TDDFT beyond the linear regime: Analysis and control of electron dynamics

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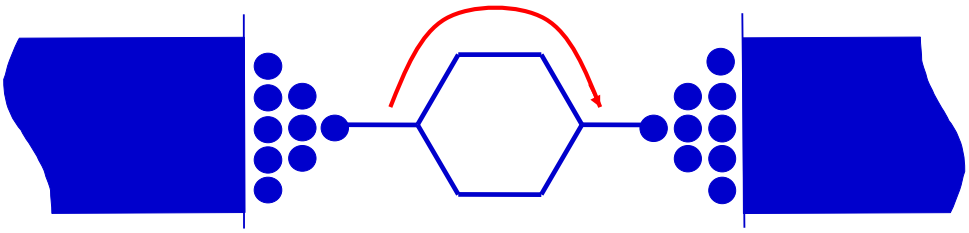
Electron dynamics happens on the femto-second time scale

Questions:

- How much time does it take to break a bond in a laser field?
- How long takes an electronic transition from one state to another?
- Can we control the path of an electronic wave packet with lasers?

Molecular Electronics

Goal: Control the path of the current with laser



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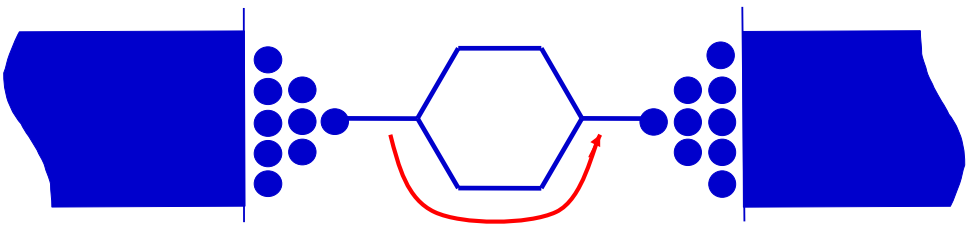
Molecular Electronics

Goal: Control the path of the current with laser



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OUTLINE

- **Basics of TDDFT**
- **Analysis**
  TD Electron Localization Function (TD-ELF): Movie of laser-induced π-π^* transition
- **Control:**
  Optimal control of
  -- the path in Hilbert space
  -- the TD density/TD current in real space

THANKS

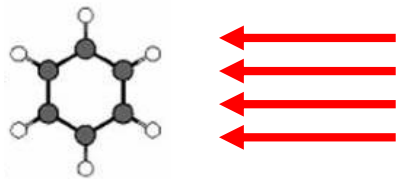
Erich Runge
Martin Petersilka
Ulrich Gossmann

Tobias Burnus
Miguel Marques
Alberto Castro

Jan Werschnik
Ioana Serban
Esa Räsänen

Basics of TDDFT

Generic situation:
Molecule in laser field



$$\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{j,\alpha} -\frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \vec{E}\cdot\vec{r}_j \cdot \sin \omega t$$

Interacting many-electron system, driven by an external field

Time-dependent Schrödinger equation

$$i\,(\partial/\partial t)\,\Psi(r_1,r_2,\ldots,r_N,t) = H(t)\Psi(r_1,r_2,\ldots,r_N,t)$$

Time-dependent density-functional formalism

E. Runge, E.K.U.G., PRL 52, 997 (1984)

Hohenberg-Kohn-type theorem:

$$v(r\,t) \xleftrightarrow{1\text{-}1} \rho(r\,t)$$

The time-dependent density determines uniquely the time-dependent external potential for fixed initial state

Kohn-Sham-type theorem:

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(r\,t) = \sum_{j=1}^{N} \left|\varphi_j(r\,t)\right|^2$$

of an auxiliary non-interacting (KS) system

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

with the local potential

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

Simplest possible approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Local Density Approximation (ALDA)

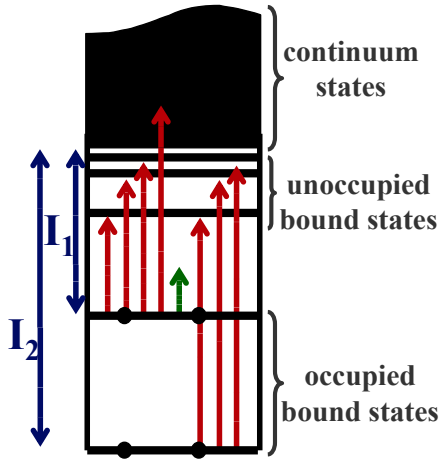
$$v_{xc}^{ALDA}(\vec{r}\,t) := v_{xc,stat}^{hom}(n)\Big|_{n=\rho(\vec{r}\,t)}$$

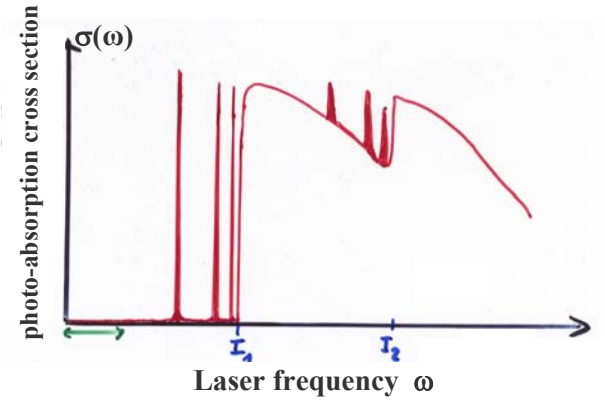
$v_{xc,stat}^{hom}$ **= xc potential of static homogeneous e-gas**

Approximation with correct asymptotic -1/r behavior: time-dependent optimized effective potential

C. A. Ullrich, U. Gossmann, E.K.U.G., PRL 74, 872 (1995)

Standard application: Photo-absorption in weak lasers





Calculate 1. Linear density response $\rho_1(r\ t)$

2. Dynamical polarizability

$$\alpha(\omega) = -\frac{e}{E}\int z\ \rho_1(\vec{r},\omega)\,d^3r$$

3. Photo-absorption cross section $\sigma(\omega) = -\frac{4\pi\omega}{c}\ \mathrm{Im}\ \alpha$

Standard linear response formalism

$H(t_0)$ = full static Hamiltonian at t_0

$$H(t_0)|m\rangle = E_m|m\rangle$$ ← **exact many-body eigenfunctions and energies of system**

full response function

$$\chi(r,r';\omega) = \lim_{\eta\to 0^+}\sum_m \left(\frac{\langle 0|\hat{\rho}(r)|m\rangle\langle m|\hat{\rho}(r)|0\rangle}{\omega-(E_m-E_0)+i\eta} - \frac{\langle 0|\hat{\rho}(r')|m\rangle\langle m|\hat{\rho}(r')|0\rangle}{\omega+(E_m-E_0)+i\eta} \right)$$

⇒ **The exact linear density response**

$$\rho_1(\omega) = \hat{\chi}(\omega)v_1(\omega)$$

has poles at the exact excitation energies $\Omega = E_m - E_0$

Discrete excitation energies from TDDFT

Goal: Use exact TDDFT representation of linear density response to determine the poles of $\rho_1(\omega)$:

$$\rho_1(\omega) = \hat{\chi}_S(\omega)\left(v_1(\omega) + \hat{W}_C\rho_1(\omega) + \hat{f}_{xc}(\omega)\rho_1(\omega)\right)$$

"^" denotes integral operator, e.g. $\hat{f}_{xc}\rho_1 \equiv \int f_{xc}(\vec{r},\vec{r}')\rho_1(\vec{r}')d^3r'$

where $\hat{\chi}_S(\vec{r},\vec{r}';\omega) = \sum_{j,k}\frac{M_{jk}(\vec{r},\vec{r}')}{\omega-(\varepsilon_j-\varepsilon_k)+i\eta}$

with $M_{jk}(\vec{r},\vec{r}') = (f_k - f_j)\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_k(\vec{r}')\varphi_k^*(\vec{r})$

$$f_m = \begin{cases} 1 \text{ if } \varphi_m \text{ is occupied in KS ground state} \\ 0 \text{ if } \varphi_m \text{ is unoccupied in KS ground state} \end{cases}$$

$\varepsilon_j - \varepsilon_k$ KS excitation energy

$$\left(\hat{1} - \hat{\chi}_S(\omega)\left[\hat{W}_C + \hat{f}_{xc}(\omega)\right]\right)\rho_1(\omega) = \hat{\chi}_S(\omega)v_1(\omega)$$

