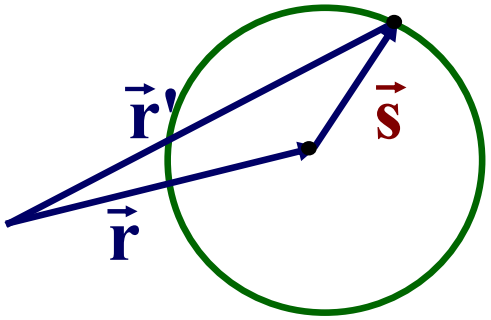
= **diagonal of two-body density matrix**

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

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

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

Coordinate transformation



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

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

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

Expand in a Taylor series:

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

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** $\vec{r}$

C_σ is always ≥ 0 (because $\mathbf{p_\sigma}$ is a probability) and $\mathbf{C_\sigma(\vec{r})}$ is not bounded from above.

Define as a useful visualization of localization
(Becke, Edgecombe, JCP 92, 5397 (1990))

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

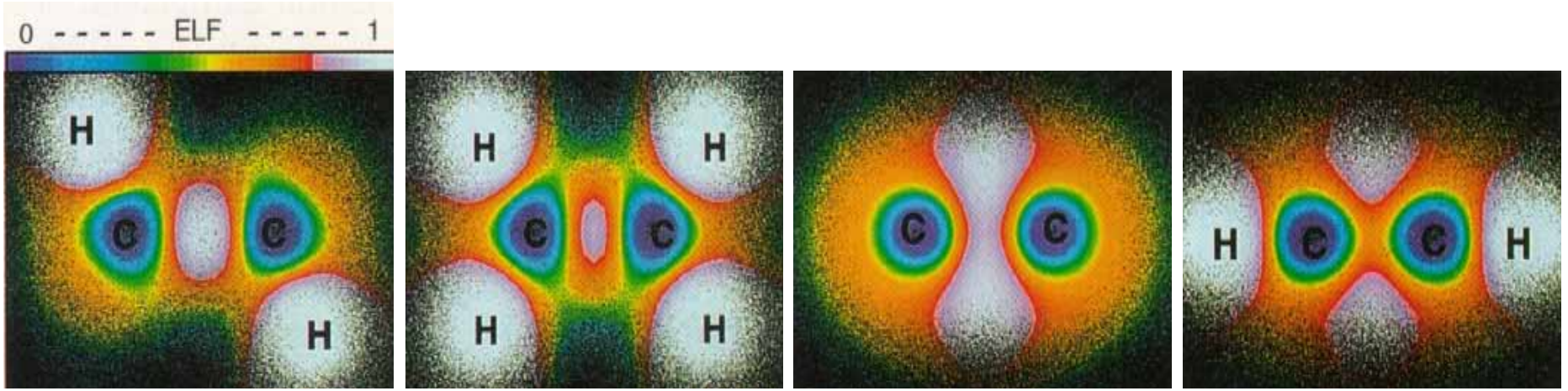
where

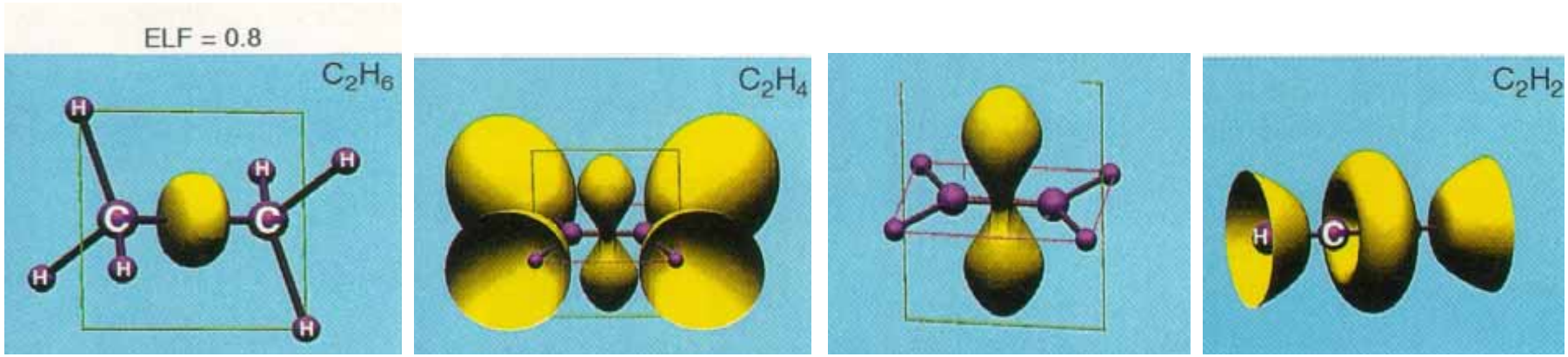
$$C_\sigma^{\mathrm{uni}}(\vec{r}) = \frac{3}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3}(\vec{r}) = \tau_\sigma^{\mathrm{uni}}(\vec{r})$$

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. Engl.* 36, 1808 (1997)

For a determinantal wave function one obtains

in the static case:

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

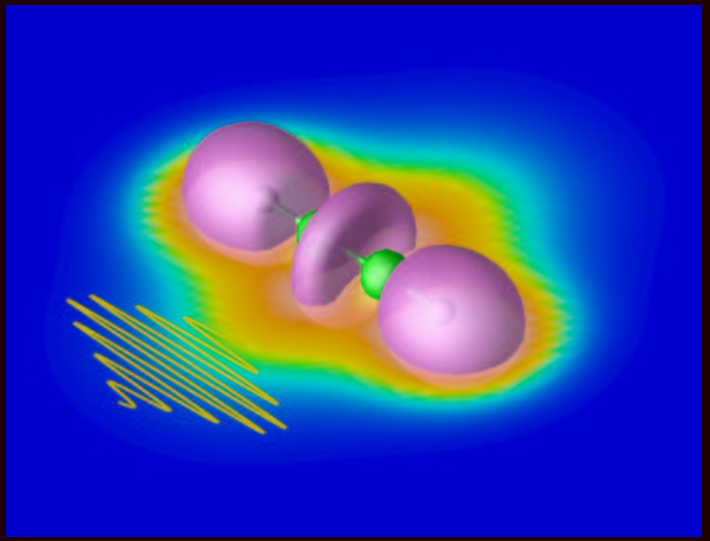
A.D. Becke, K.E. Edgecombe, *J.Chem. Phys.* 92, 5397 (1990)

in the time-dependent case:

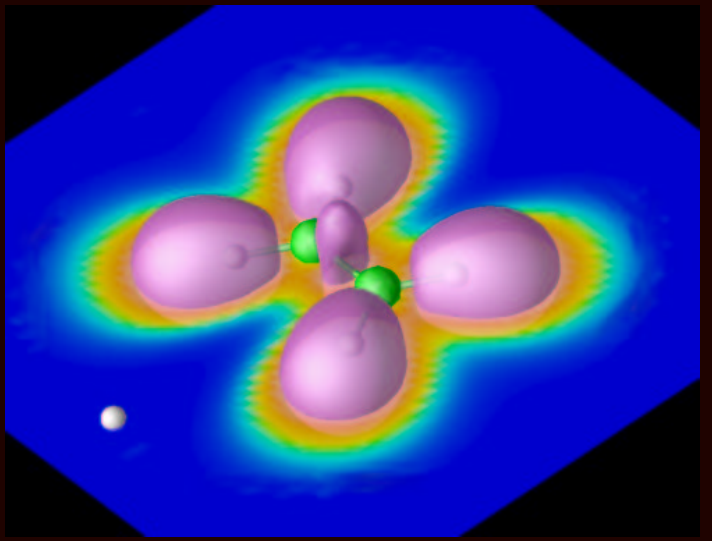
$$C_\sigma^{det}(\vec{r},t) = \sum_{i=1}^{N_\sigma} \left|\nabla \varphi_{i\sigma}(\vec{r},t)\right|^2 - \frac{1}{4}\frac{(\nabla \rho_\sigma(\vec{r},t))^2}{\rho_\sigma(\vec{r},t)} - j_\sigma(\vec{r},t)^2/\rho_\sigma(\vec{r},t)$$

T. Burnus, M. Marques, E.K.U.G., *Phys. Rev. A (Rapid Comm)* 71, 010501 (2005)

Ethyne (acetylene) in a strong laser field

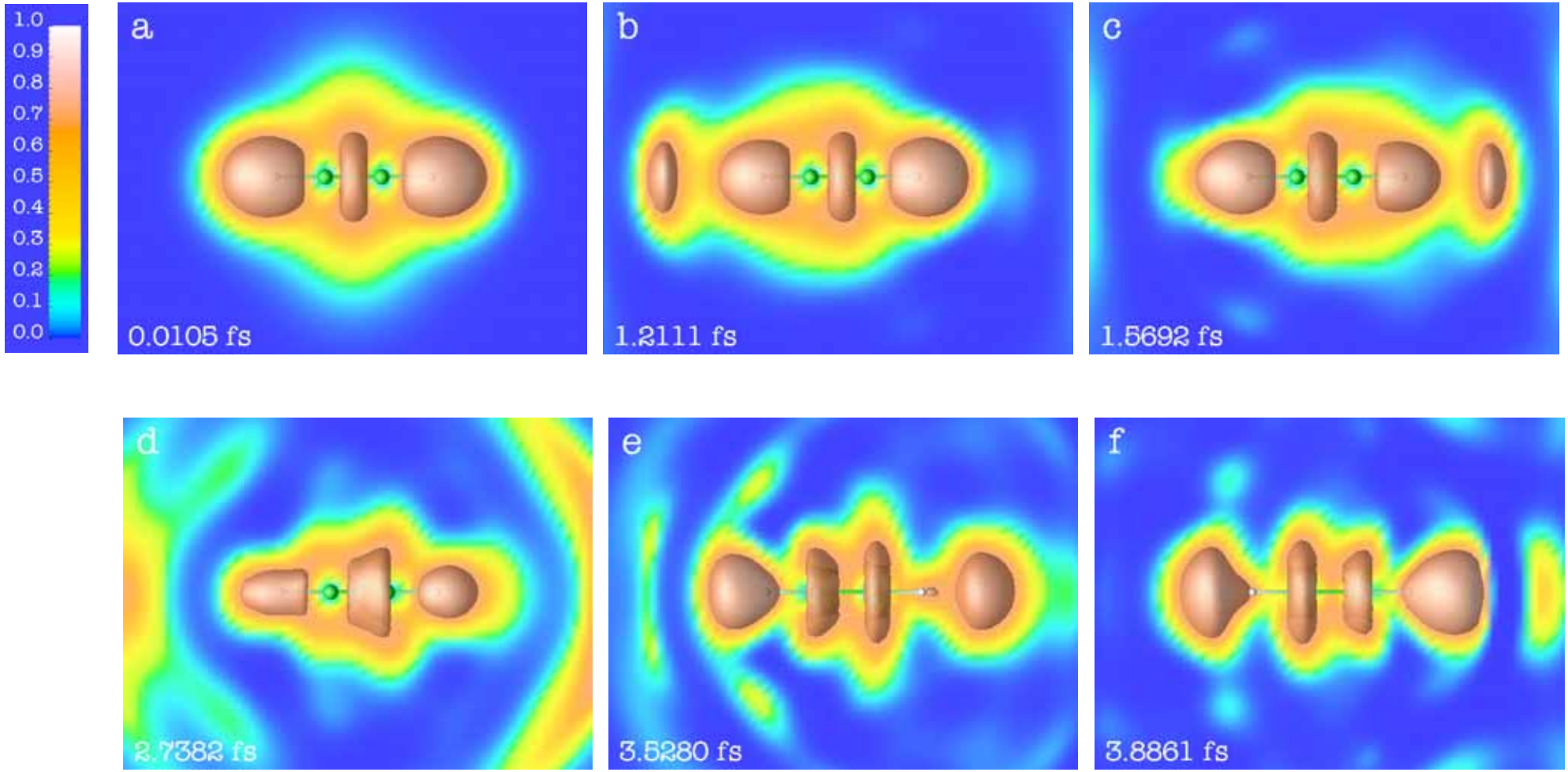


Scattering of a high energetic proton on ethene (ethylene)



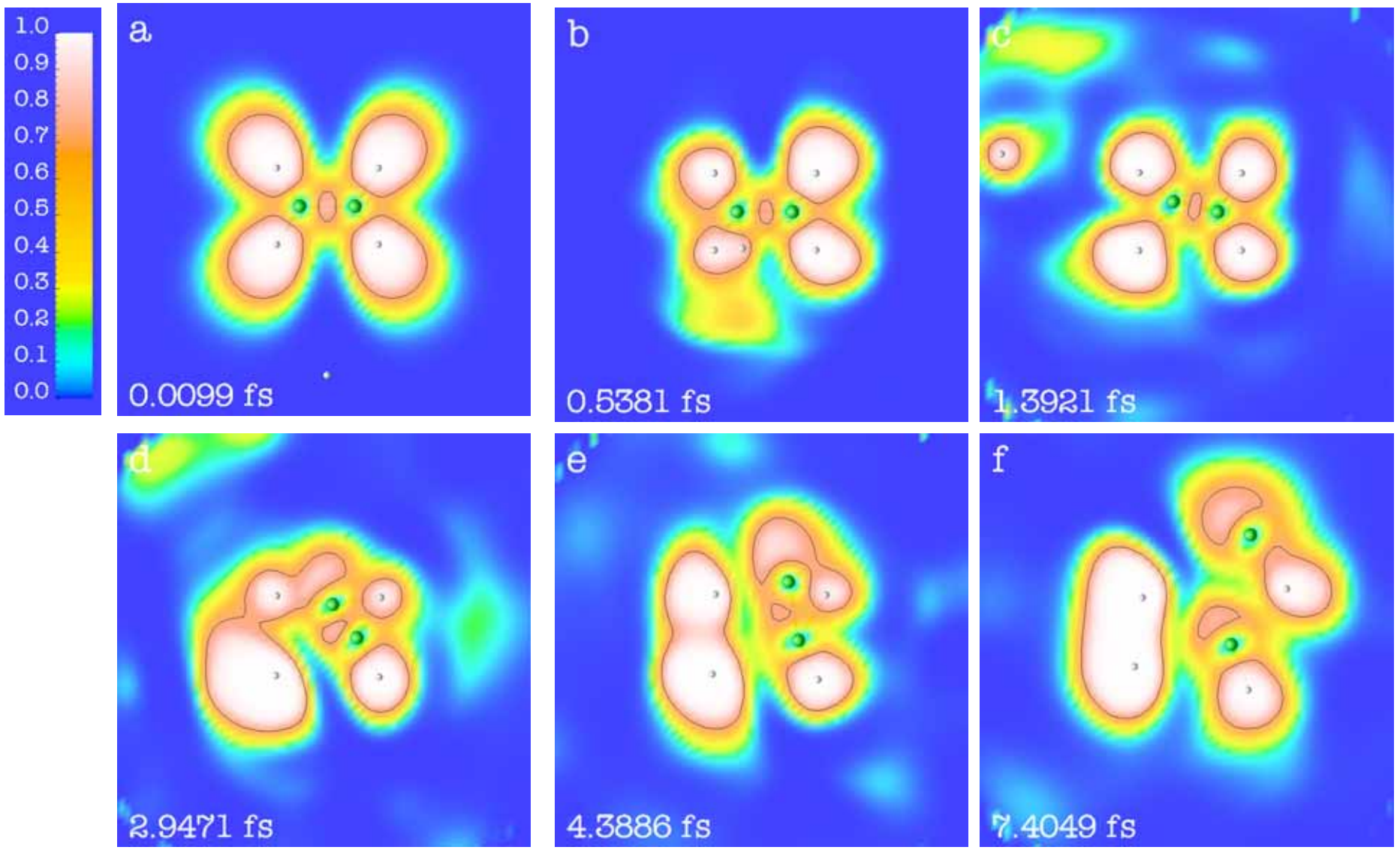
TD-ELF Examples

Ethyne (acetylene) in a strong laser field



TD-ELF Examples

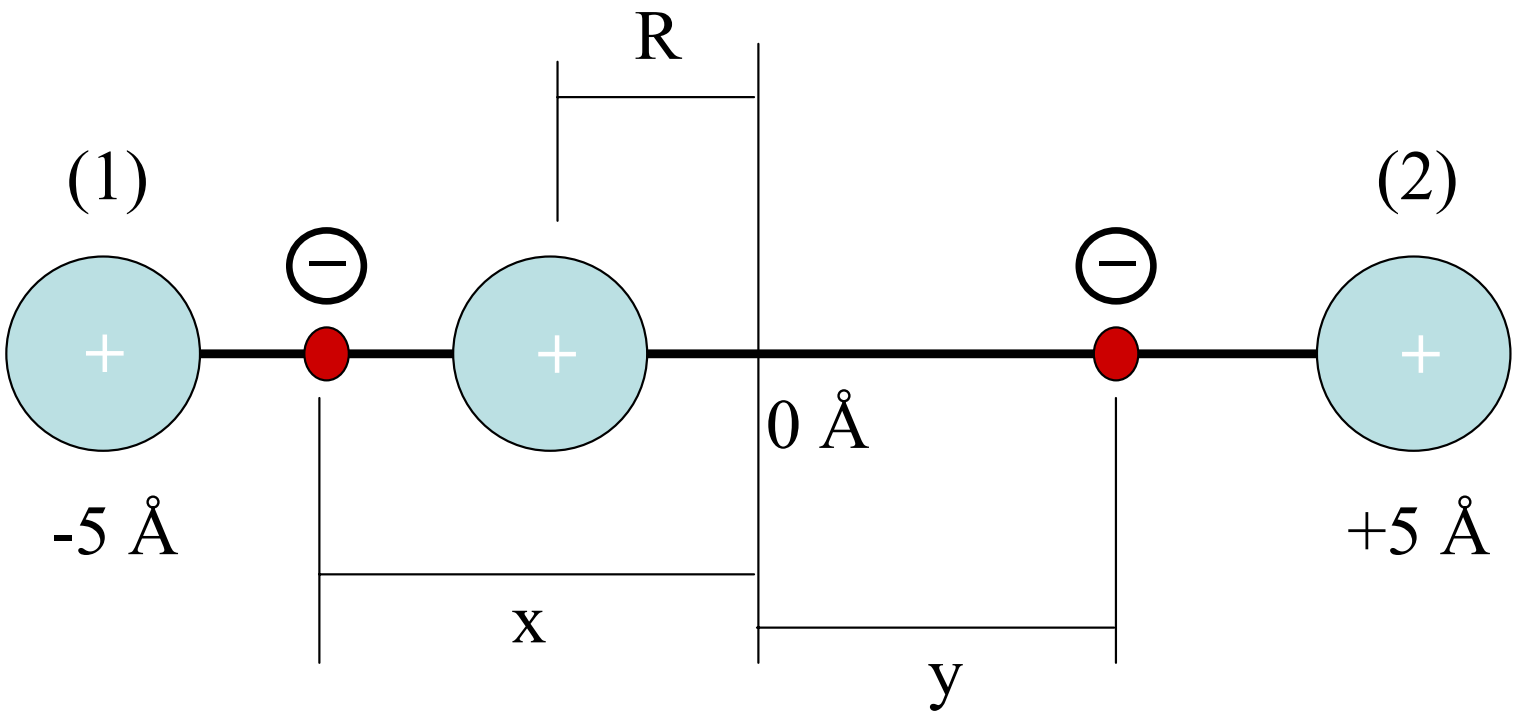
Scattering of an energetic proton from ethene (ethylene)