$\rho_1(\omega) \to \infty$ for $\omega \to \Omega$ (exact excitation energy) but right-hand side remains finite for $\omega \to \Omega$

hence $\left(\hat{1} - \hat{\chi}_S(\omega)\left[\hat{W}_C + \hat{f}_{xc}(\omega)\right]\right)\xi(\omega) = \lambda(\omega)\xi(\omega)$

$\lambda(\omega) \to 0$ for $\omega \to \Omega$

This condition rigorously determines the exact excitation energies, i.e.,

$$\left(\hat{1} - \hat{\chi}_S(\Omega)\left[\hat{W}_C + \hat{f}_{xc}(\Omega)\right]\right)\xi(\Omega) = 0$$

This leads to the (non-linear) eigenvalue equation

(See T. Grabo, M. Petersilka, E. K. U. G., J. Mol. Struc. (Theochem) 501, 353 (2000))

$$\sum_{q'}\left(A_{qq'}(\Omega)+\omega_q\delta_{qq'}\right)\beta_{q'}=\Omega\beta_q$$

where

$$A_{qq'}=\alpha_{q'}\int d^3r\int d^3r'\,\Phi_q(r)\left(\frac{1}{|r-r'|}+f_{xc}(r,r',\Omega)\right)\Phi_{q'}(r')$$

$q=(j,a)$ double index $\qquad \alpha_q=f_a-f_j$

$\Phi_q(r)=\varphi_a^*(r)\varphi_j(r) \qquad \omega_q=\varepsilon_a-\varepsilon_j$

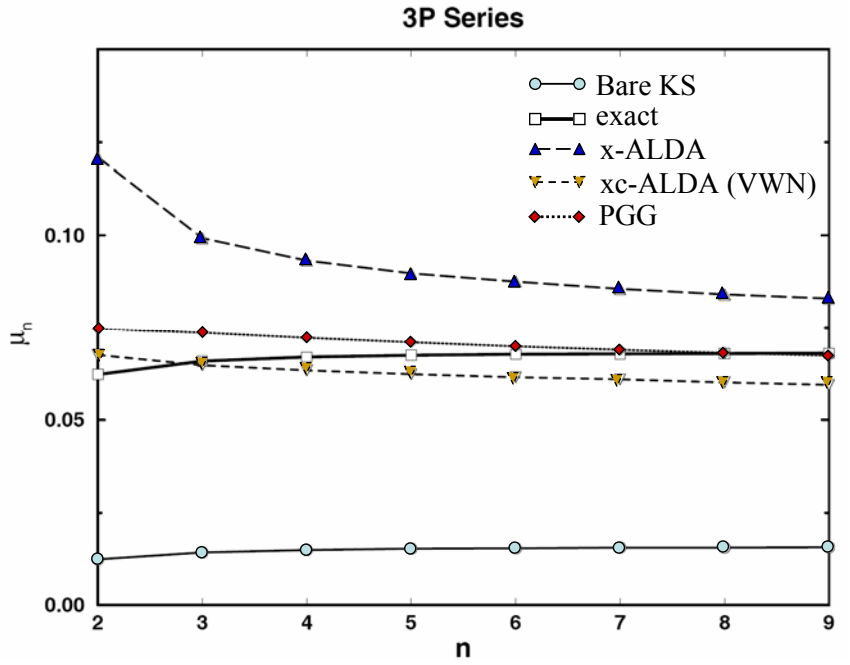
Atom	Experimental Excitation Energies $^1S\rightarrow{}^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	$\Delta\epsilon_{KS}+K$
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

$$\Delta E=\underbrace{\Delta\epsilon_{KS}}_{\epsilon_j-\epsilon_k}+K$$

$$K=\int d^3r\int d^3r'\,\varphi_j(r)\varphi_j^*(r')\varphi_k(r')\varphi_k^*(r)\left(\frac{1}{|r-r'|}+f_{xc}(r,r')\right)$$

Quantum defects in Helium $E_n = -\frac{1}{2(n-\mu_n)^2}$ [a.u.]



M. Petersilka, U.J. Gossmann, E.K.U.G., in: Electronic Density Functional Theory: Recent Progress and New Directions, J.F. Dobson, G. Vignale, M.P. Das, ed(s), (Plenum, New York, 1998), p 177 - 197.

To study the dynamics of electrons we have to propagate the TDKS equations

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

in real time.

Time-Dependent Electron Localization Function

How can one give a mathematical meaning to intuitive 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)

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

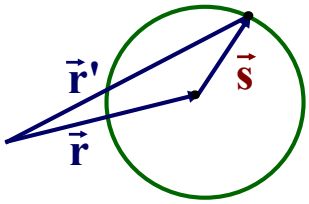
= diagonal of two-body density matrix

= 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 same 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 p_σ is a probability) and $C_\sigma(\vec{r})$ is not bounded from above.

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

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

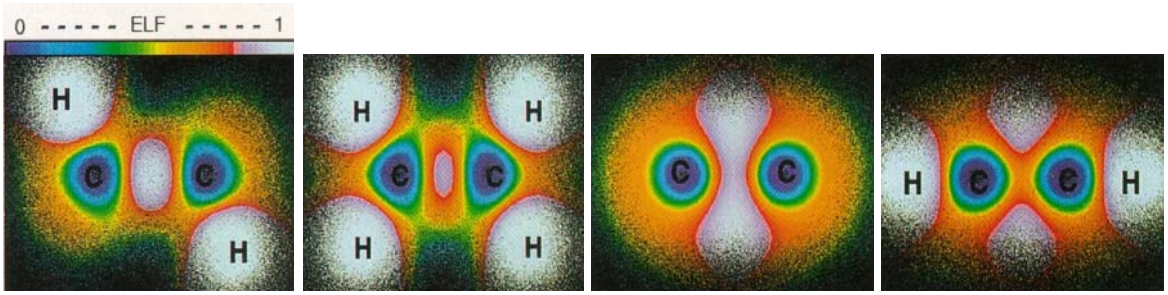
where

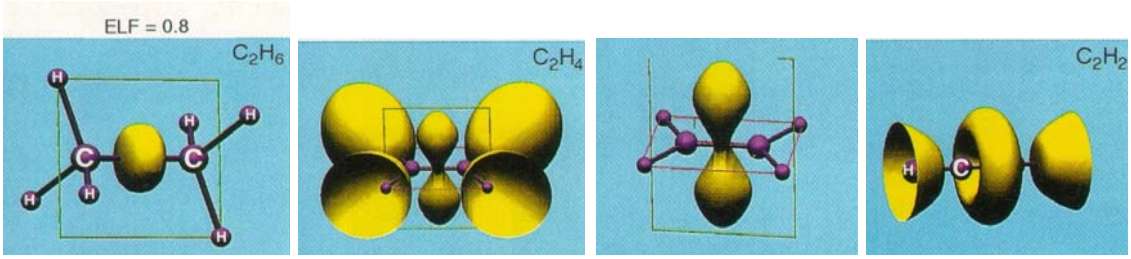
$$C_\sigma^{uni}(\vec{r}) = \frac{3}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3}(\vec{r}) = \tau_\sigma^{uni}(\vec{r})$$

is the kinetic energy density of the uniform gas.

Advantage: ELF is dimensionless and $0 \leq ELF \leq 1$

ELF





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

For a determinantal wave function one obtains

in the static case:

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

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

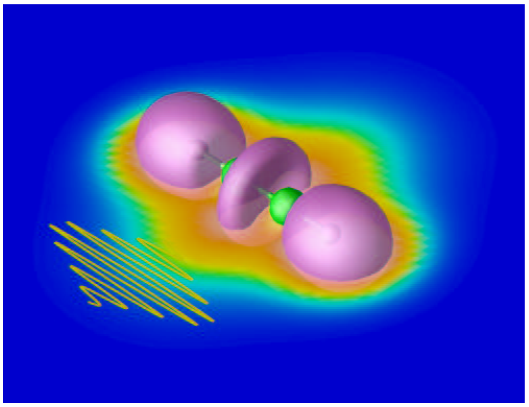
in the time-dependent case:

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

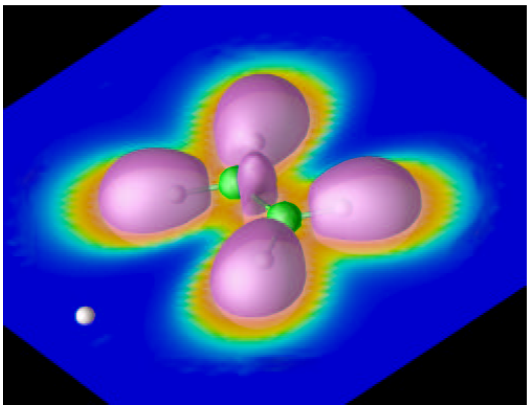
T. Burnus, M. Marques, E.K.U.G., PRA (Rapid Comm) 71, 010501 (2005)

J. Dobson, J. Chem. Phys. 98, 8870 (1993)

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

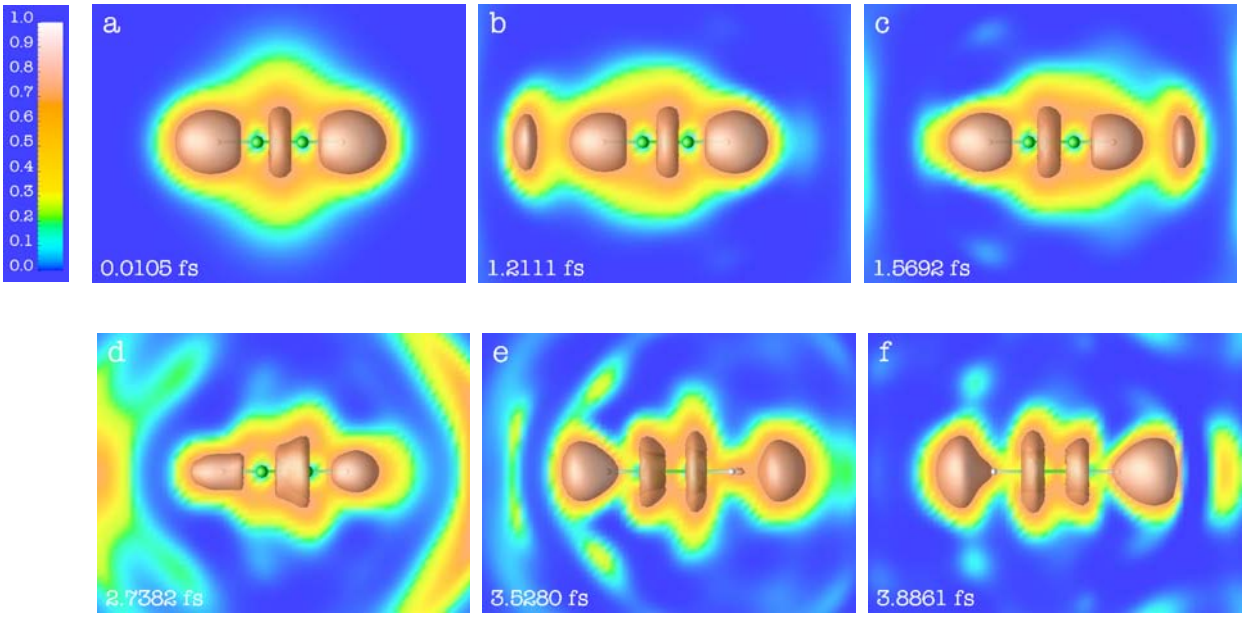


Scattering of a proton from ethylene
(E_{kin}(proton) = 2 keV)



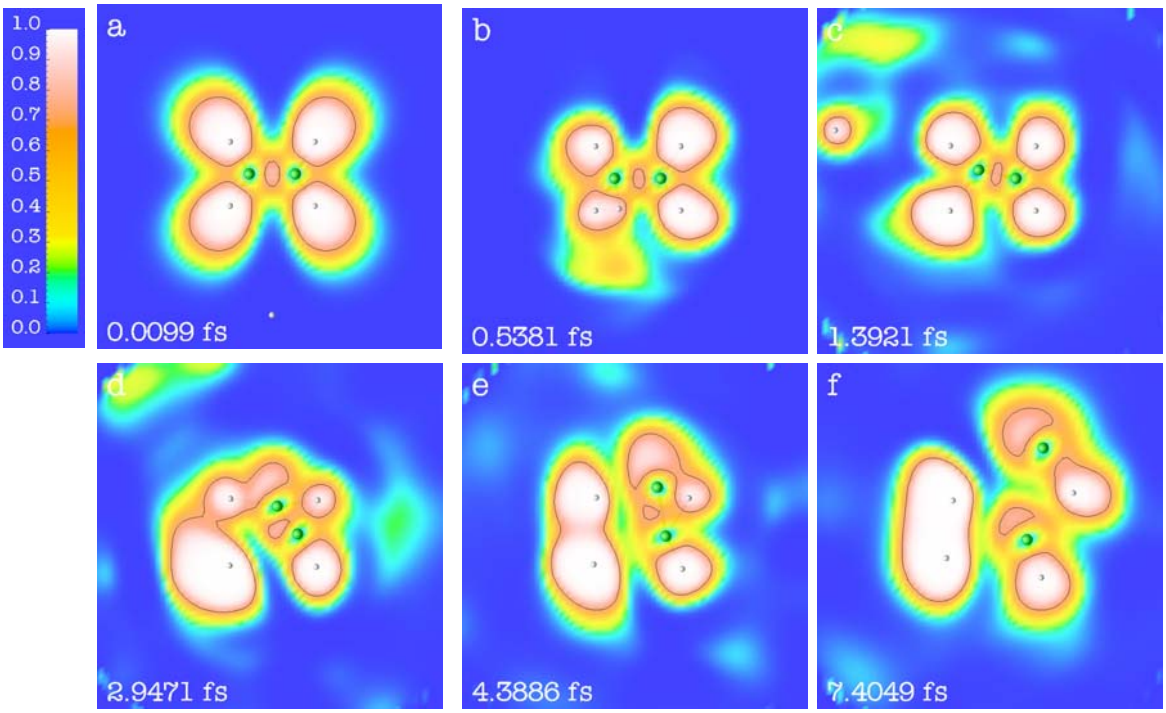
TD-ELF Examples

Ethyne (acetylene) in a strong laser field



TD-ELF Examples

Scattering of a proton from 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 ?**

Use TD Kohn-Sham equations (E. Runge, EKUG, PRL **52**, 997 (1984))

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

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

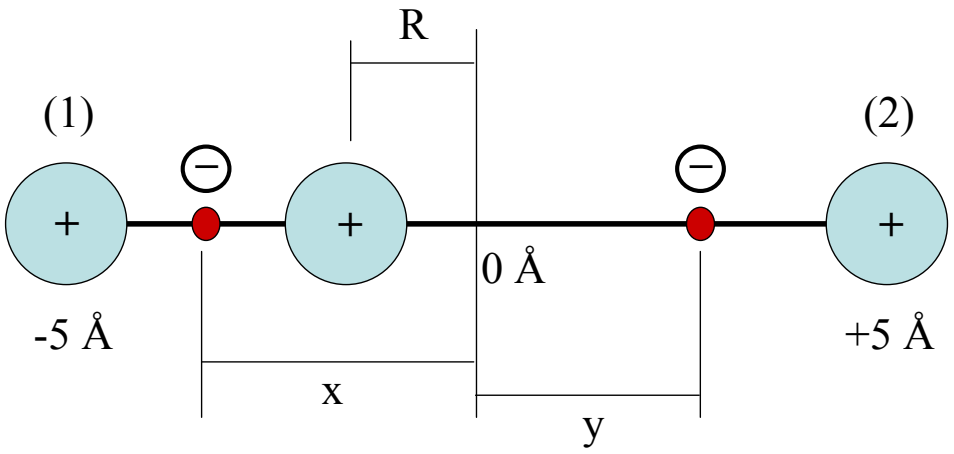
propagated numerically on real-space grid using **octopus** code

www.tddft.org

- more TDELF movies
- download **octopus**

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).