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 ?**

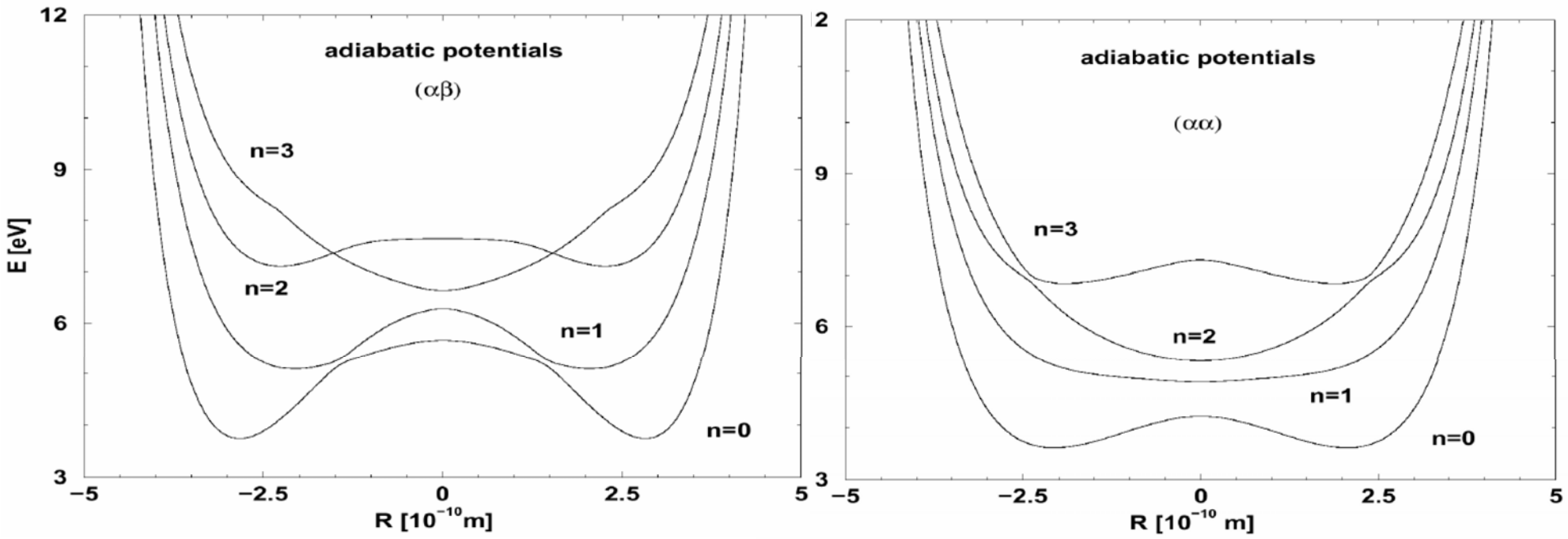
MODEL



Nuclei (1) and (2) are heavy: Their positions are fixed

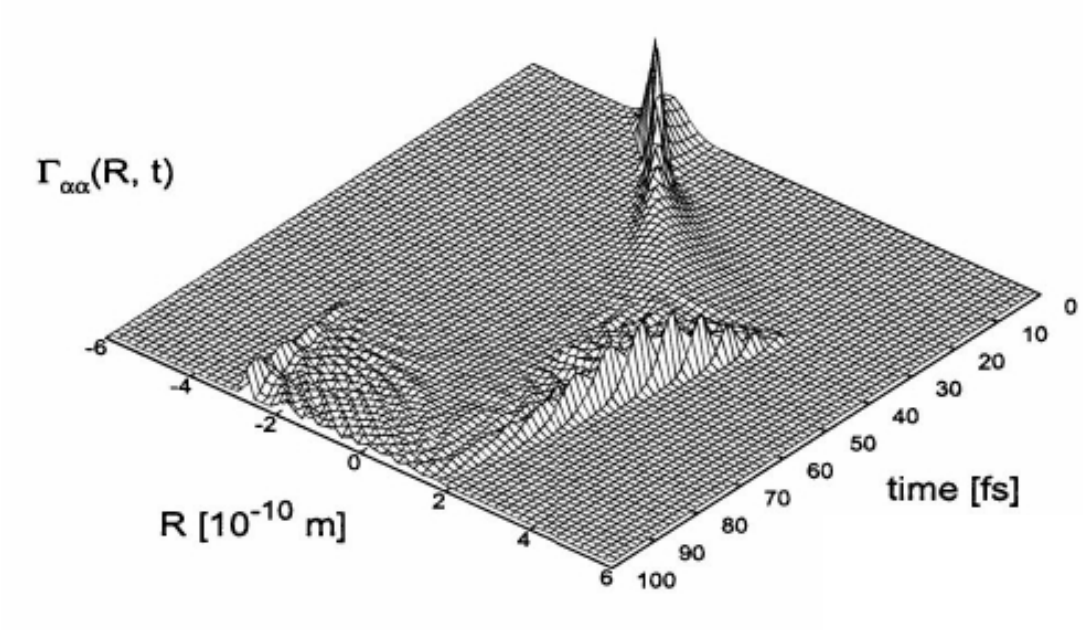
Anti-parallel spins

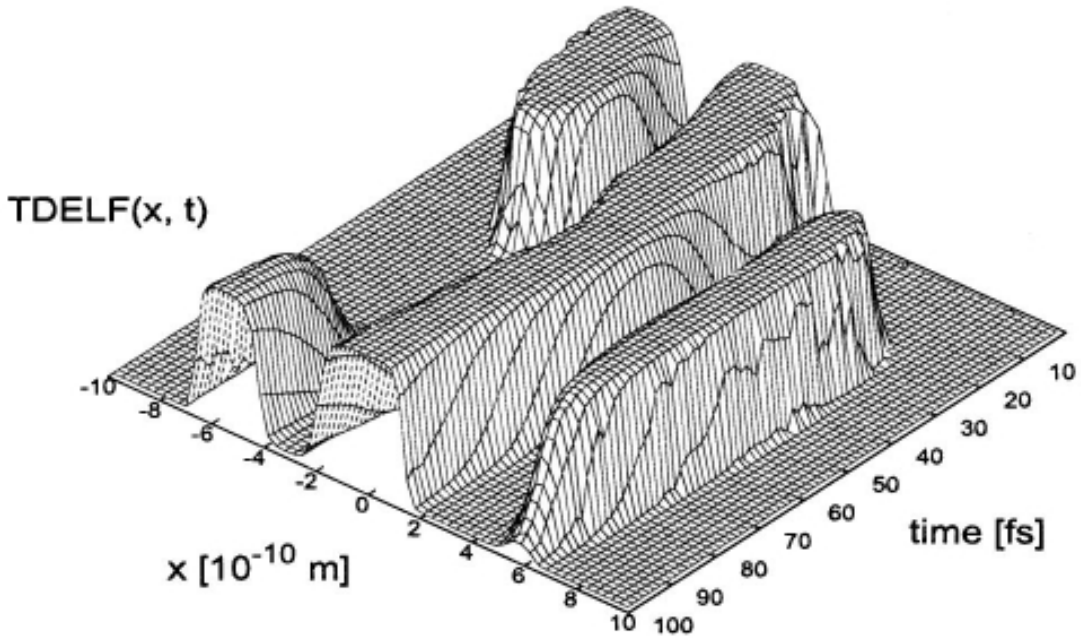
Parallel spins



M. Erdmann, E.K.U.G., V. Engel, JCP 121, 9666 (2004)

Parallel spins





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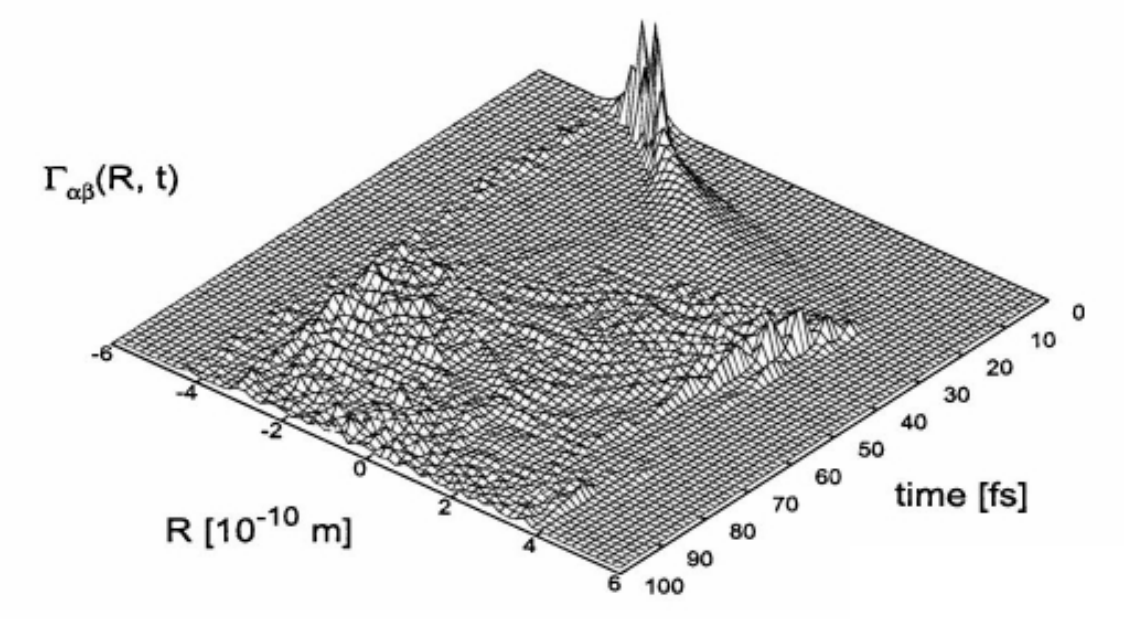
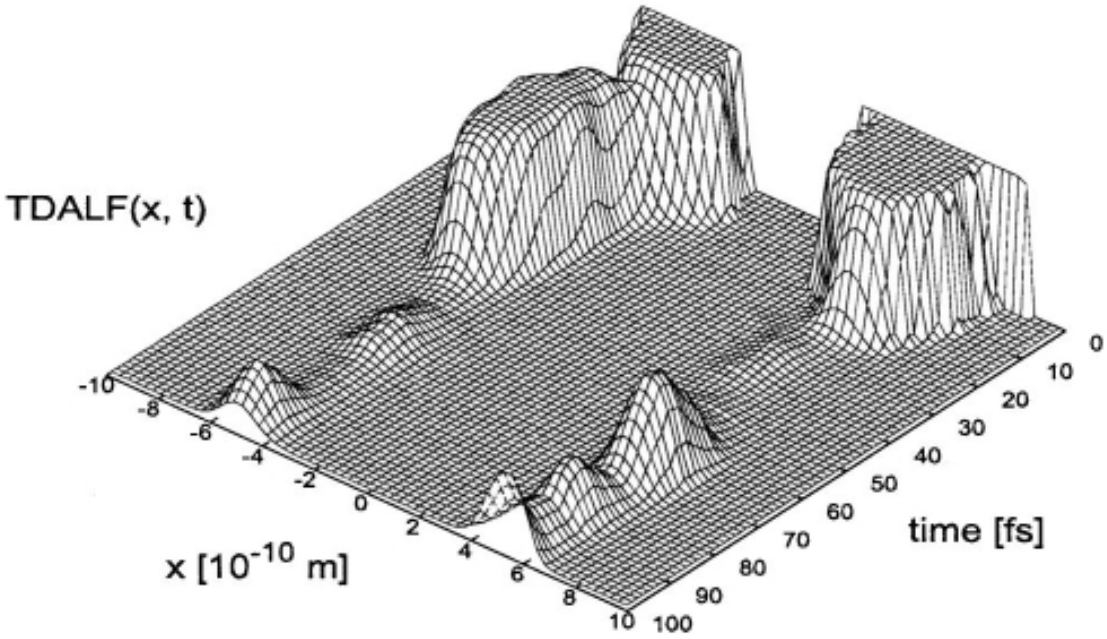
Anti-parallel spins





TD-ELF is a measure of non-adiabaticity

Optimal Control Theory (OCT)

Normal question:

What happens if a system is exposed to a given laser pulse?

Inverse question (solved by OCT):

Which is the laser pulse that achieves a prescribed goal?

possible goals:

a) **system should end up in a given final state ϕ_f at the end of the pulse**

b) **wave function should follow a given trajectory in Hilbert space**

c) **density should follow a given classical trajectory r(t)**

Optimal control of static targets (standard formulation)

For <u>given</u> target state Φ_f , maximize the functional:

$$J_1 = \left| \left\langle \Psi(T) \middle| \Phi_f \right\rangle \right|^2 = \left\langle \Psi(T) \middle| \Phi_f \right\rangle \left\langle \Phi_f \middle| \Psi(T) \right\rangle = \left\langle \Psi(T) \middle| \hat{O} \middle| \Psi(T) \right\rangle$$

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$\hat{O}$

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$\hat{O}$

with the constraints:

$$J_2 = -\alpha \left[\int_0^T dt \varepsilon^2(t) - E_0 \right]$$

E_0 = <u>given</u> fluence

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$$J_3[\varepsilon,\Psi,\chi] = -2\,\mathrm{Im}\int_0^T dt\left\langle \chi(t)\middle|-i\partial_t - \left[\hat{T}+\hat{V}-\mu\varepsilon(t)\right]\middle|\Psi(t)\right\rangle$$

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TDSE

Control equations

Set the total variation of $J = J_1 + J_2 + J_3$ equal to zero:

1. Schrödinger equation with initial condition:

$$\delta_\chi J = 0 \rightarrow \boxed{i\partial_t \psi(t) = \hat{H}(t)\psi(t), \quad \psi(0) = \phi}$$

2. Schrödinger equation with final condition:

$$\delta_\psi J = 0 \rightarrow \boxed{i\partial_t \chi(t) = \hat{H}(t)\chi(t), \quad \chi(T) = \hat{O}\psi(T)}$$

3. Field equation:

$$\delta_\varepsilon J = 0 \rightarrow \boxed{\varepsilon(t) = \frac{1}{\alpha}\,\mathrm{Im}\left\langle \chi(t)\middle|\hat{\mu}\middle|\psi(t)\right\rangle}$$