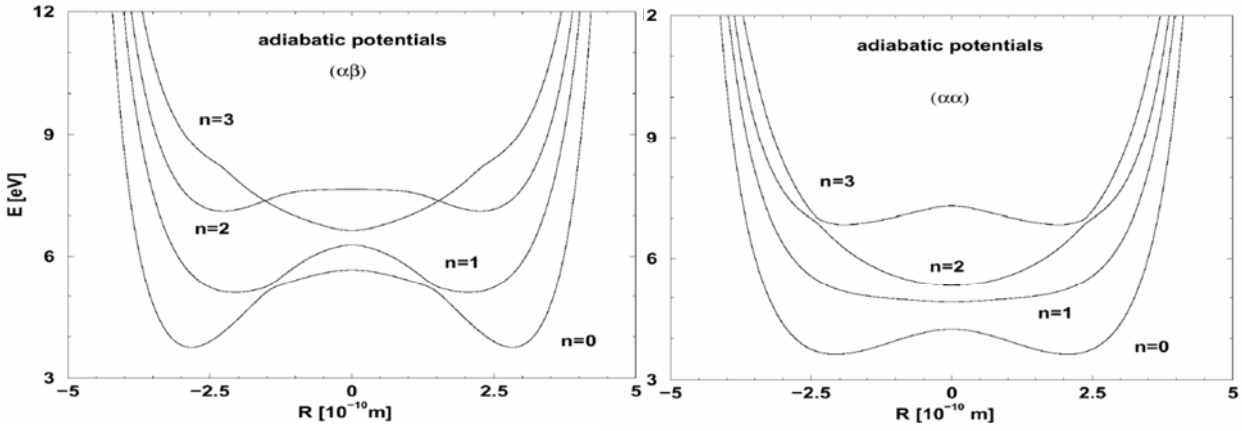
MODEL



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

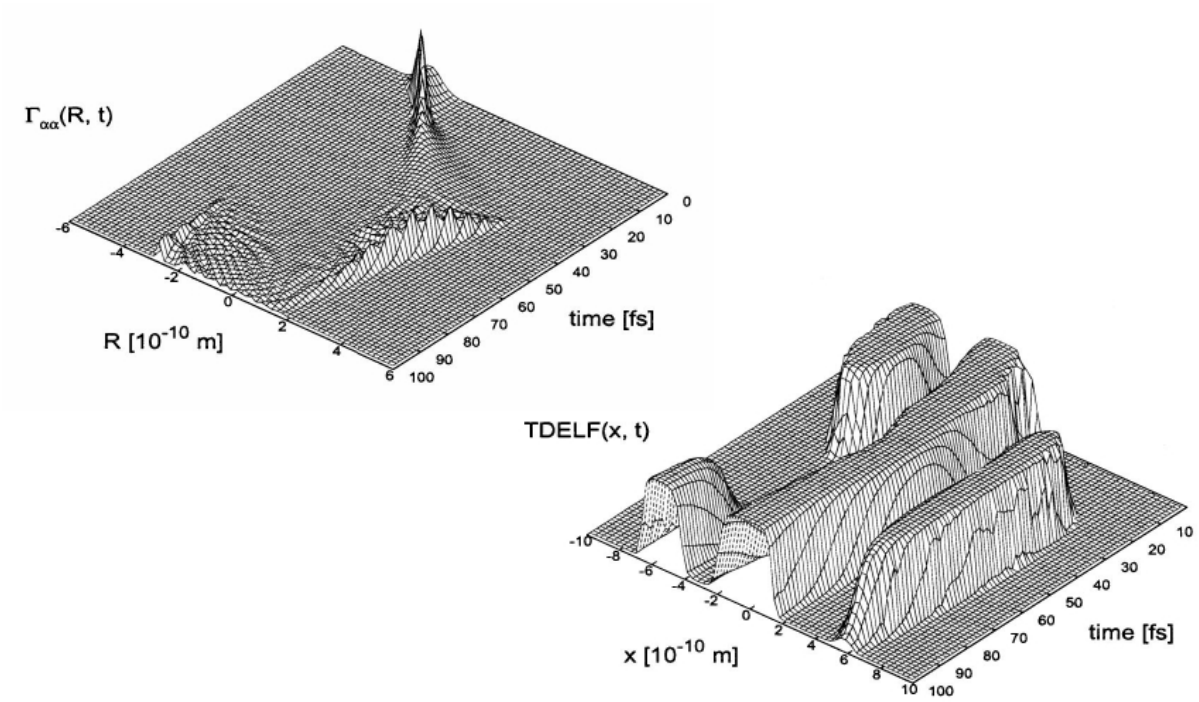
Anti-parallel spins

Parallel spins



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

Parallel spins



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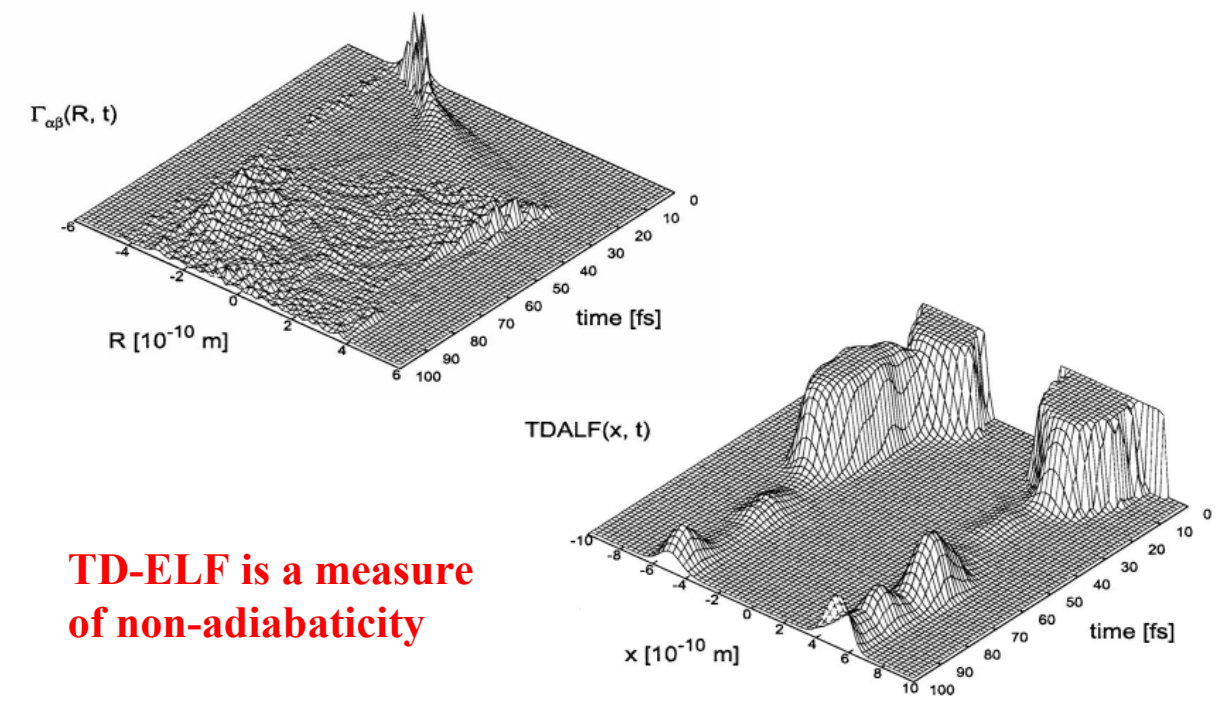

TD-ELF is a measure of non-adiabaticity

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)

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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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E_0 = <u>given</u> fluence

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

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

TDSE

Optimal control of static targets (standard formulation)

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

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$\hat{O}$

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TDSE

GOAL: Maximize $J = J_1 + J_2 + J_3$

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

Control equations

Algorithm

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:

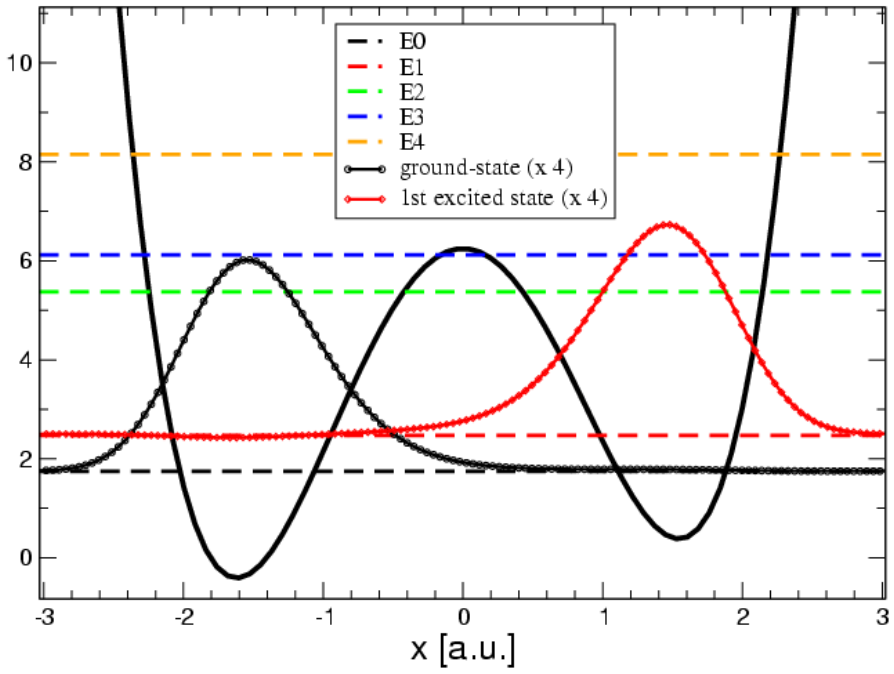
$$\delta_\varepsilon J = 0 \rightarrow \boxed{\varepsilon(t) = \frac{1}{\alpha}\,\mathrm{Im}\langle \chi(t)|\hat{\mu}|\psi(t)\rangle}$$