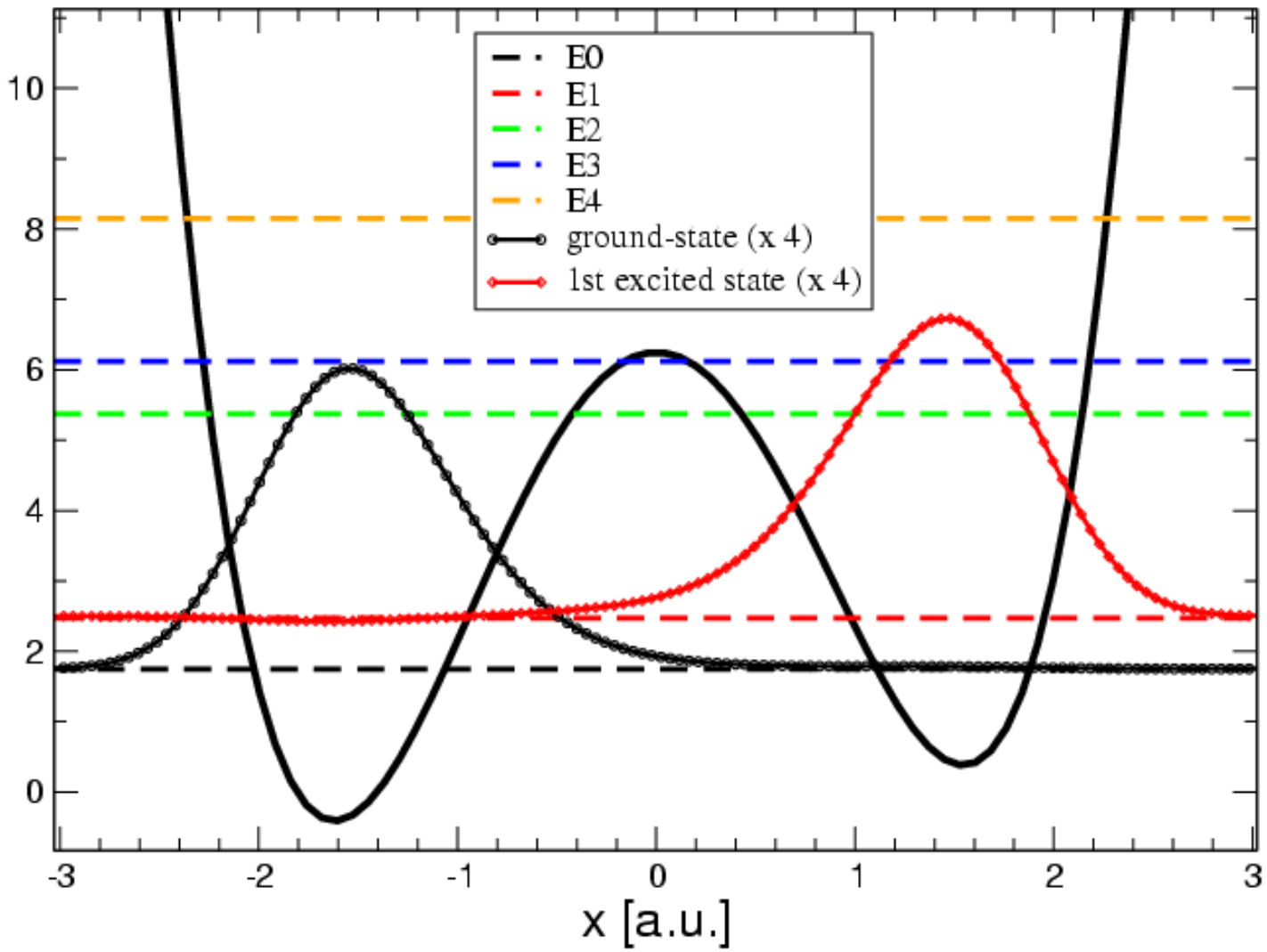
algorithm

Forward propagation of TDSE $\Rightarrow \Psi^{(k)}$

Backward propagation of TDSE $\Rightarrow \chi^{(k)}$

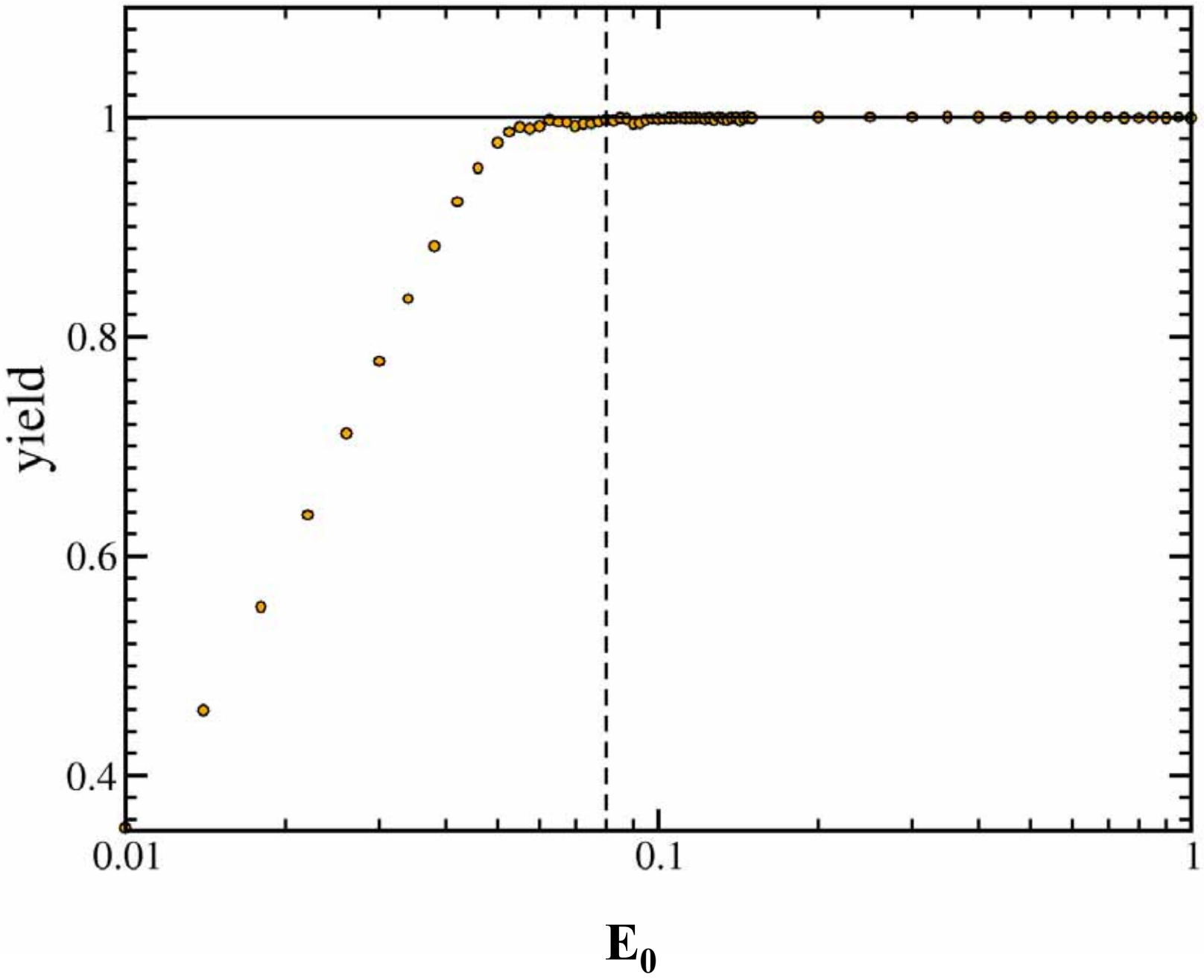
new field: $$\tilde{\varepsilon}^{(k+1)}(t) = -\frac{1}{\alpha}\,\mathrm{Im}\left\langle \chi^{(k)}(t)\left|\hat{\mu}\right|\Psi^{(k)}(t)\right\rangle$$

(W. Zhu, J. Botina, H. Rabitz, J. Chem. Phys. 108, 1953 (1998))



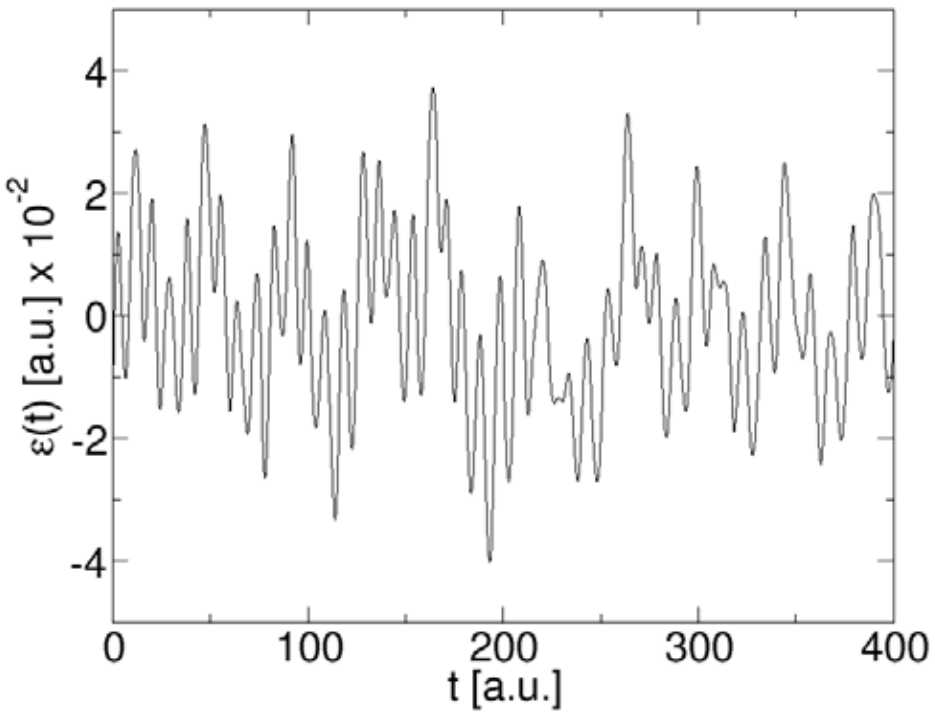
target state: ϕ_f = first excited state

(lives in the well on the right-hand side)

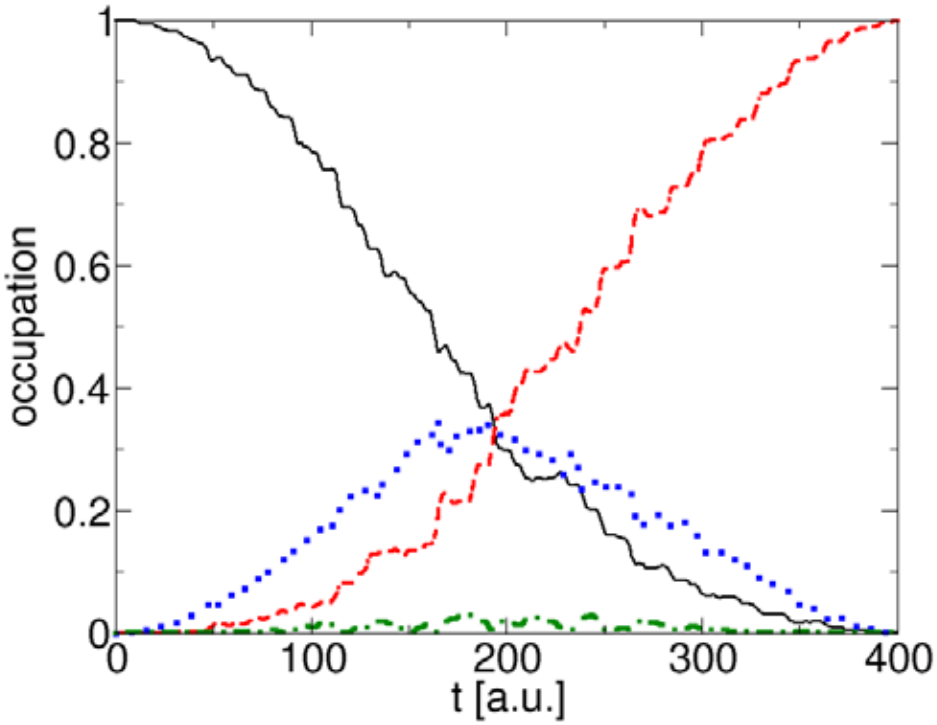

yield
1
0.8
0.6
0.4
0.01
0.1
1
E0

Optimization results

Optimized pulse

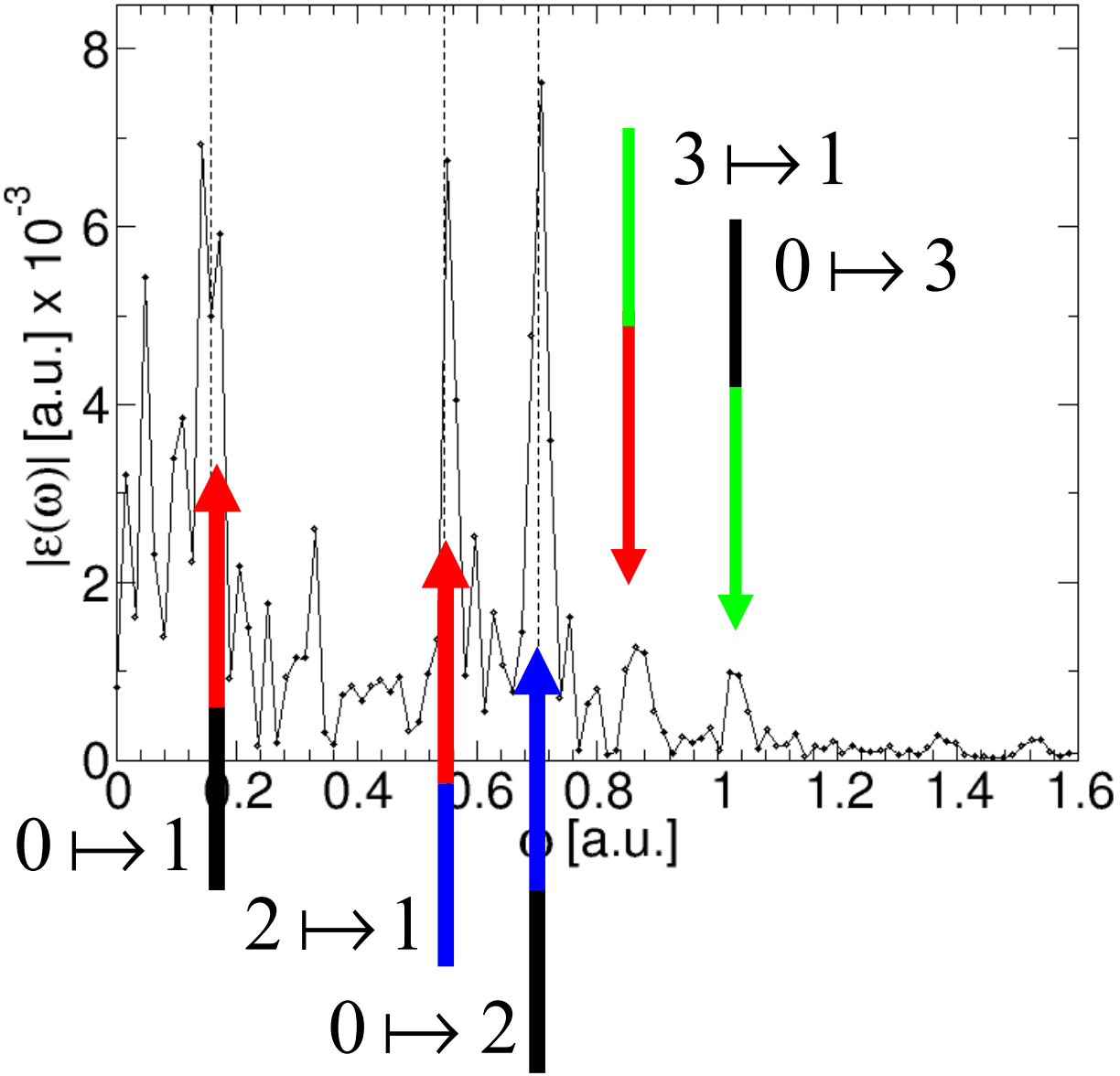


Occupation numbers

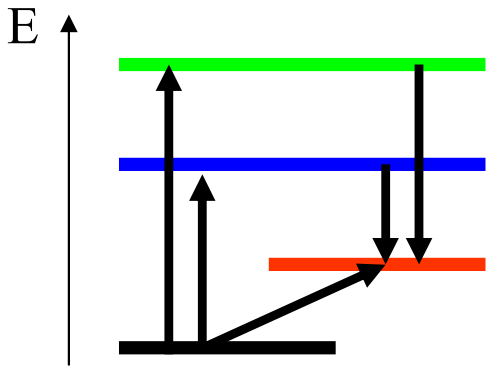


$$\left|\langle 1|\psi(T)\rangle\right|^2 = 99.91\%$$

Spectrum



OCT finds a combination of several transition processes



Filter algorithm

Forward propagation of TDSE $\Rightarrow \Psi^{(k)}$

Backward propagation of TDSE $\Rightarrow \chi^{(k)}$

new field: $$\tilde{\varepsilon}^{(k+1)}(t) = -\frac{1}{\alpha}\,\mathrm{Im}\left\langle \chi^{(k)}(t)\left|\hat{\mu}\right|\Psi^{(k)}(t)\right\rangle$$

(W. Zhu, J. Botina, H. Rabitz, J. Chem. Phys. 108, 1953 (1998))

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(W. Zhu, J. Botina, H. Rabitz, J. Chem. Phys. 108, 1953 (1998))

With spectral constraint:

$$\varepsilon^{(k+1)}(t) := \mathcal{F}\left[f(\omega)\times\mathcal{F}\left[\tilde{\varepsilon}^{(k+1)}(t)\right]\right]$$

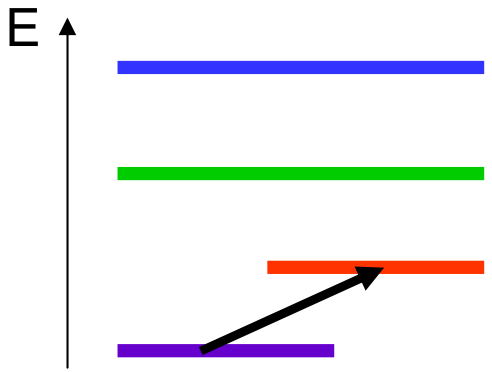
filter function: $$f(\omega) = \exp\left[-\gamma(\omega-\omega_0)^2\right] + \exp\left[-\gamma(\omega+\omega_0)^2\right]$$

or $$f(\omega) = 1 - \exp\left[-\gamma(\omega-\omega_0)^2\right] - \exp\left[-\gamma(\omega+\omega_0)^2\right]$$

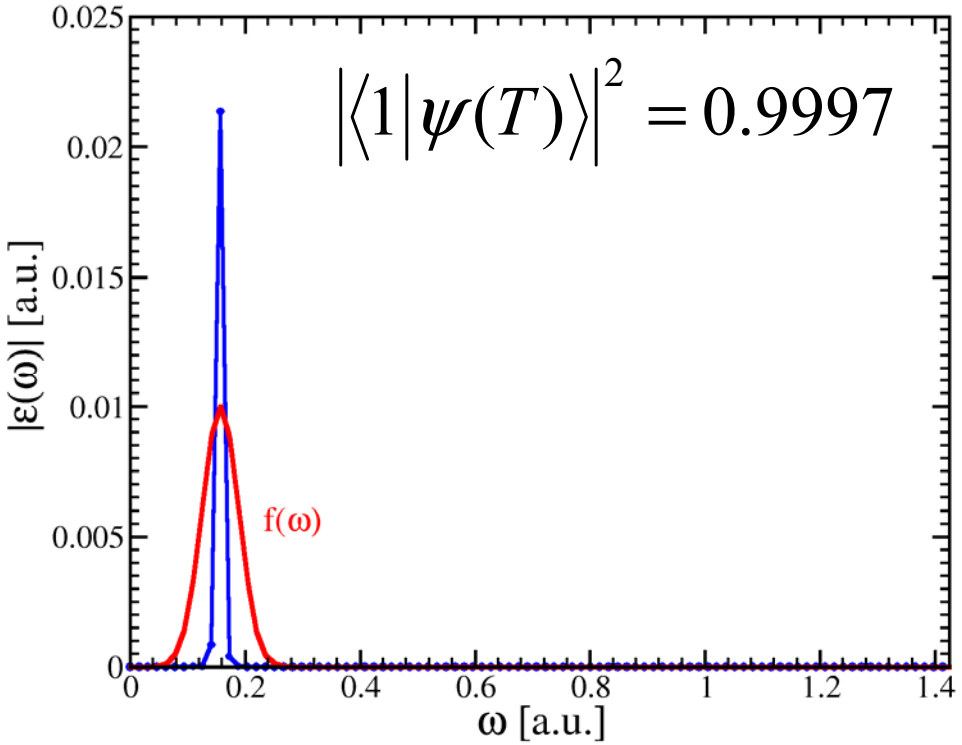
J. Werschnik, E.K.U.G., J. Opt. B 7, S300 (2005)

Frequency constraint:

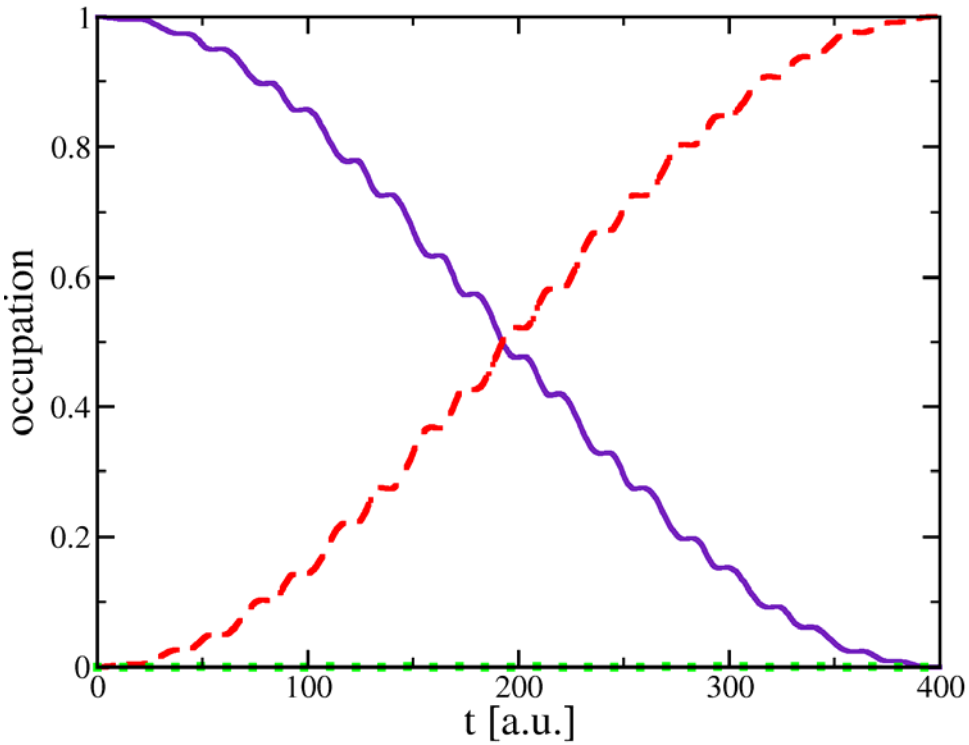
Only direct transition frequency ω_0 allowed



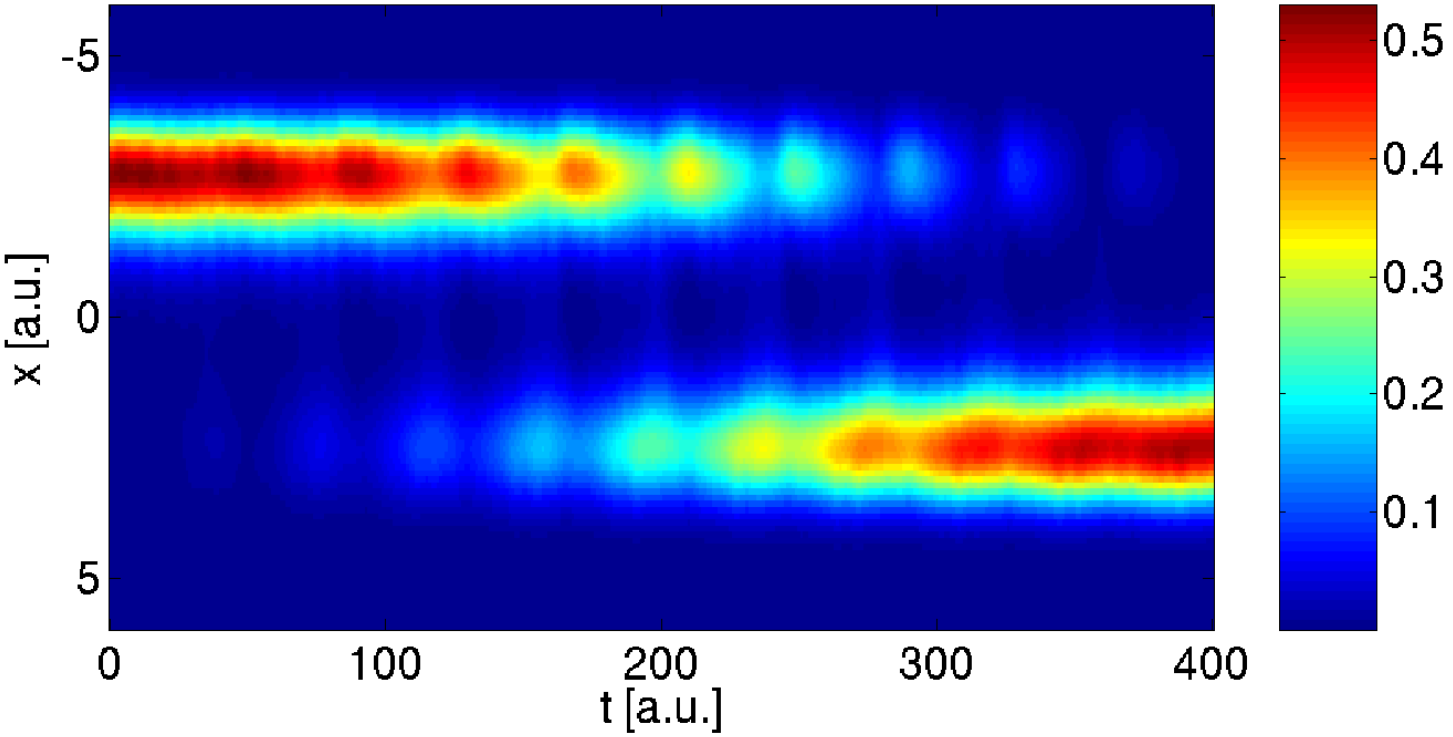
Spectrum of optimized pulse



occupation numbers



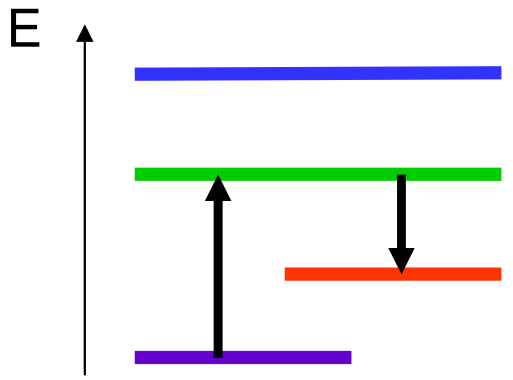
Time-Dependent Density



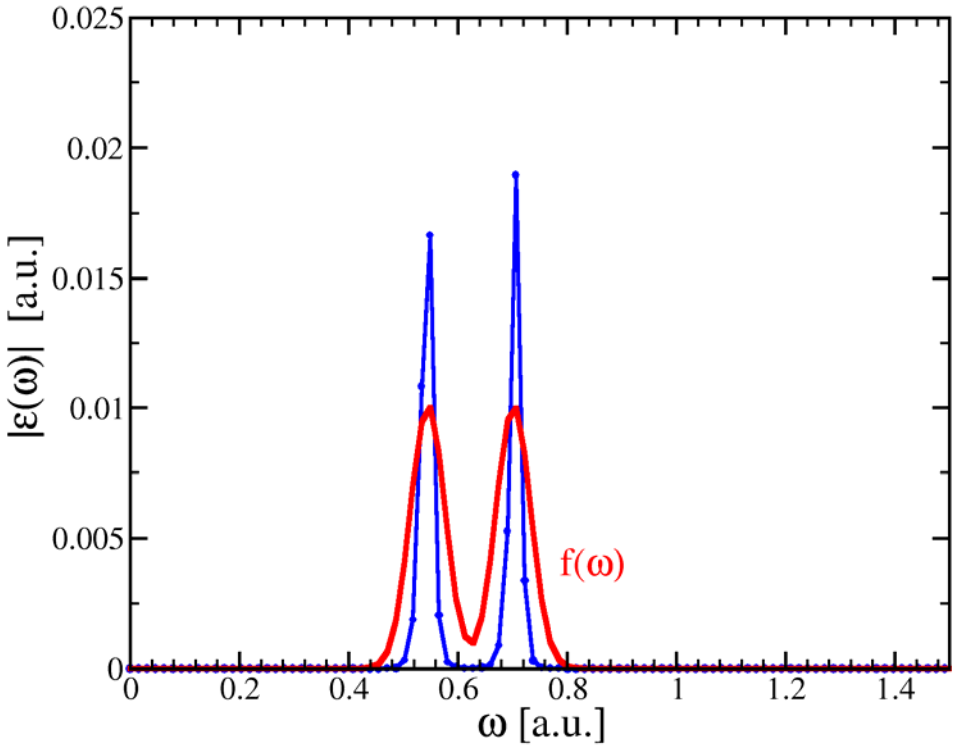
Frequency constraint:

Selective transfer via intermediate state $|2\rangle$

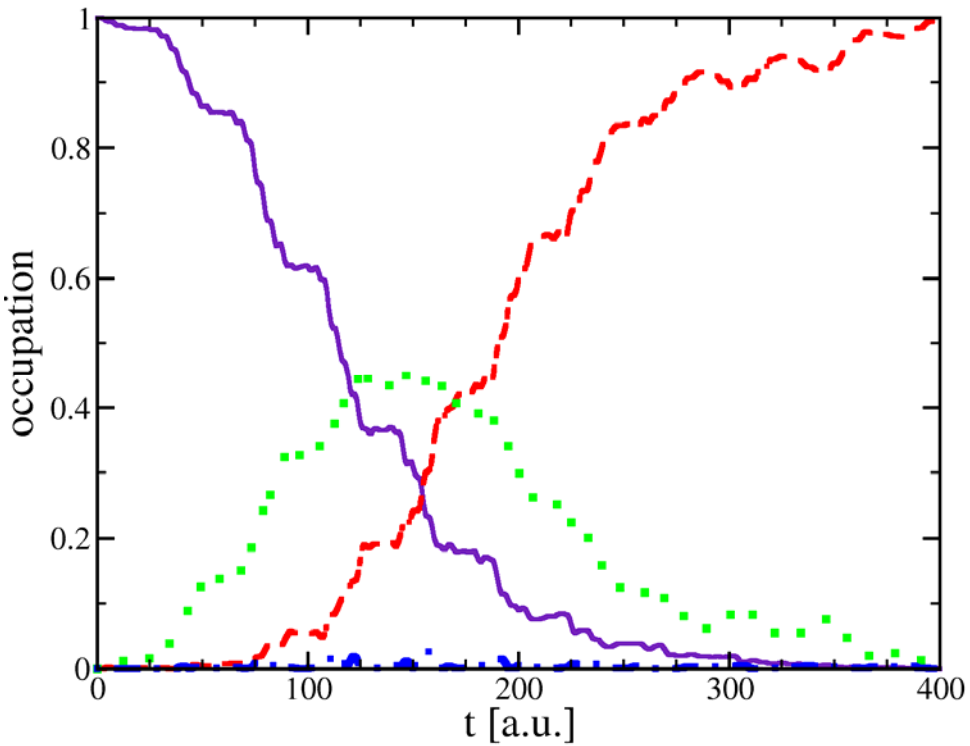
$$|0\rangle \xrightarrow{\omega_{02}} |2\rangle \xrightarrow{\omega_{21}} |1\rangle$$



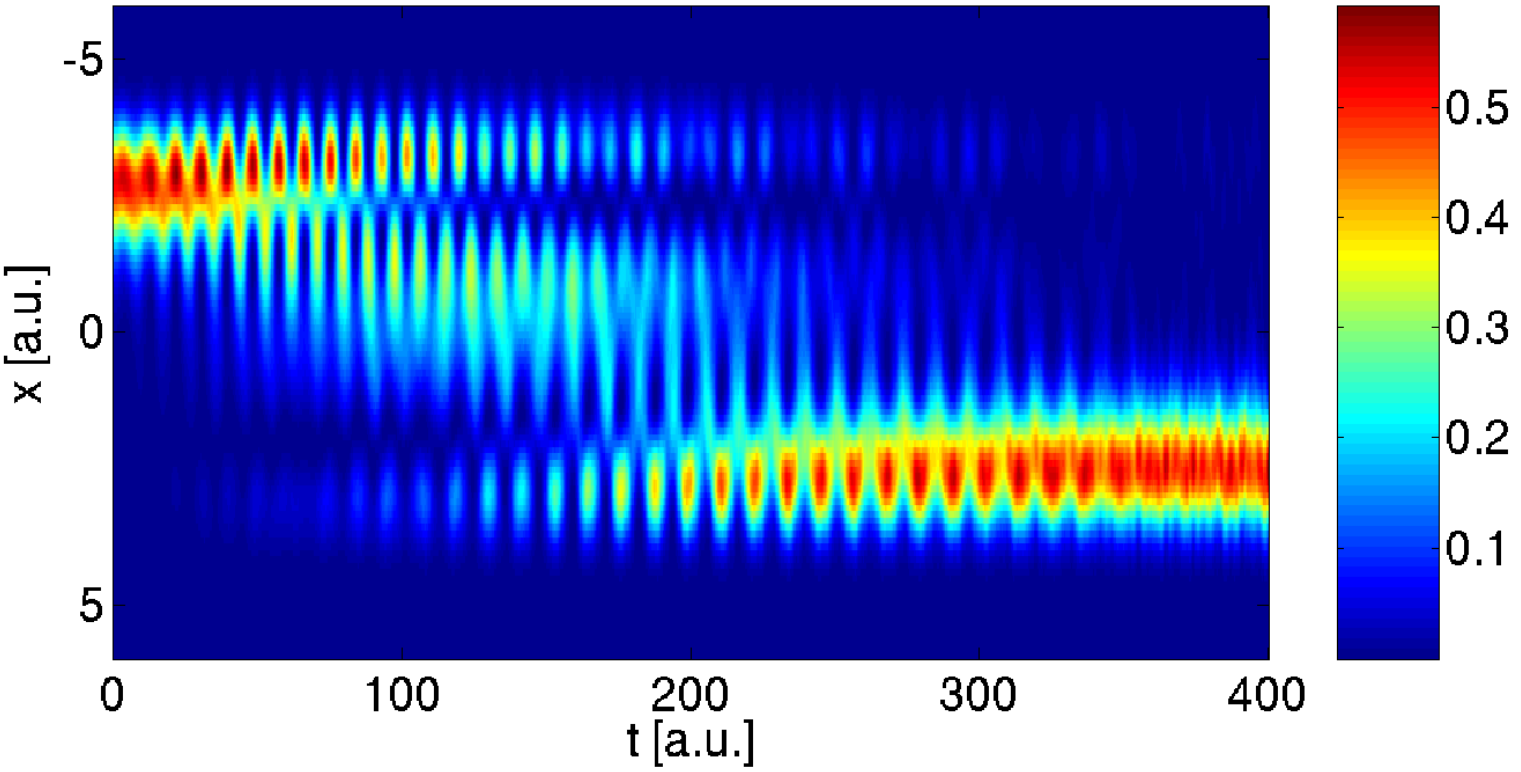
Spectrum of optimized pulse



occupation numbers



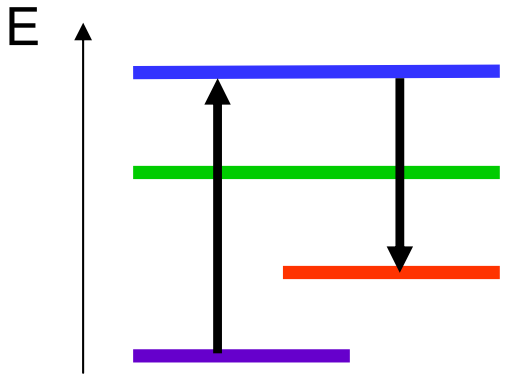
Time-Dependent Density

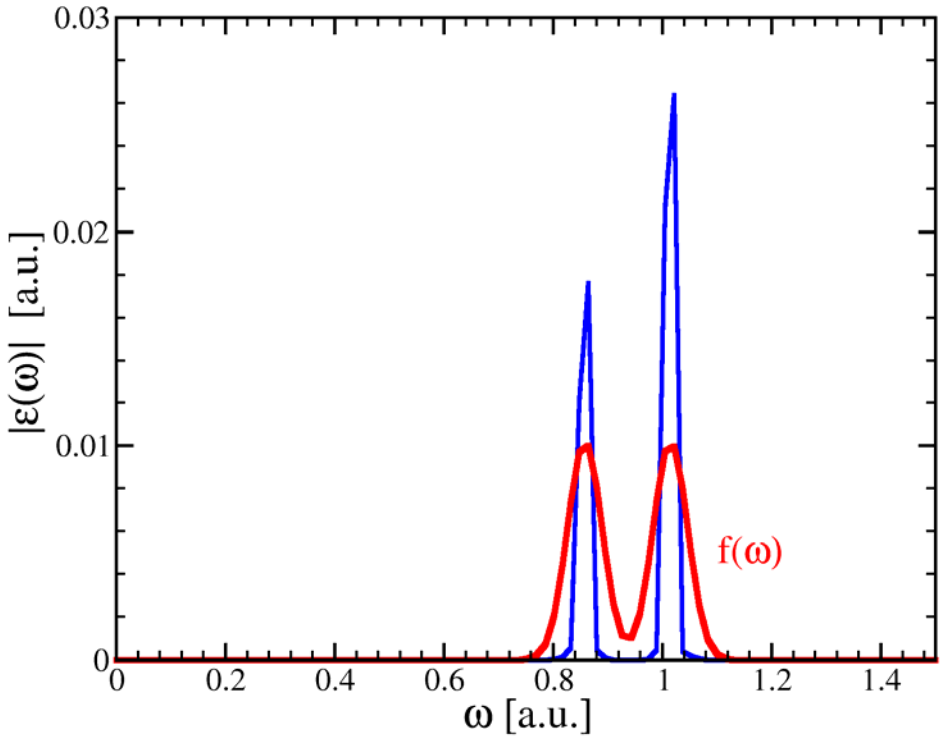


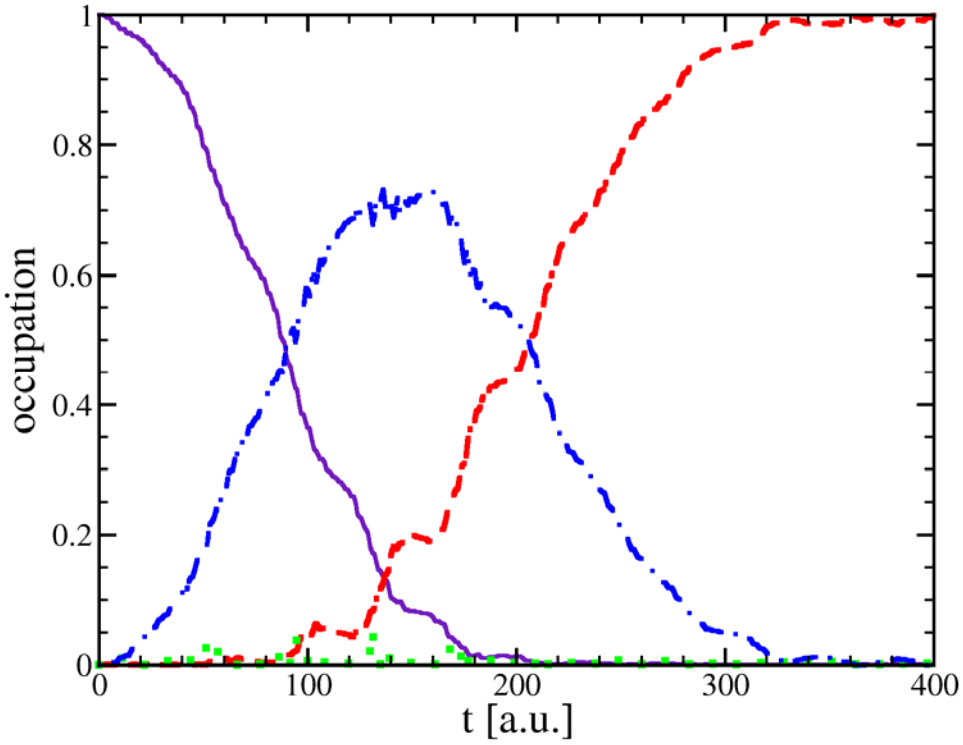
Frequency constraint:

Selective transfer via intermediate state $|3\rangle$

$$|0\rangle \xrightarrow{\omega_{03}} |3\rangle \xrightarrow{\omega_{31}} |1\rangle$$

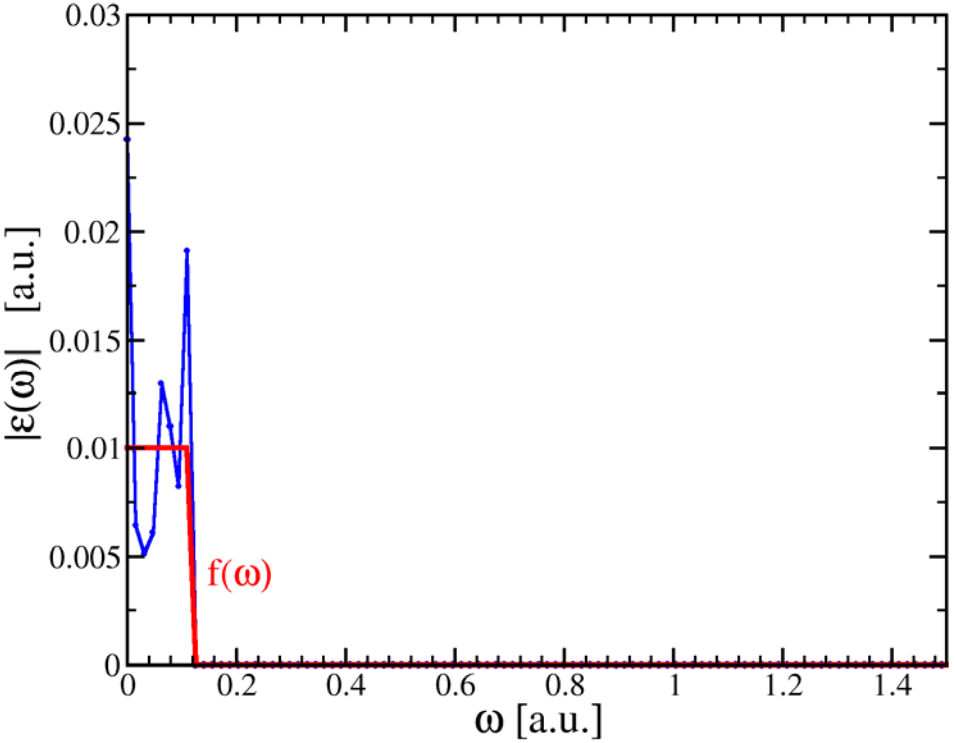




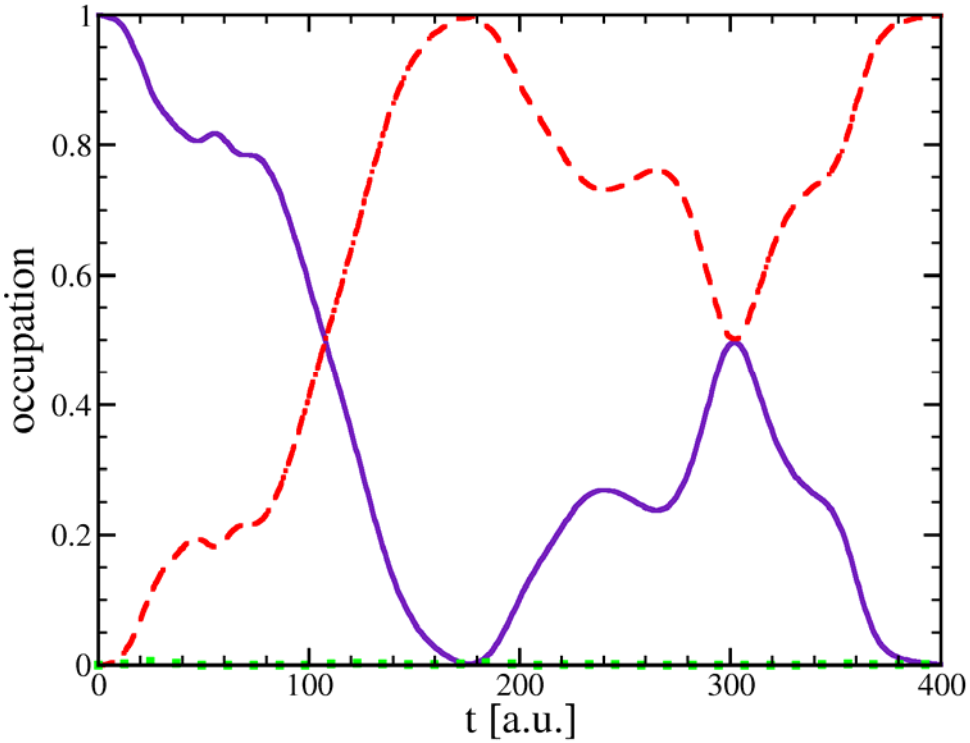


Frequency constraint: All resonances excluded

Spectrum of optimized pulse



occupation numbers



All pulses shown give practically 100% occupation at the end of the pulse

OPTIMAL CONTROL OF TIME-DEPENDENT TARGETS

I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

Maximize $J = J_1 + J_2 + J_3$

$$J_1[\Psi] = \frac{1}{T}\int_0^T dt \left\langle \Psi(t) \middle| \hat{O}(t) \middle| \Psi(t) \right\rangle$$

$$J_2 = -\alpha\left[\int_0^T dt\,\varepsilon^2(t) - E_0\right]$$

$$J_3[\varepsilon,\Psi,\chi] = -2\,\mathrm{Im}\int_0^T dt \left\langle \chi(t) \middle| -i\partial_t - \left[\hat{T} + \hat{V} - \mu\varepsilon(t)\right] \middle| \Psi(t) \right\rangle$$

Control equations

- Set total functional derivative to zero

1. Schrödinger equation with initial condition:

$$\left[i\partial_t - \hat{H}(t)\right]\psi(t) = 0, \qquad \psi(0) = \phi$$

2. Inhomogenous TDSE :

$$\left[i\partial_t - \hat{H}(t)\right]\chi(t) = -\frac{i}{T}\hat{O}(t)\psi(t), \qquad \chi(T) = 0$$

3. Field equation:

$$\varepsilon(t) = \frac{1}{\alpha}\,\mathrm{Im}\left\langle \chi(t)\middle|\hat{\mu}\middle|\psi(t)\right\rangle$$

Two-level system

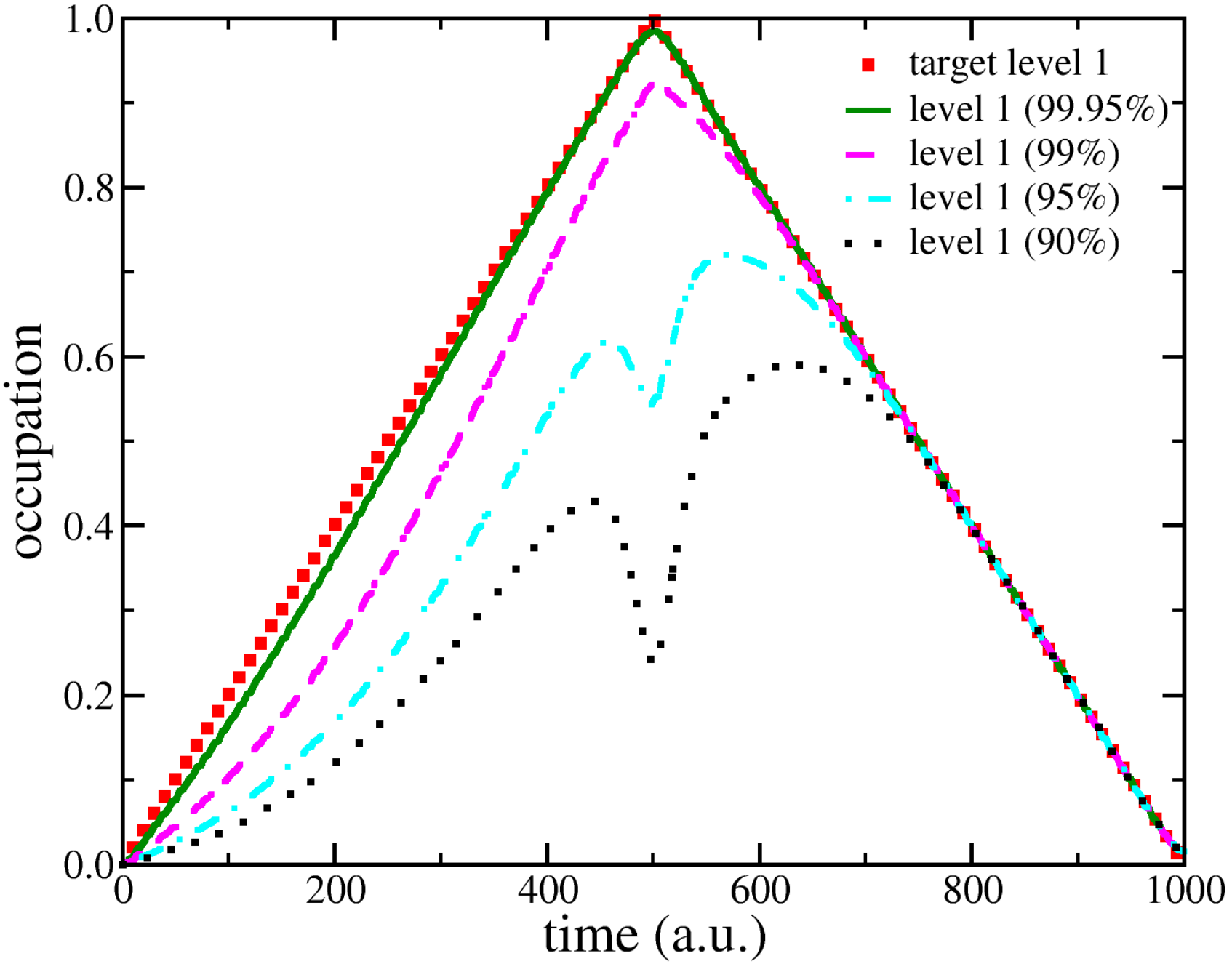
Control of time-dependent occupation numbers:

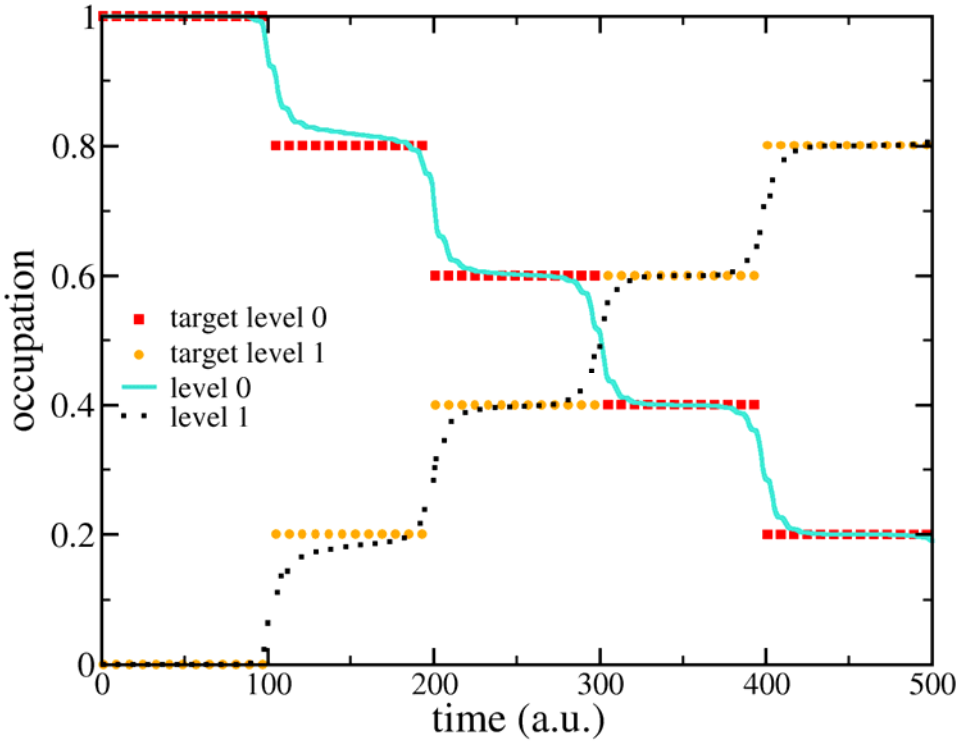
$$\hat{O}(t) = |\Phi(t)\rangle\langle\Phi(t)|$$

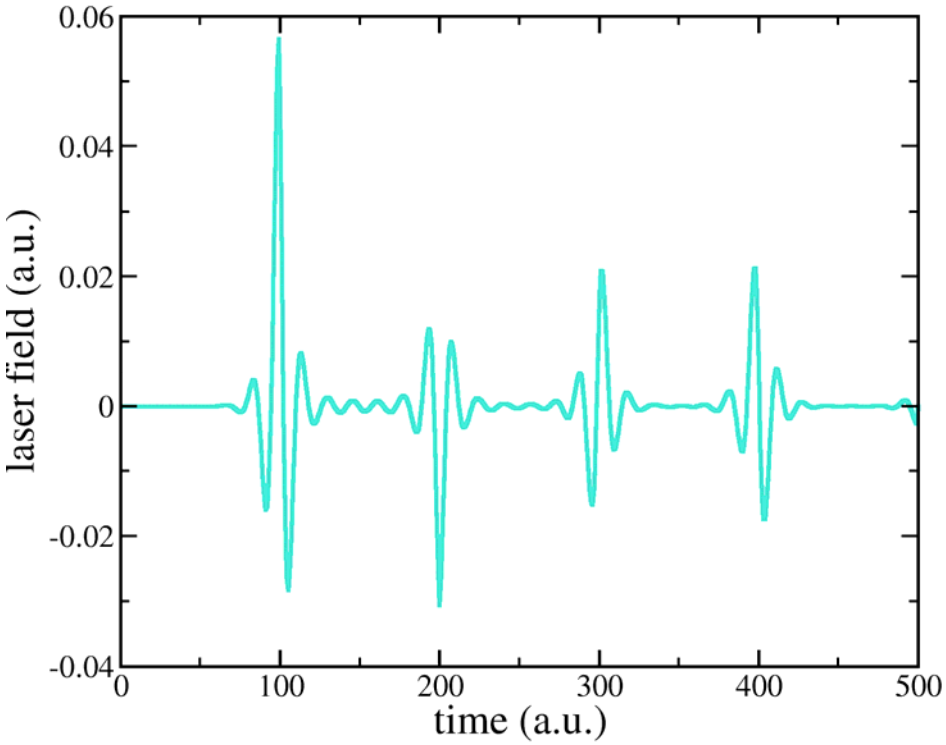
with $|\Phi(t)\rangle = \alpha_0(t)e^{-i\varepsilon_o t}|0\rangle + \alpha_1(t)e^{-i\varepsilon_1 t}|1\rangle$