Forward propagation

Backward propagation

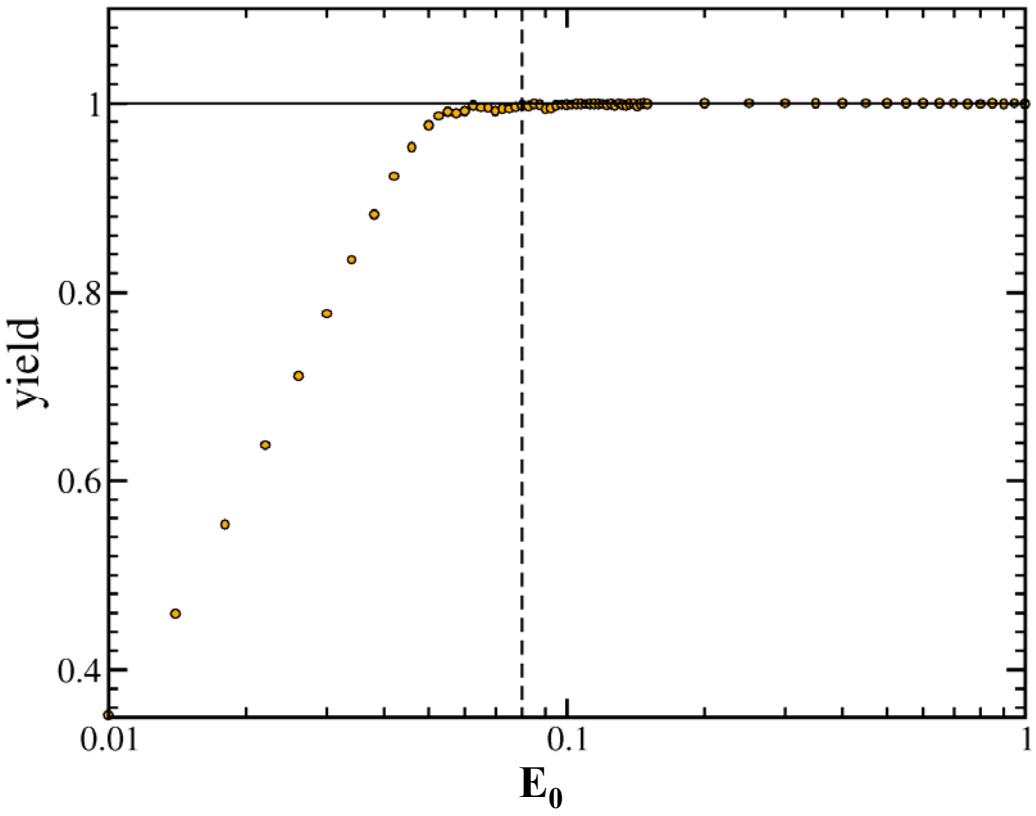
New laser field

Algorithm monotonically convergent: W. Zhu, J. Botina, H. Rabitz, J. Chem. Phys. 108, 1953 (1998))



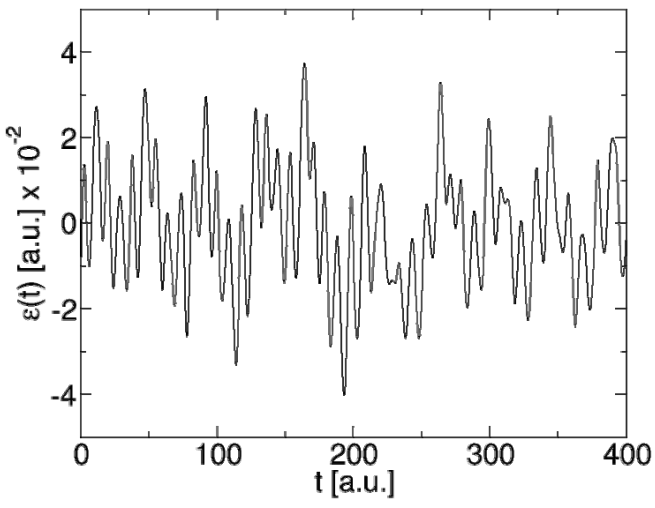
target state: ϕ_f = first excited state

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

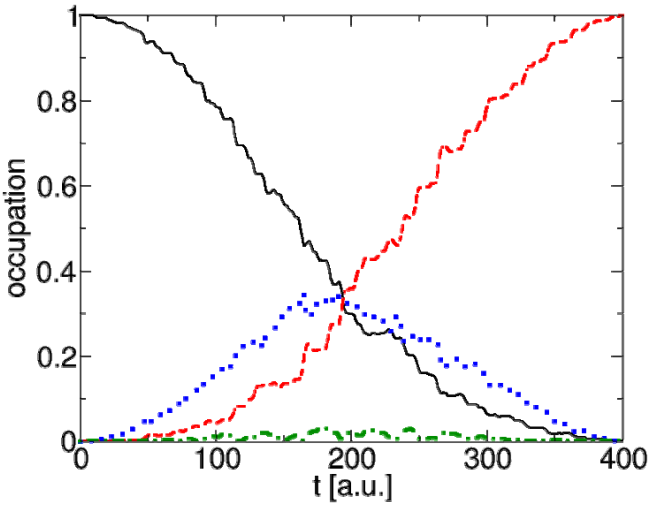


Optimization results

Optimized pulse

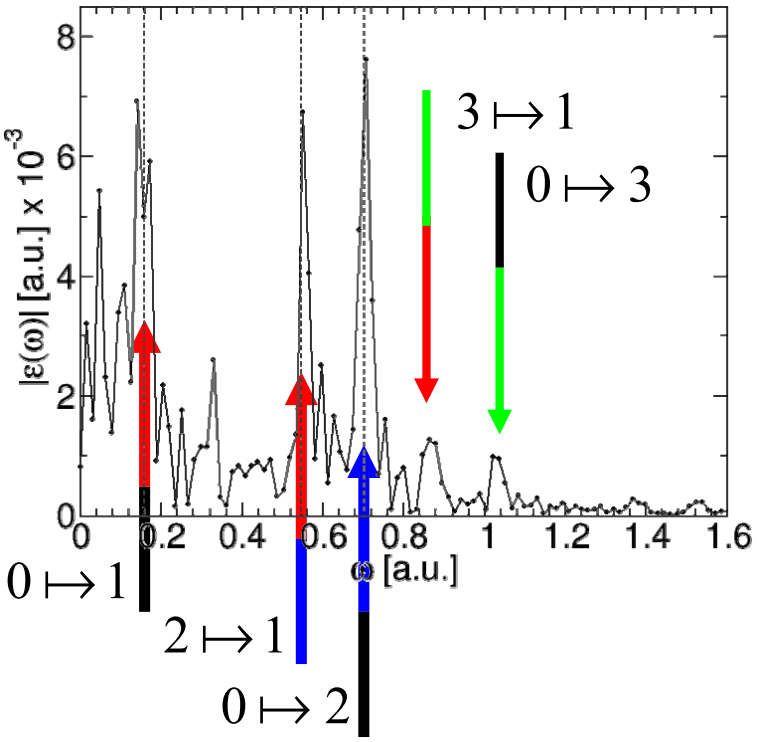


Occupation numbers

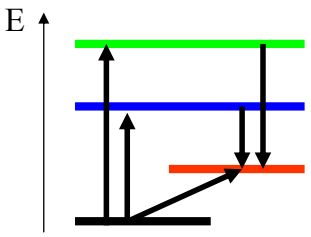


$$\left|\langle 1|\psi(T)\rangle\right|^2 = 99.91\%$$

Spectrum



OCT finds a combination of several transition processes



algorithm

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

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

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

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

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))

With spectral constraint:

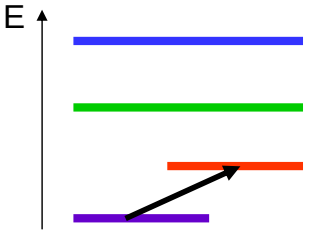
$$\varepsilon^{(k+1)}(t) := \mathcal{F}\left[f(\omega)\times \mathcal{F}\left[\tilde{\varepsilon}^{(k+1)}(t)\right]\right]$$

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

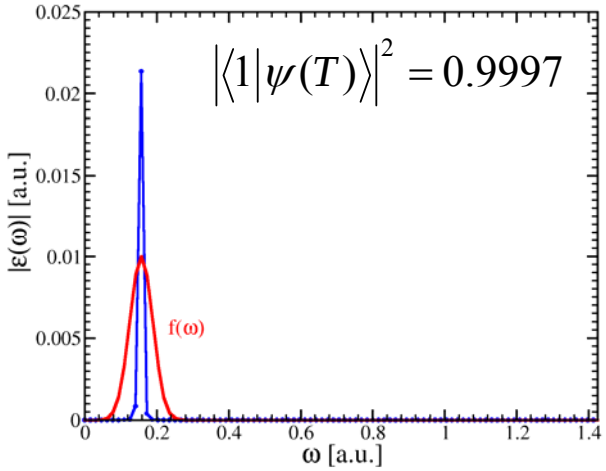
or $$f(\omega) = 1 - \exp\left[-\gamma(\omega-\omega_0)^2\right] - \exp\left[-\gamma(\omega+\omega_0)^2\right]$$

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

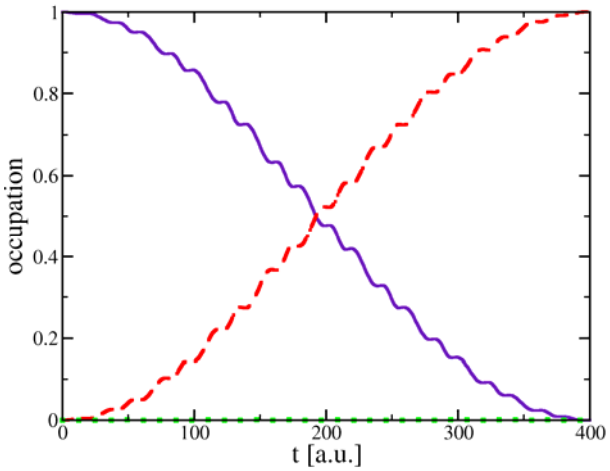
Frequency constraint:
Only direct transition frequency ω_0 allowed



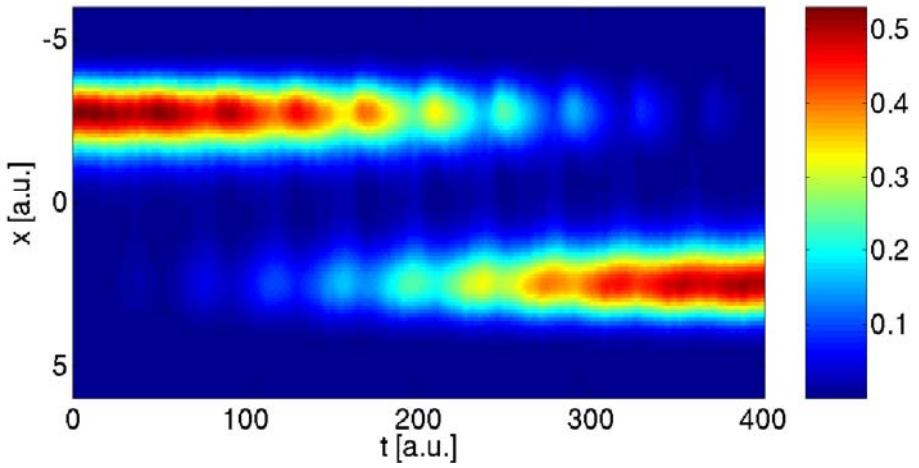
Spectrum of optimized pulse



occupation numbers

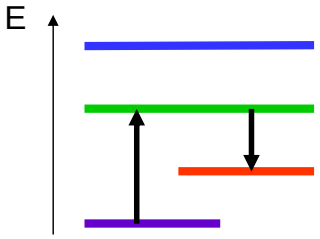


Time-Dependent Density

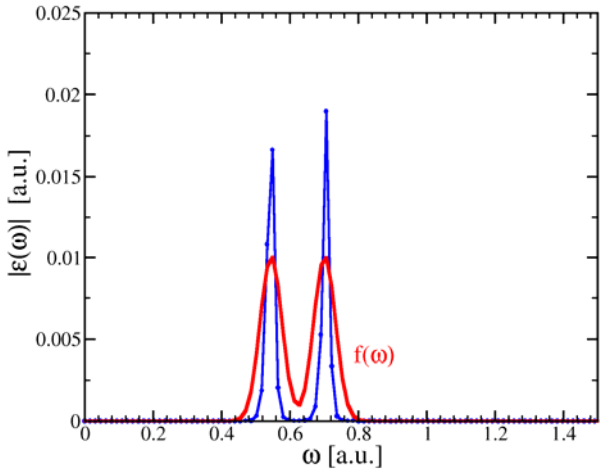


<u>Frequency constraint</u>:
Selective transfer via intermediate state $|2\rangle$

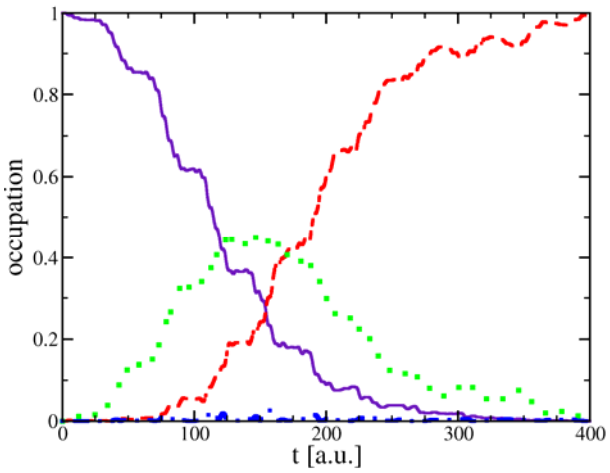
$$|0\rangle \xrightarrow{\omega_{02}} |2\rangle \xrightarrow{\omega_{21}} |1\rangle$$



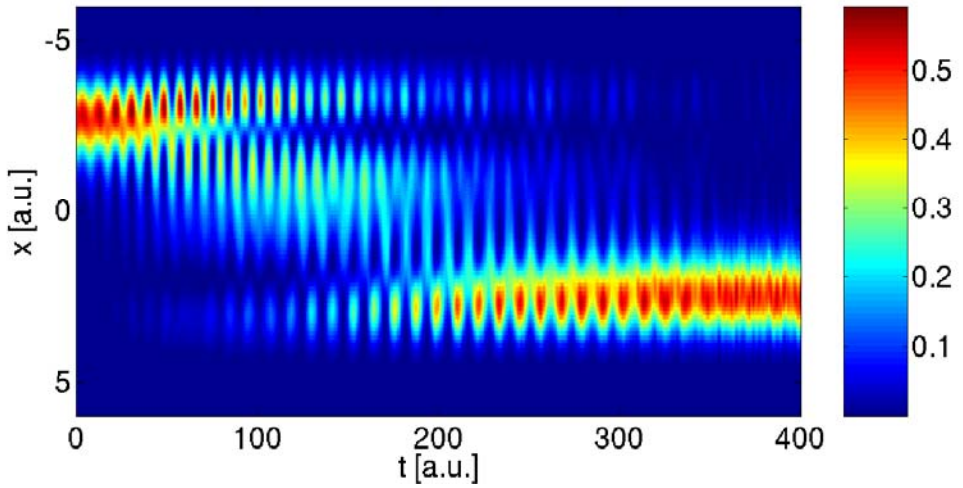
Spectrum of optimized pulse



occupation numbers

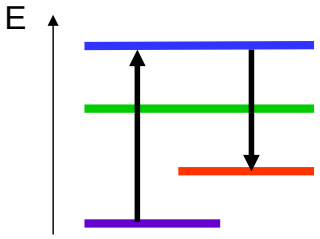


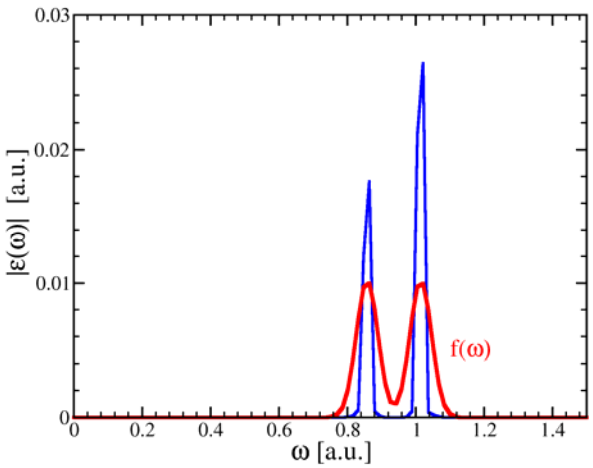
Time-Dependent Density

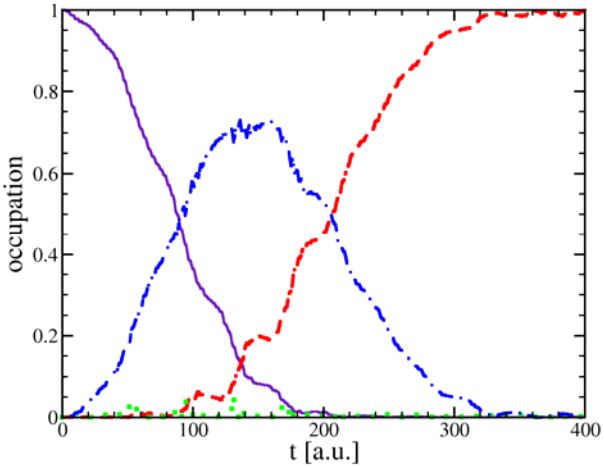


<u>Frequency constraint</u>:
Selective transfer via intermediate state $|3\rangle$