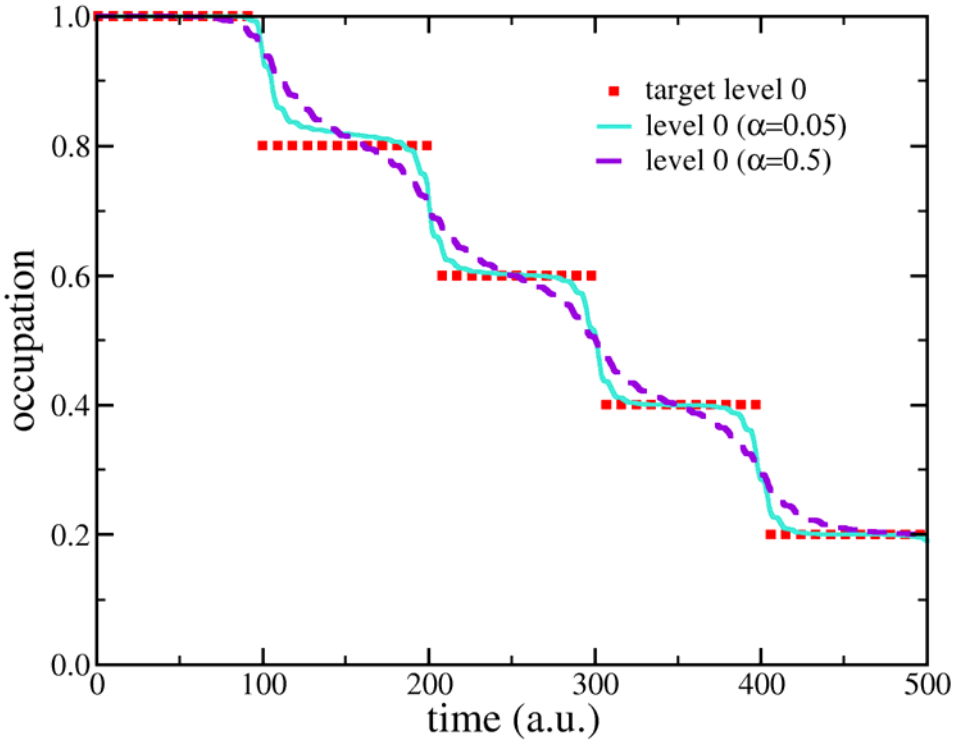
$|\alpha_0(t)|^2$ **and** $|\alpha_1(t)|^2$ **are <u>given</u> target occupations with**

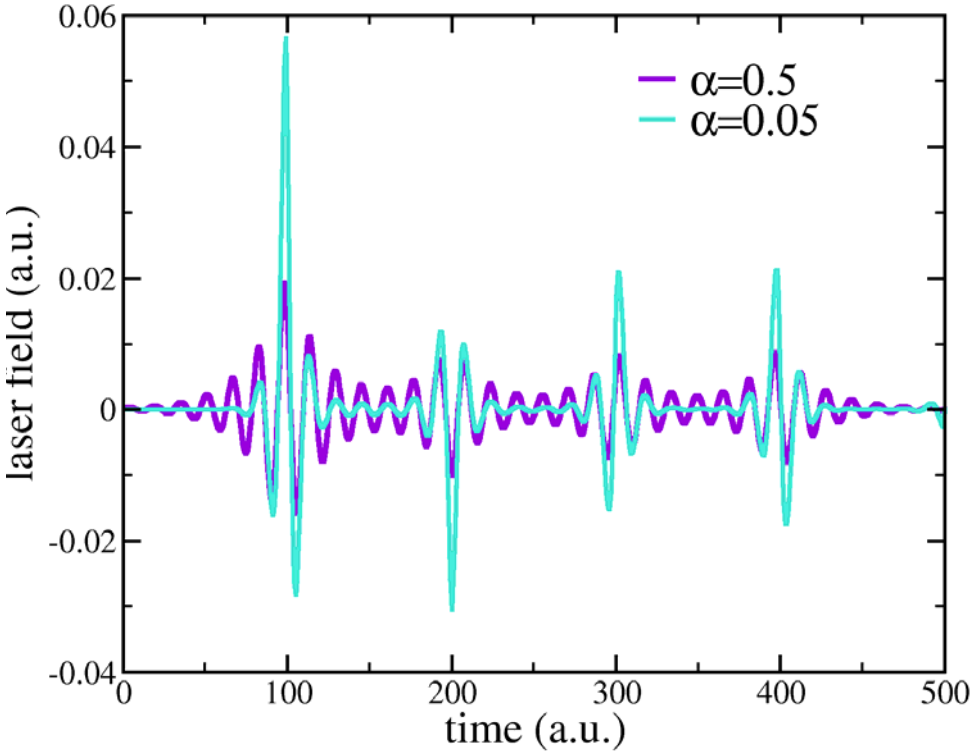
$$|\alpha_0(t)|^2 + |\alpha_1(t)|^2 = 1$$


1.0
0.8
0.6
0.4
0.2
0.0
occupation
0
200
400
600
800
1000
time (a.u.)
target level 1
level 1 (99.95%)
level 1 (99%)
level 1 (95%)
level 1 (90%)


occupation
time (a.u.)
target level 0
target level 1
level 0
level 1
0
0.2
0.4
0.6
0.8
1
0
100
200
300
400
500


laser field (a.u.)
time (a.u.)
0.06
0.04
0.02
0
-0.02
-0.04
0
100
200
300
400
500


target level 0
level 0 (α=0.05)
level 0 (α=0.5)
occupation
time (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500


α=0.5
α=0.05
laser field (a.u.)
time (a.u.)
0.06
0.04
0.02
0
-0.02
-0.04
0
100
200
300
400
500

Control of time-dependent density

$$\hat{O}(t) = \delta(x - x_0(t)) \approx \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-x_0(t))^2/2\sigma^2}$$

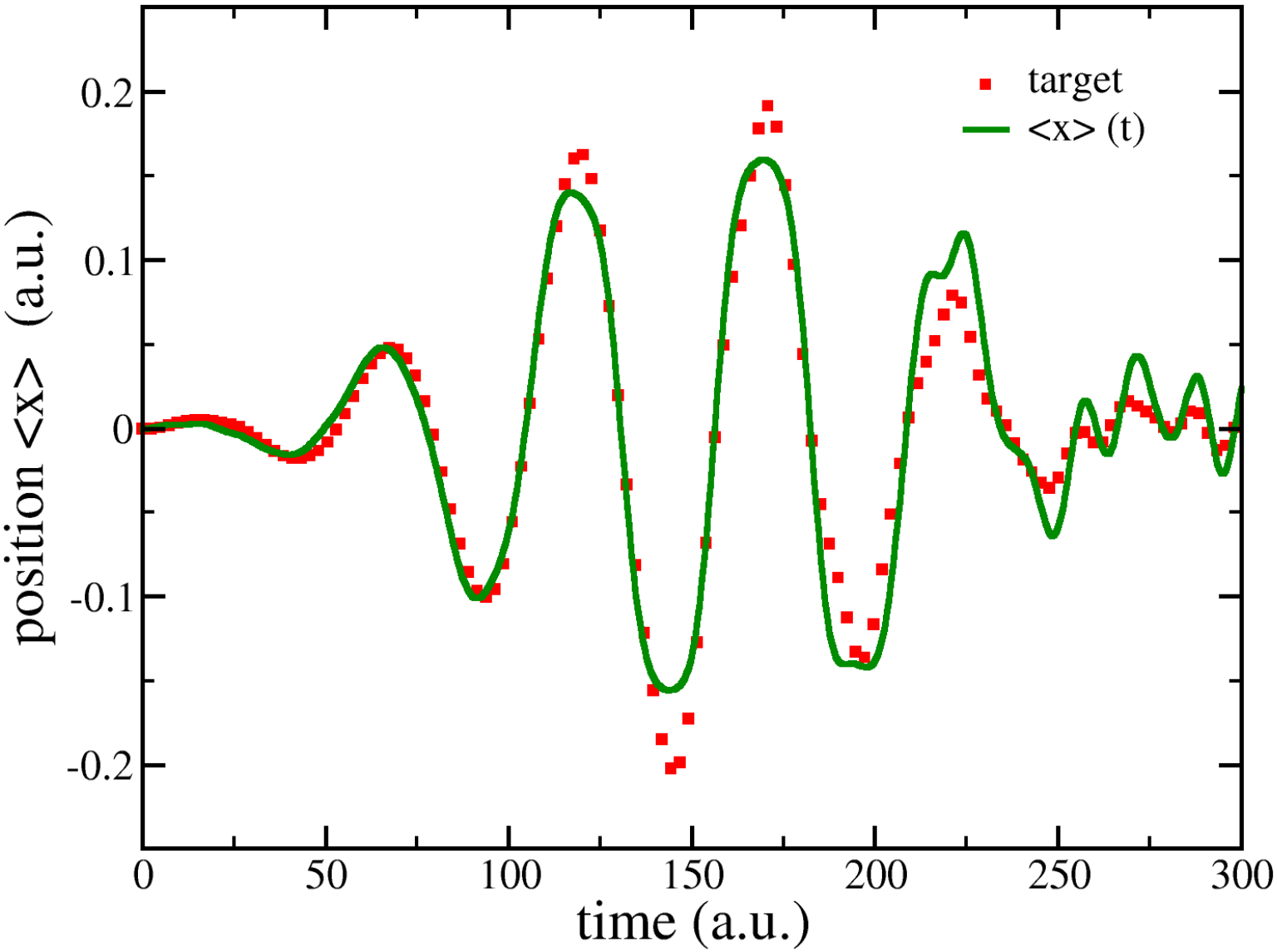
with <u>given</u> trajectory $x_0(t)$**.**

Algorithm maximizes the density along the path $x_0(t)$:

$$\max \int_0^T dt \left\langle \psi(t) \middle| \delta(x - x_0(t)) \middle| \psi(t) \right\rangle$$