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

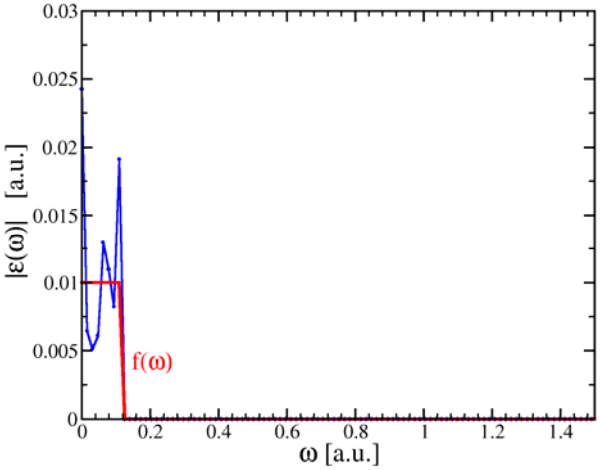




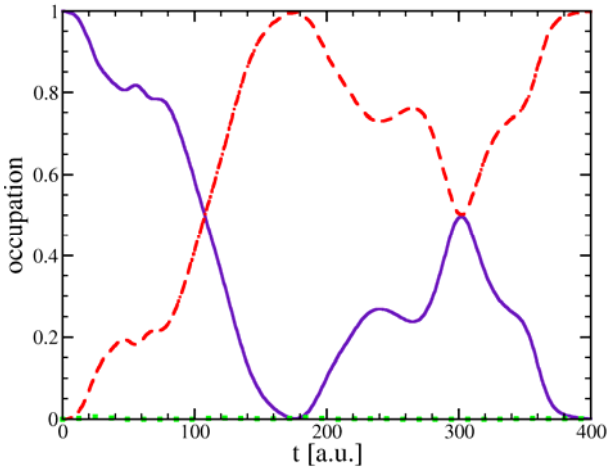


Frequency constraint: All resonances excluded

Spectrum of optimized pulse



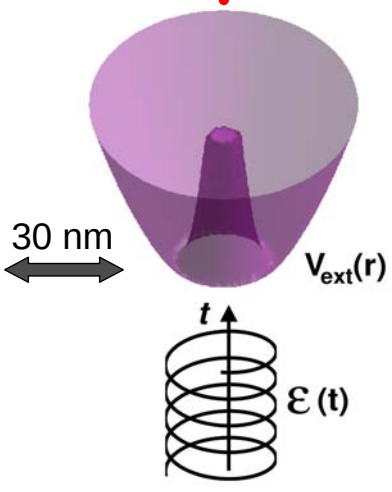
occupation numbers

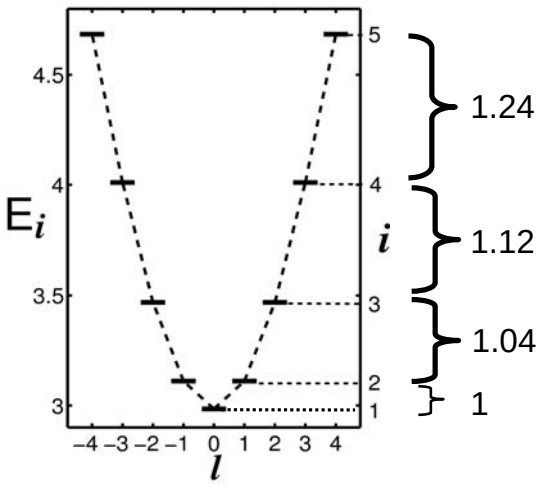


Quantum ring: Control of circular current

- TD-SE: $$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\hat{H}_0 + e\,\mathbf{r}\,\epsilon(t)\right]\Psi(\mathbf{r},t)$$

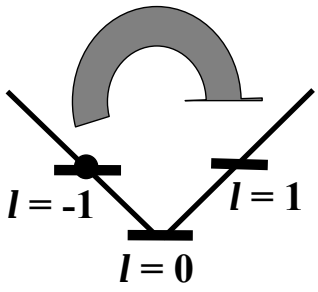
$$\hat{H}_0 = -\frac{\hbar^2}{2m^*}\nabla^2 + \frac{1}{2}m^*\omega_0^2 r^2 + V_0 e^{-r^2/d^2} \qquad \epsilon(t) = (\epsilon_x(t), \epsilon_y(t))$$

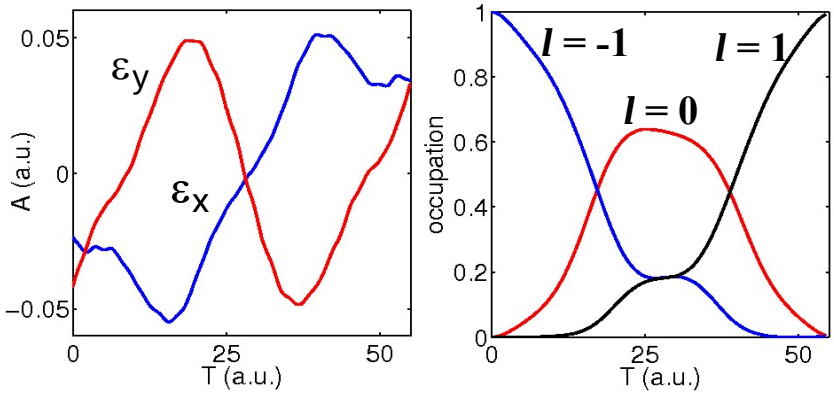




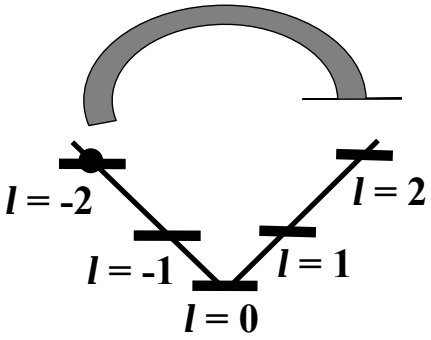
Change in chirality

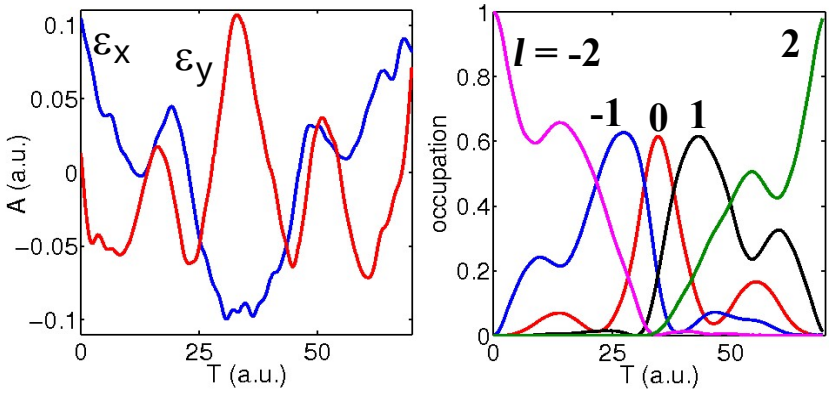
E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U.G.
PRL 98, 157404 (2007)