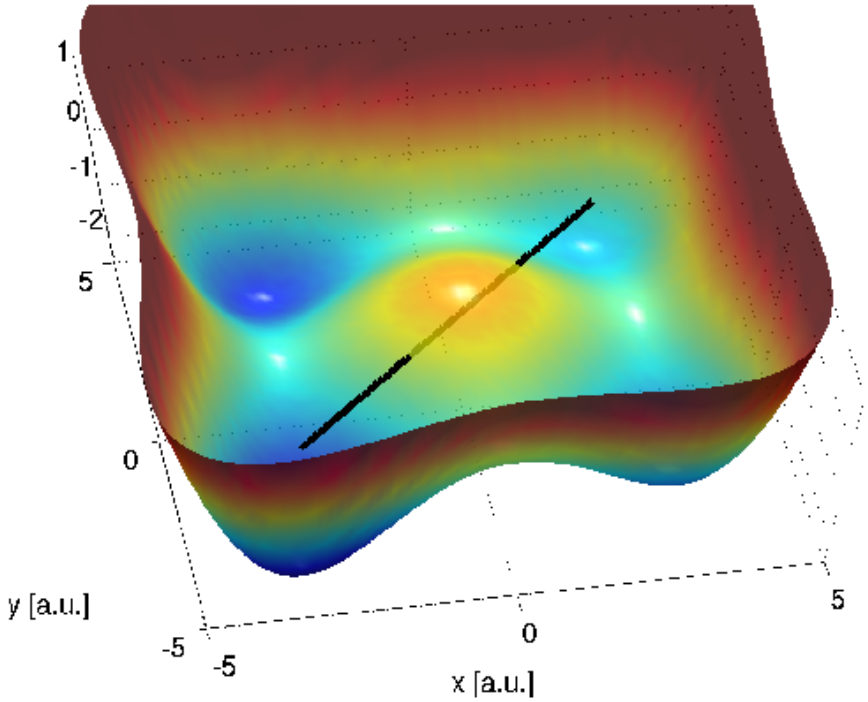
$$= \max \int_0^T dt \, n(x_0(t), t)$$

Control of time-dependent density of a 1D-hydrogen atom

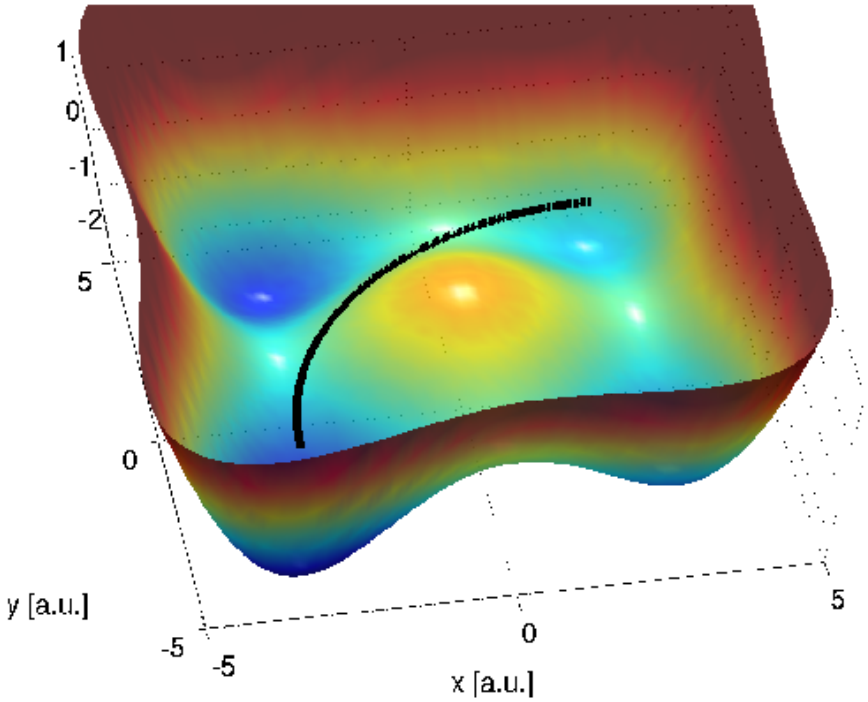


Control of charge transfer along selected pathways

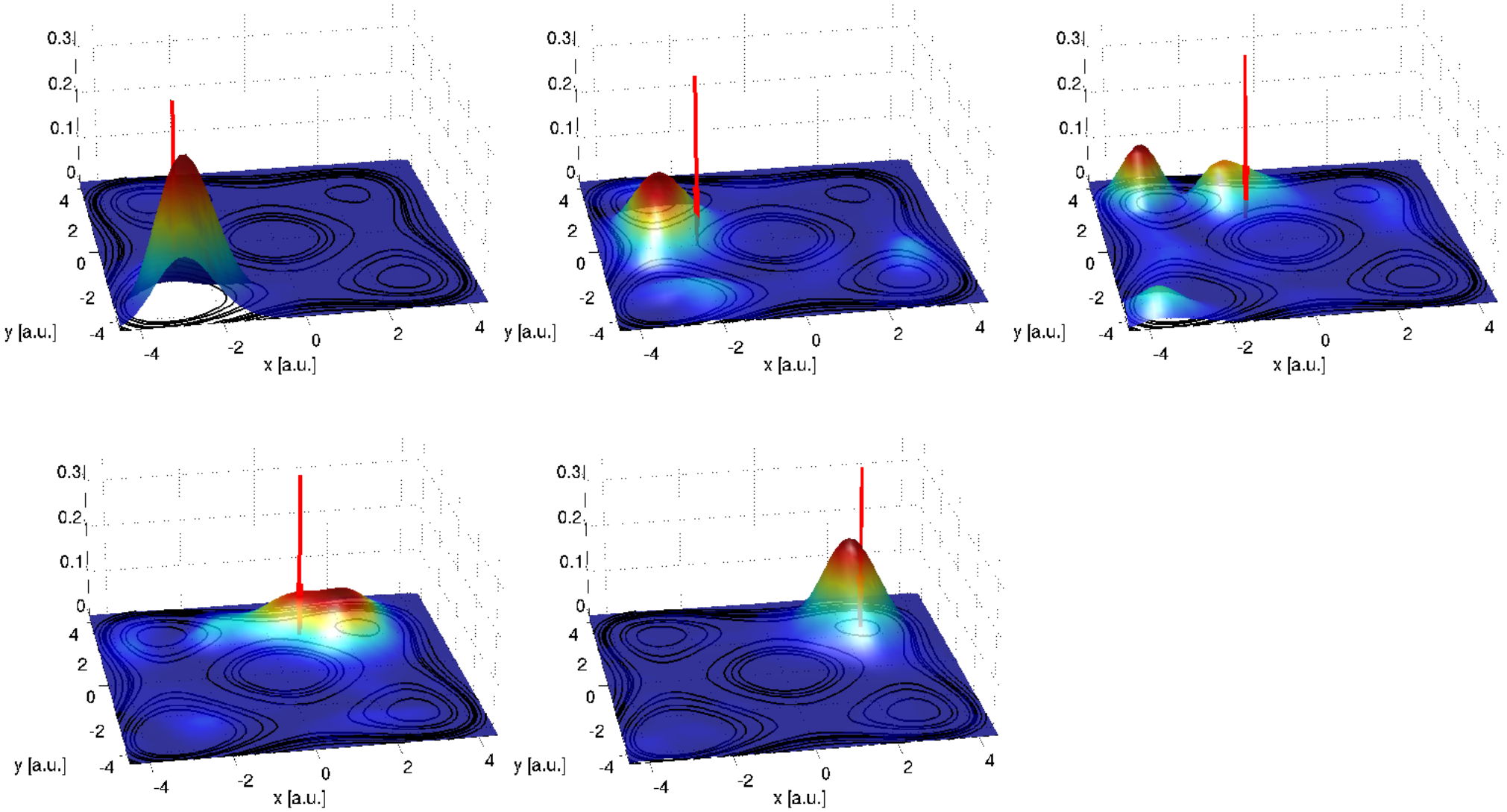
Trajectory 1



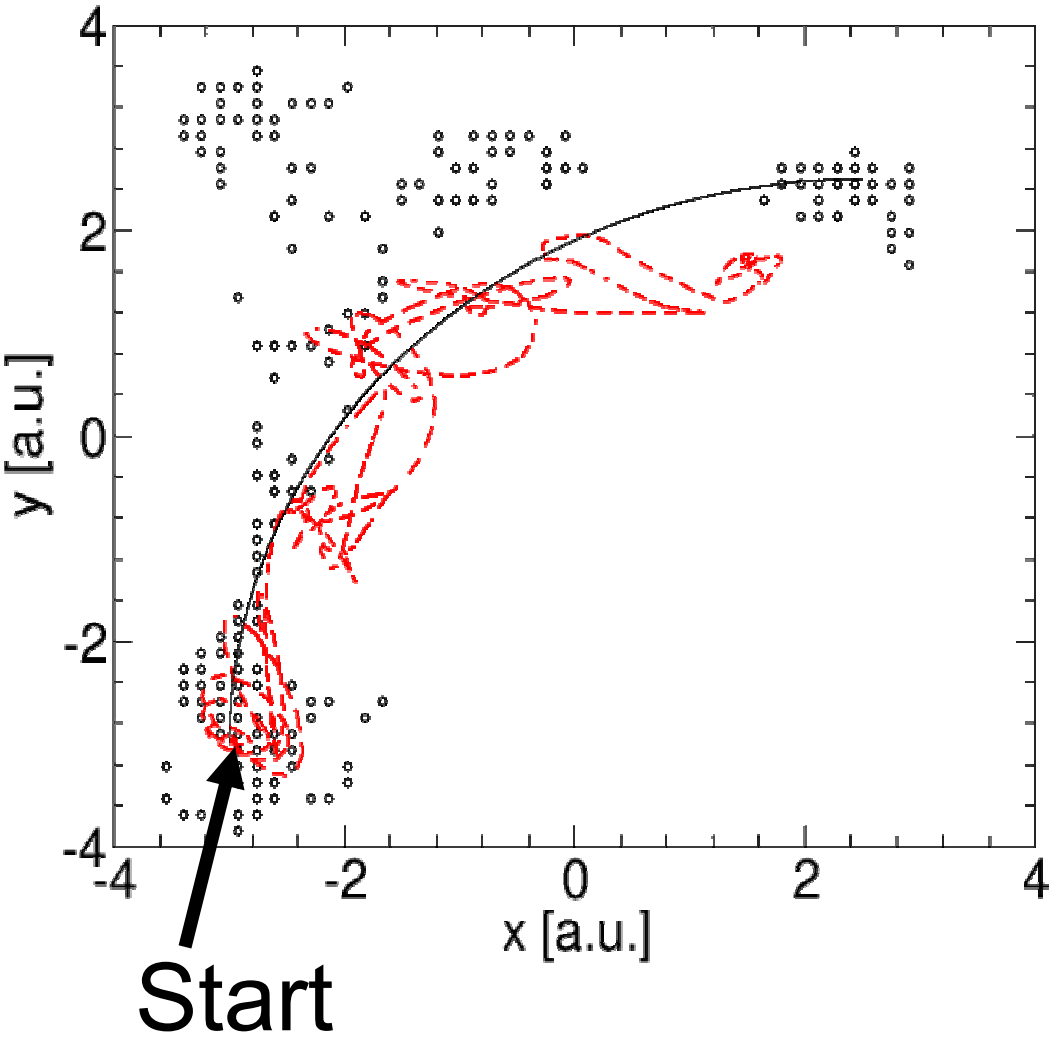
Trajectory 2

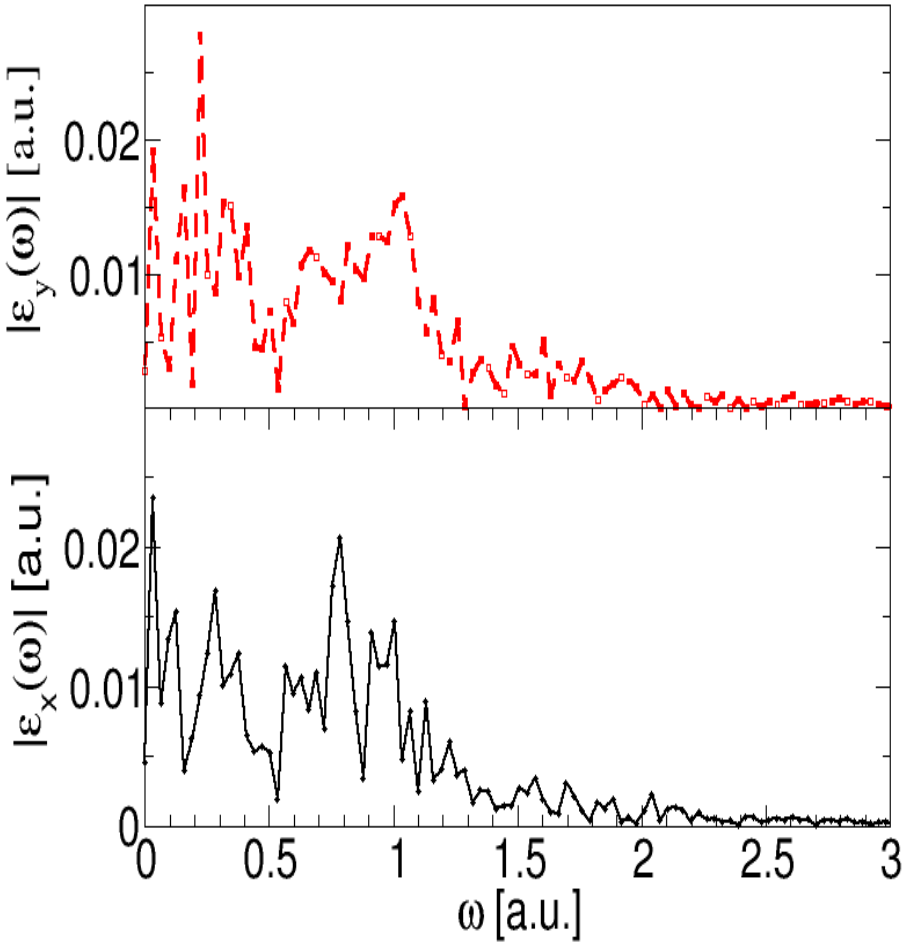


Time-evolution of wavepacket with the optimal laser pulse for trajectory 2

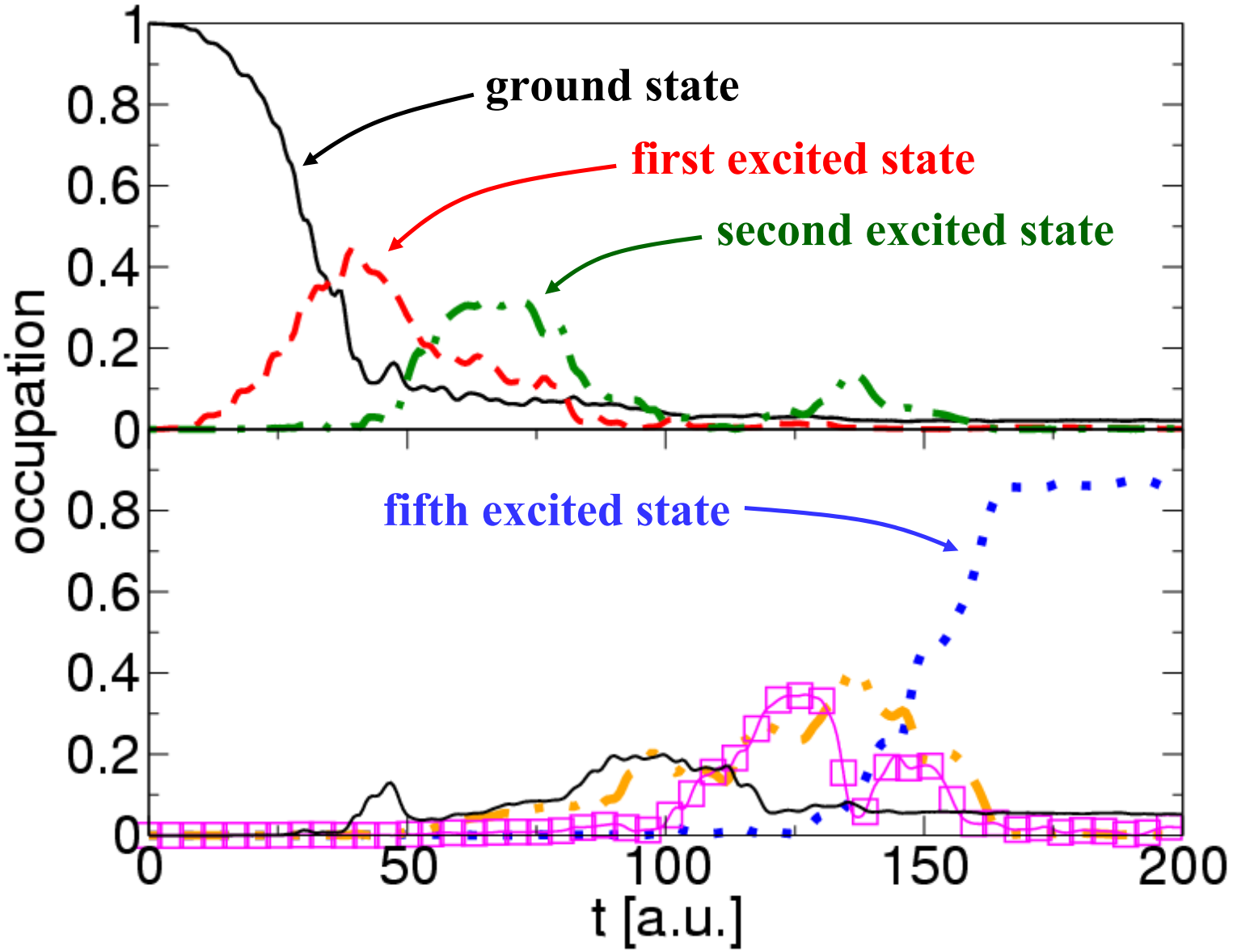


Trajectory 2: Results

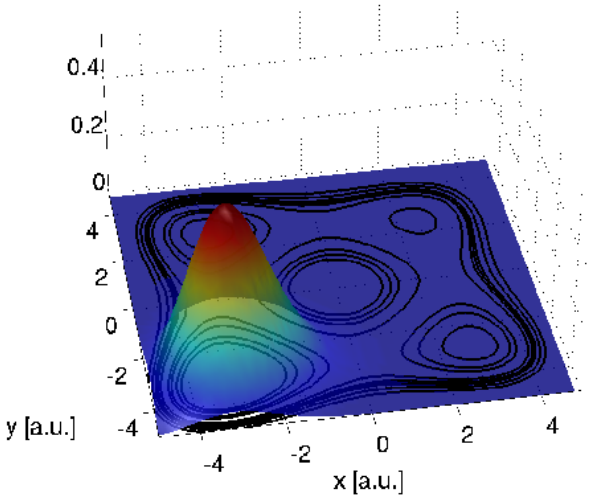


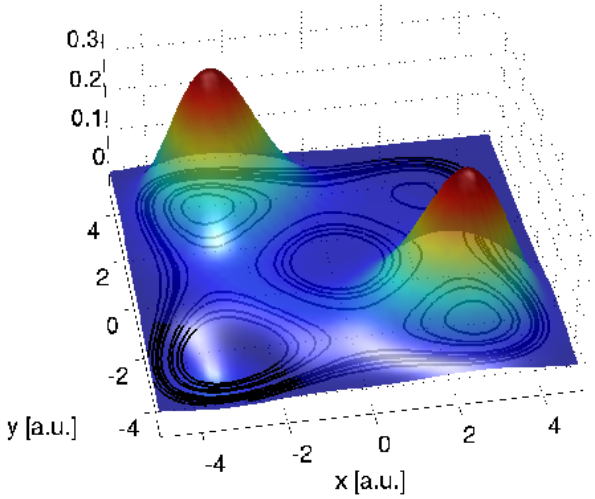


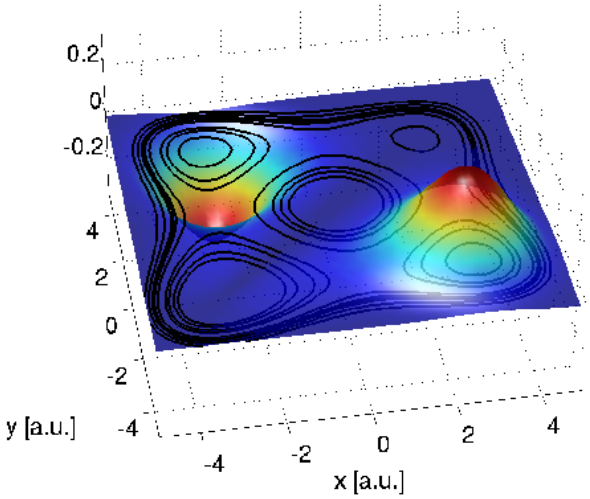
Populations of eigenstates

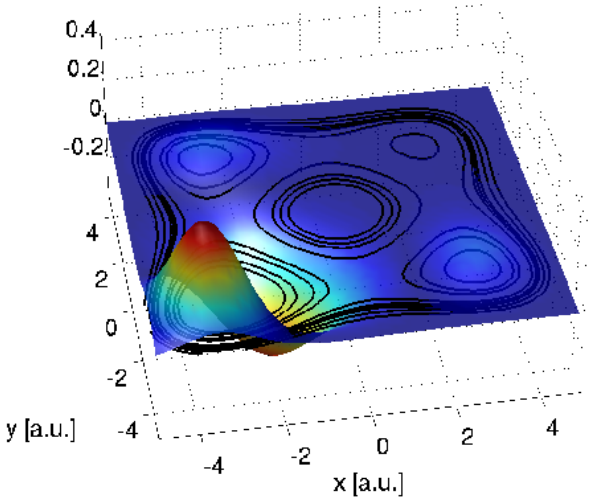


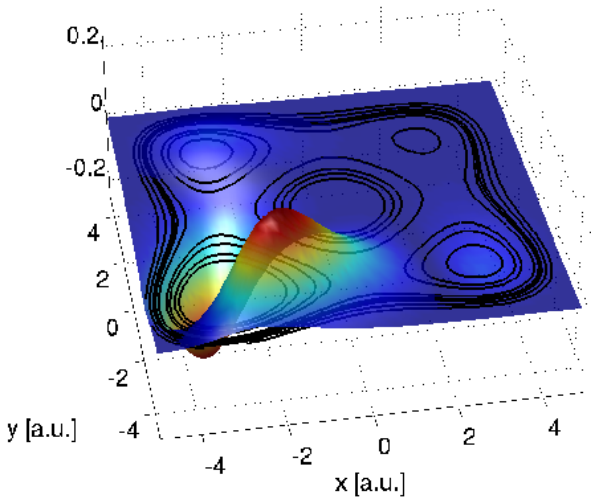
Densities of lowest six eigenstates

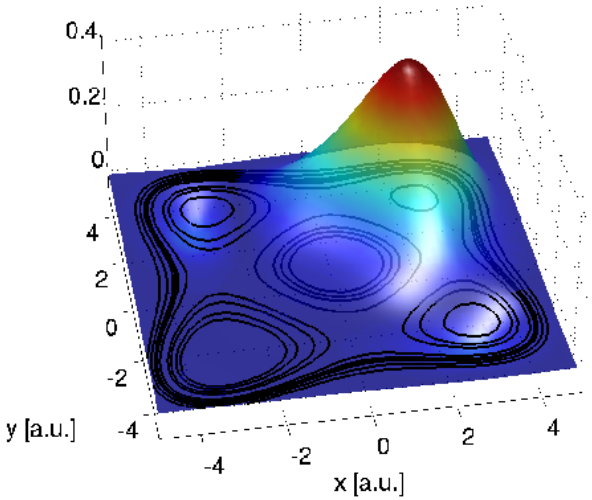












Control of many-body systems

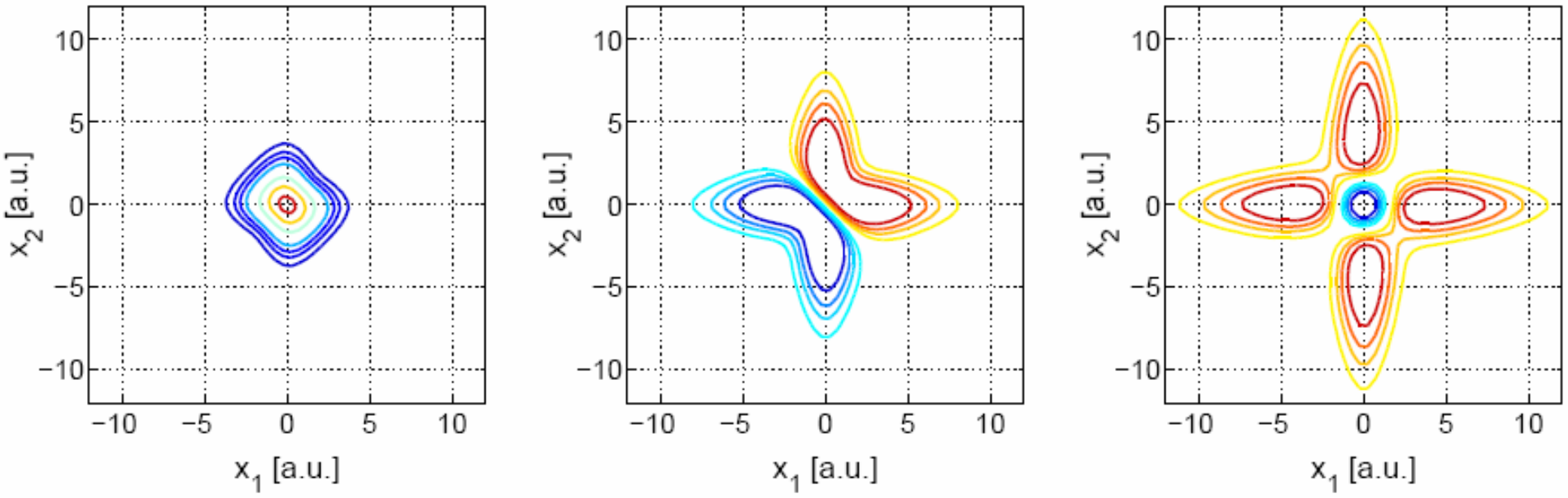
- So far only one electron

- OCT is easily extended to many-body problems: The one-body SE is simply replaced by the many-body SE

1D Helium model

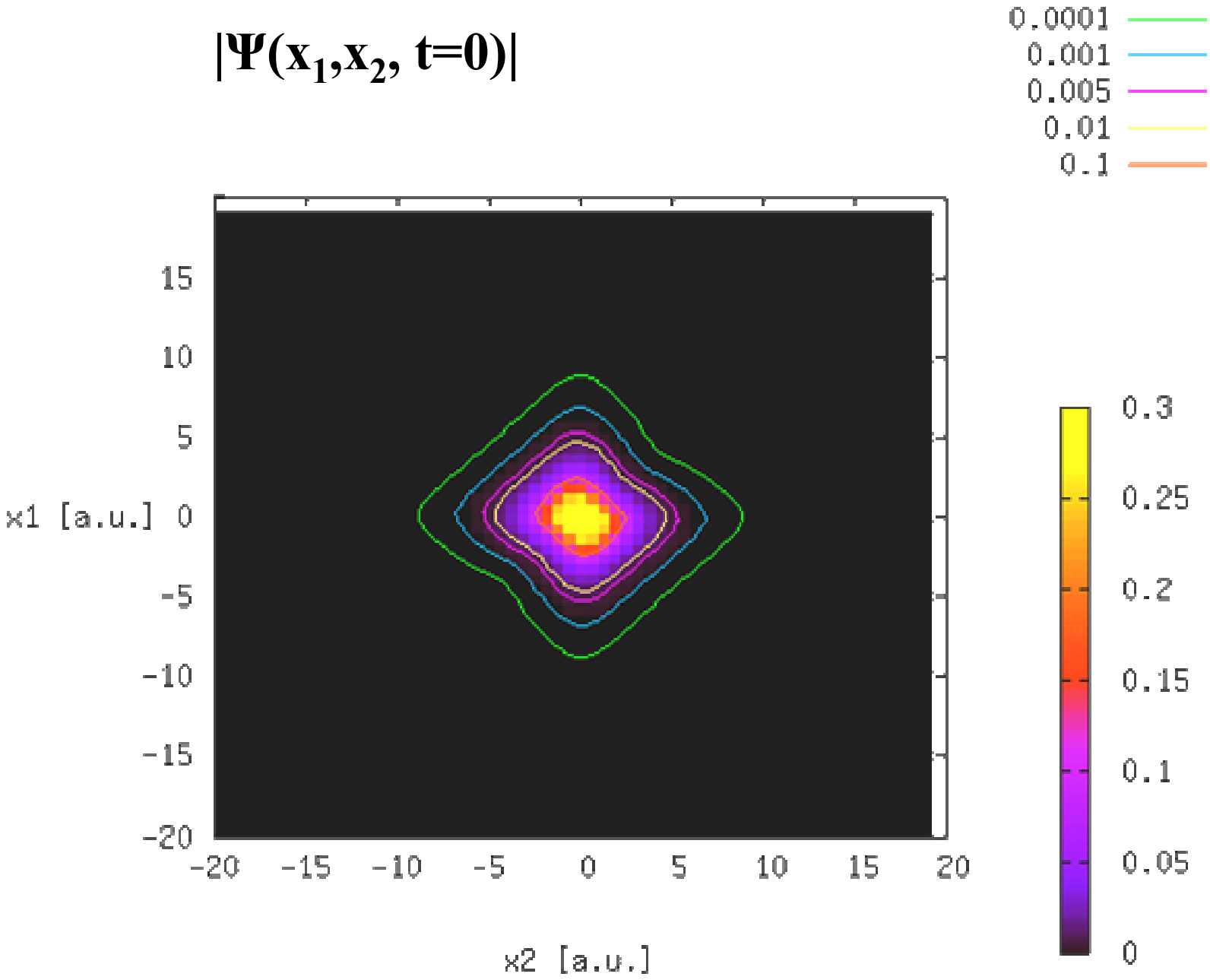
$$\hat{H} = -\frac{1}{2}\frac{\partial^2}{\partial x_1^2} - \frac{1}{2}\frac{\partial^2}{\partial x_2^2} - \frac{Z}{\sqrt{x_1^2+1}} - \frac{Z}{\sqrt{x_2^2+1}} + \frac{1}{\sqrt{(x_1-x_2)^2+1}}$$

Singlet states:



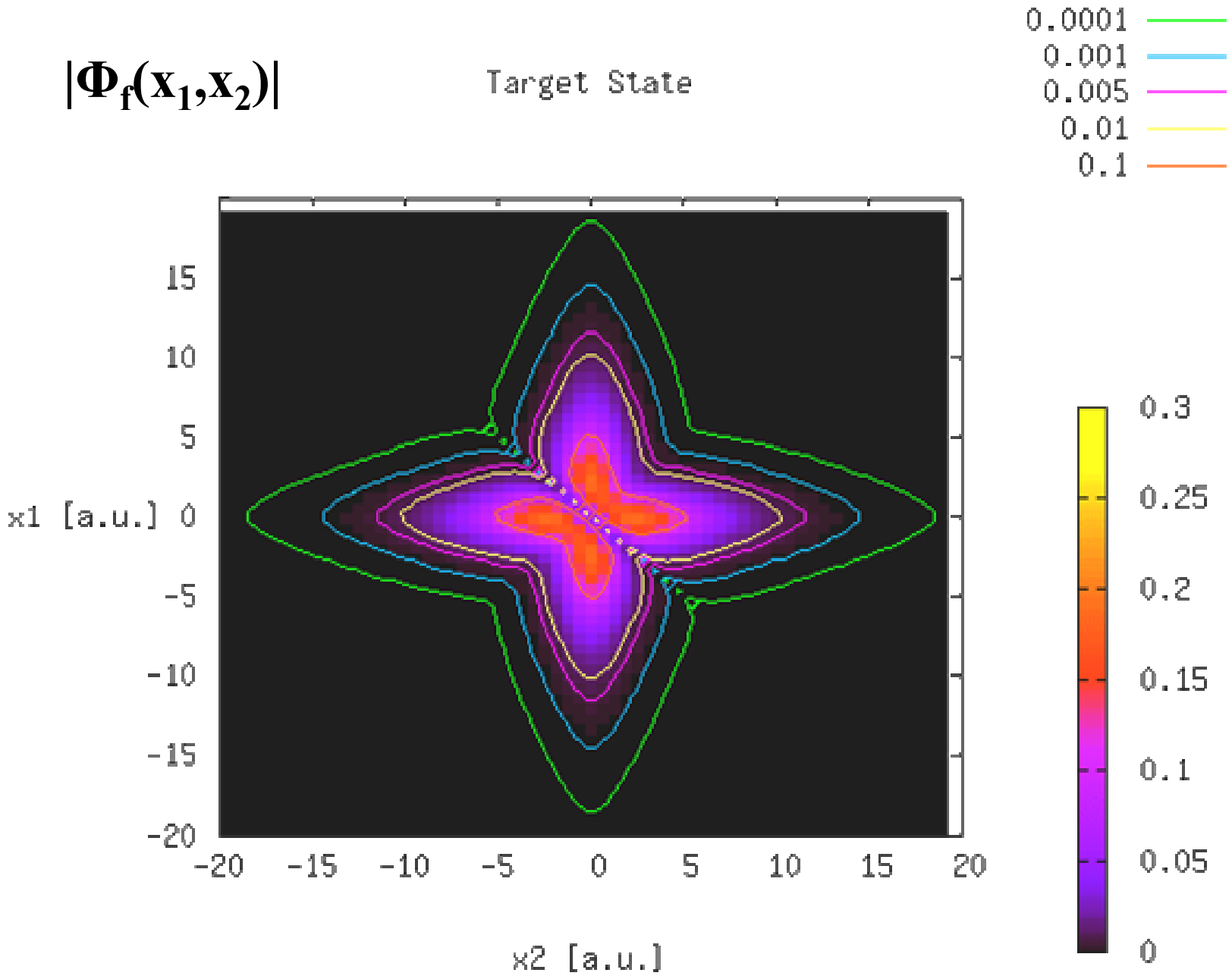
Initial-state = ground-state (singlet)

$|\Psi(x_1,x_2, t=0)|$



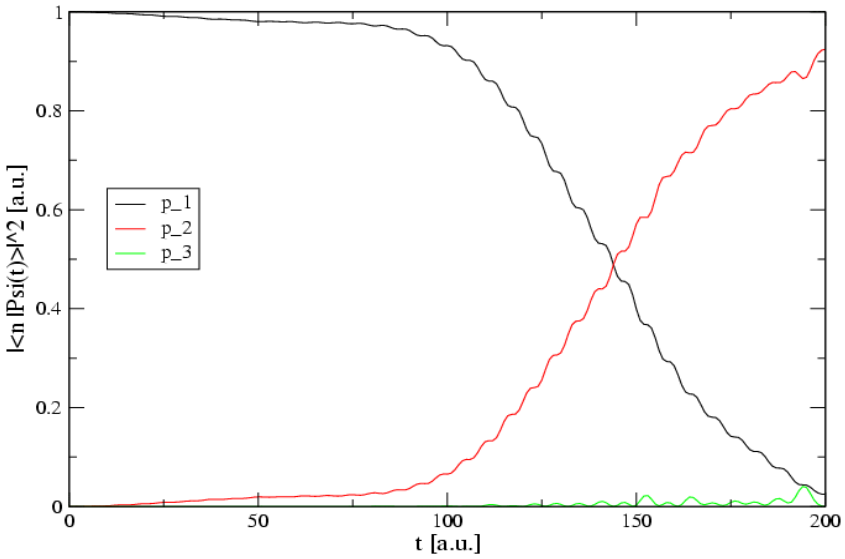
Target-state = 1st excited-state (singlet)

$|\Phi_f(x_1,x_2)|$



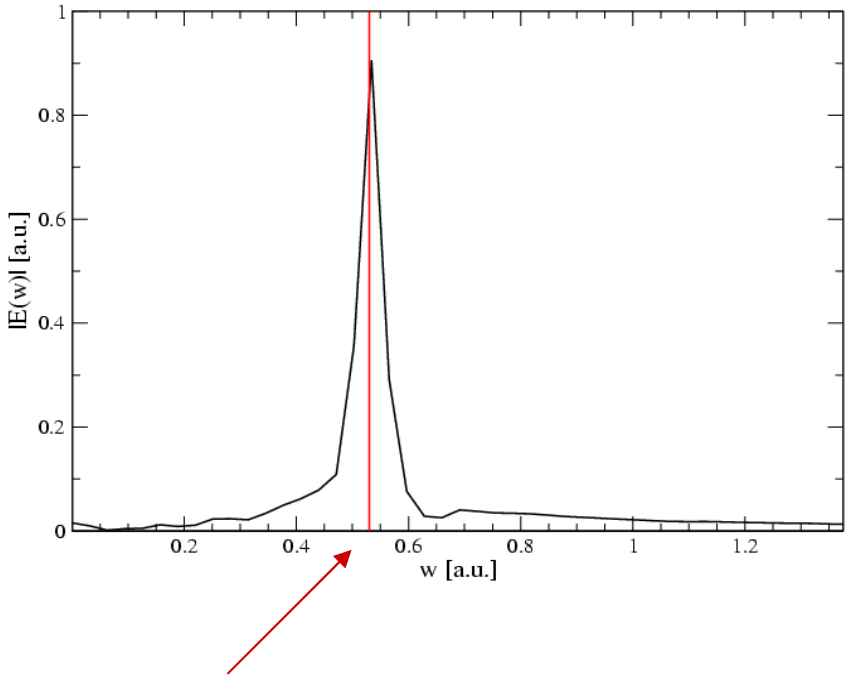
Results 1D Helium

Populations of exact eigenstates



$$\left| \left\langle \Psi(T) \middle| \Phi_f \right\rangle \right|^2 = 0.93$$

Spectrum of optimized pulse



Optimization finds the correct transition frquency

Control of many-body systems

- Problem: For 3 or more degrees of freedom, the full solution of the TDSE becomes computationally very hard

→ **Instead of solving the many-body TDSE, invoke TDDFT**

TDDFT+OCT: A perfect couple

- Laser pulses from OCT are determined iteratively – TDDFT is computationally efficient (local potential)

- Excitation energies from TDDFT (in linear response) are often quite o.k. – important to find an optimal pulse that works

TDDFT+OCT: Equations

- TDKS equations as a constraints:

$$J = J_1 - \alpha \int_0^T dt\, \varepsilon^2(t)$$

$$- 2\,\mathrm{Im} \sum_{j=1}^{N} \int_0^T dt \left\langle \lambda_j(t) \middle| i\partial_t - \hat{h}_{KS}(t) \middle| \phi_j^{KS}(t) \right\rangle$$

$$\hat{h}_{KS}(t) = -\frac{\nabla^2}{2} + v_{KS}[n](\vec{r}, t)$$

every KS-orbital gets a Lagrange multiplier

TDDFT+OCT: Control equations

1. Kohn-Sham equation with initial condition:

$$\delta_{\lambda_m} J = 0 \rightarrow \boxed{\left[i\partial_t - \hat{h}_{KS}[n](t) \right] \phi_m^{KS}(t) = 0, \quad \phi_m^{KS}(0) = \varphi_m^{KS}}$$

2. TDSE equation with final condition and inhomogeneity:

$$\delta_{\phi_m^{KS}} J = 0 \rightarrow \boxed{\left[i\partial_t - \hat{h}_{KS}(t) \right] \lambda_m(t) = -iD_{KS}[\lambda_j(t), \phi_j^{KS}(t)], \quad \lambda_m(T) = \hat{O}\left[\phi_j^{KS}(T) \right]}$$

$$j = 1, .., N$$

3. Field equation:

$$\delta_\varepsilon J = 0 \rightarrow \boxed{\varepsilon(t) = \frac{1}{\alpha} \sum_{j=1}^{N} \mathrm{Im} \left\langle \lambda_j(t) \middle| \hat{\mu} \middle| \phi_j^{KS}(t) \right\rangle}$$

use available iterative schemes to solve eqs.

Problem: Non-interacting fermions are generally not controllable

TWO NONINTERACTING ELECTRONS IN SINGLET STATE

1st electron: initial $\varphi_0(r)\chi_\uparrow \xrightarrow{\text{TDSE}}$ final $\varphi_f(r)\chi_\uparrow$

2nd electron: initial $\varphi_0(r)\chi_\downarrow \xrightarrow{\text{TDSE}}$ final $\varphi_f(r)\chi_\downarrow$

Initial two-body state:

$$\Psi_0 = \varphi_0(r_1)\varphi_0(r_2)\chi_{\text{singlet}}$$

Final two-body state:

$$\Psi_f = \varphi_f(r_1)\varphi_f(r_2)\chi_{\text{singlet}}$$

Maximize overlap between Ψ_f and lowest excited state

$$\Psi_1 = \frac{1}{\sqrt{2}}\left[\varphi_0(r_1)\varphi_1(r_2) + \varphi_0(r_2)\varphi_1(r_1)\right]\chi_{\text{singlet}}$$

$$\langle \Psi_1 | \Psi_f \rangle = \frac{2}{\sqrt{2}} \langle \varphi_0 | \varphi_f \rangle \langle \varphi_1 | \varphi_f \rangle$$

$$\varphi_f(r) = \sum_j \alpha_j \varphi_j(r)$$

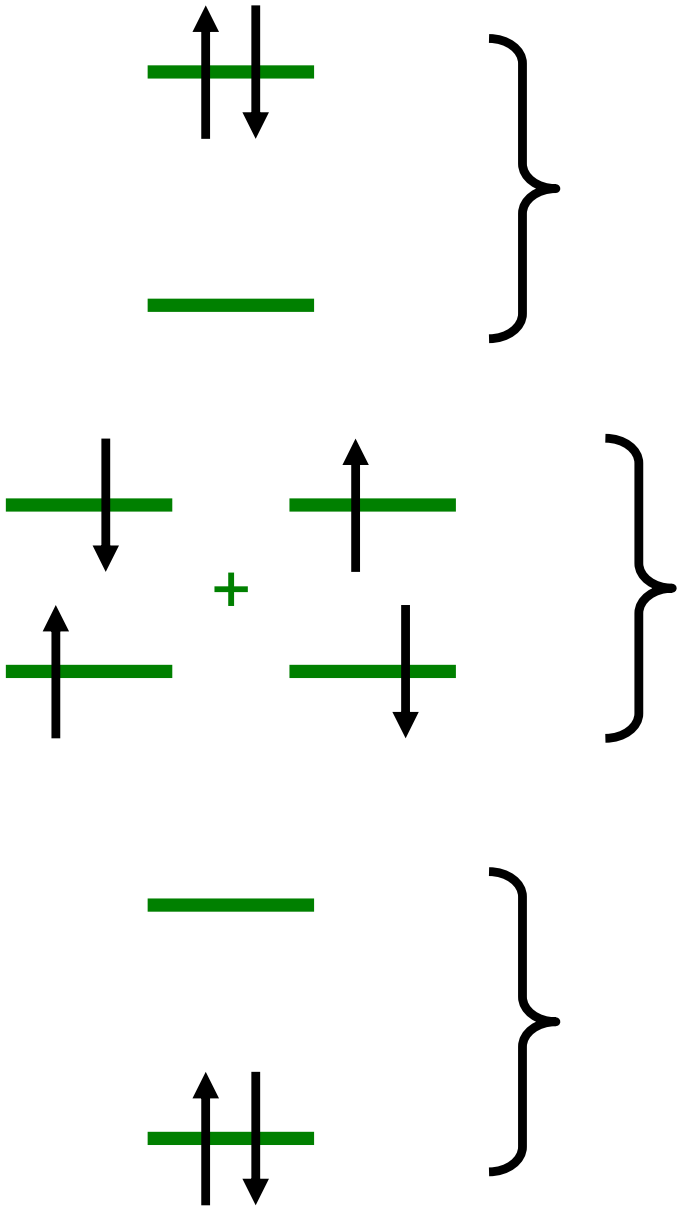
$$\left|\langle \Psi_1 | \Psi_f \rangle\right|^2 = 2|\alpha_0|^2|\alpha_1|^2 = 2|\alpha_0|^2\left(1 - |\alpha_0|^2\right)$$

$$\text{Maximum of } f(x) = 2x(1-x) \text{ is at } x = \frac{1}{2}$$

$$\text{Value of } f(x) \text{ at maximum} = \frac{1}{2}$$

J Werschnik, K Burke, EKUG, JCP 123, 062206 (2005)

Energies of the 2-electron system



Not controllable!!

Problems, Problems, Problems…

- Non-interacting system is not controllable!!

  Does it matter in KS context? NO!

  (exact KS potential would also produce overlap ½ or less.)

- Real task: Find functional of KS orbitals which, when maximized, finds a pulse that drives the INTERACTING system from $\Psi(t=0)$ to the excited many-body state Φ_f (i.e. overlap with a KS determinnt does not matter).

- The real problem: We still have to maximize $\left| \left\langle \Psi(T) | \Phi_f \right\rangle \right|^2$.

  But neither Ψ nor Φ_f are available in KS framework.

We still want to maximize $\left|\left\langle \Psi(T)\middle|\Phi_f\right\rangle\right|^2$.

Bold attempt: Maximize $\left|\left\langle \Psi^{KS}(T)\middle|\Phi_f^{KS}\right\rangle\right|^2$ instead!

Result not bad: For 1D-Helium, the pulse optimized in this way yields, when inserted in the INTERACTING TDSE, an occupation of 70 % for the 1st excited many-body state! (The fully interacting optimization yields 93%)


Thanks !