Optimized pulse and occupation numbers for l=-1 => l=1





Optimized pulse and occupation numbers for l=-2 => l=2

OPTIMAL CONTROL OF TIME-DEPENDENT TARGETS

Maximize $J = J_1 + J_2 + J_3$

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

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

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

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

Control equations

1. Schrödinger equation with initial condition:

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

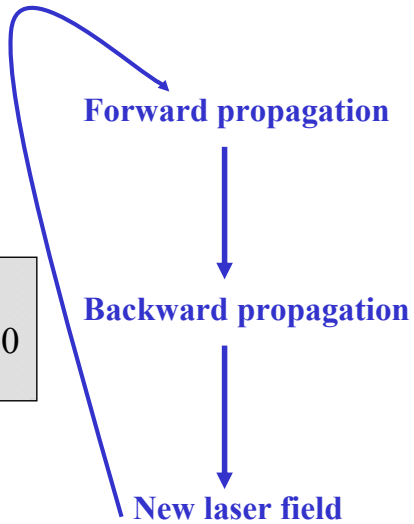
2. Schrödinger equation with final condition:

$$\delta_\psi J = 0 \rightarrow \boxed{\text{Inhomogenous TDSE}: \left[i\partial_t - \hat{H}(t)\right]\chi(t) = -\frac{i}{T}\hat{O}(t)\psi(t), \quad \chi(T) = 0}$$

3. Field equation:

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

Algorithm



Y. Ohtsuki, G. Turinici, H. Rabitz, JCP 120, 5509 (2004)
I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

Control of path in Hilbert space

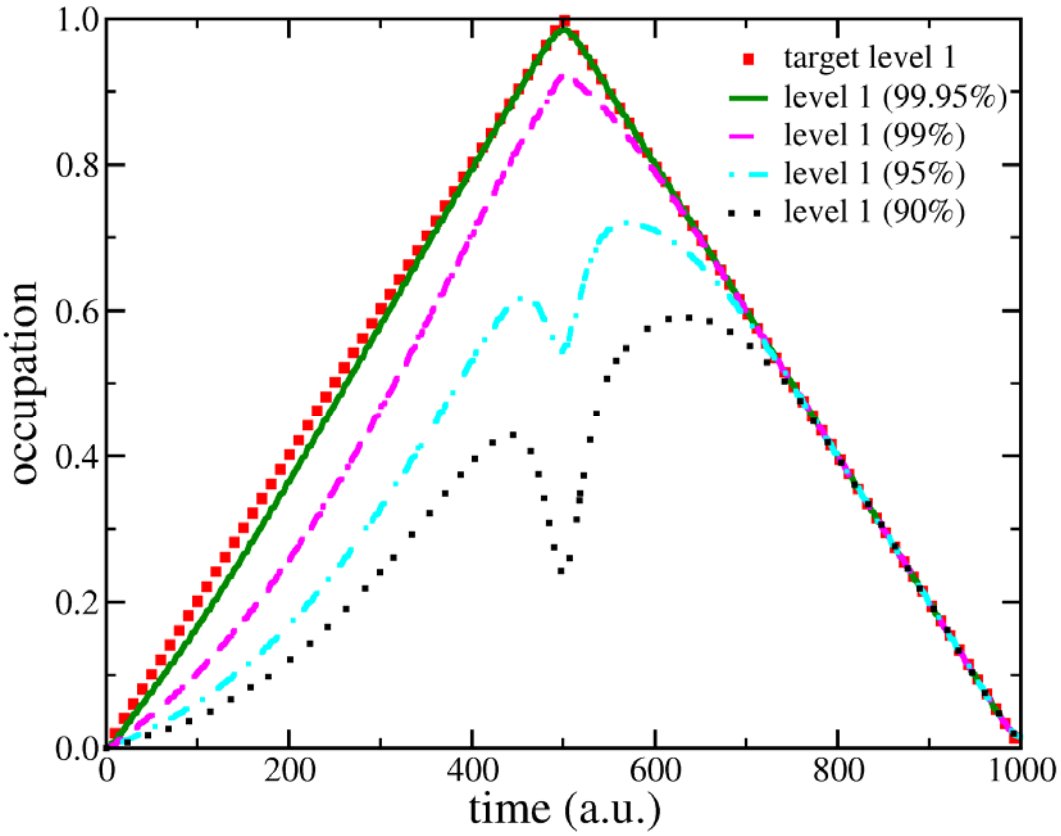
I. Serban, J. Werschnik, E.K.U.G. Phys. Rev. A 71, 053810 (2005)

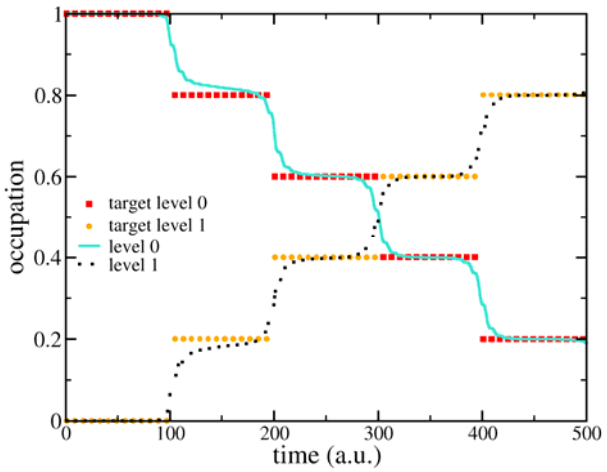
$$\hat{O}(t) = |\Phi(t)\rangle\langle\Phi(t)|$$

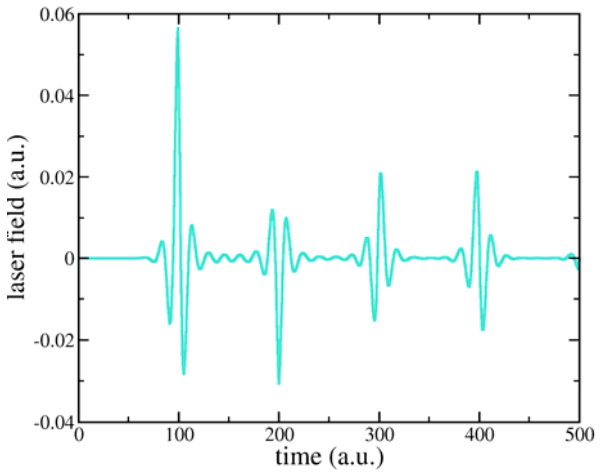
with $|\Phi(t)\rangle = \alpha_0(t)e^{-i\varepsilon_0 t}|0\rangle + \alpha_1(t)e^{-i\varepsilon_1 t}|1\rangle$

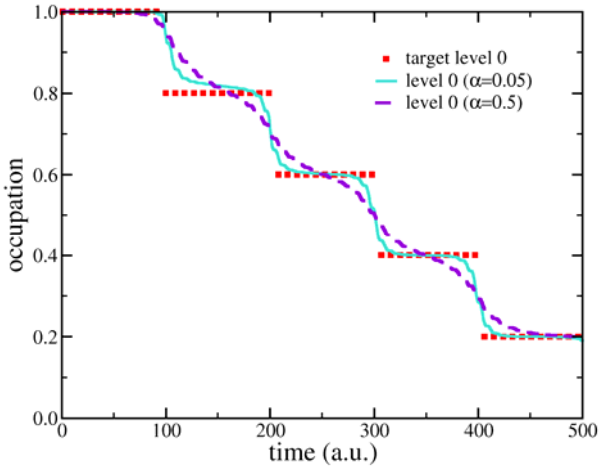
$|\alpha_0(t)|^2$ **given target occupation, and** $|\alpha_1(t)|^2 = 1 - |\alpha_0(t)|^2$

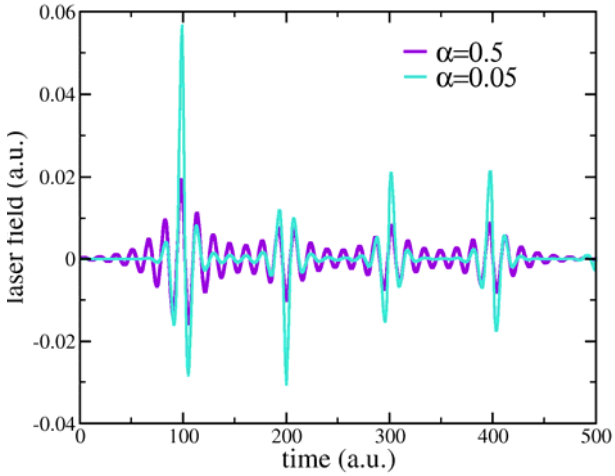
Goal: Find laser pulse that reproduces $|\alpha_0(t)|^2$


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


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


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





Control path in real space

$$\hat{O}(t) = \delta(r - r_0(t)) \approx \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(r-r_0(t))^2/2\sigma^2}$$

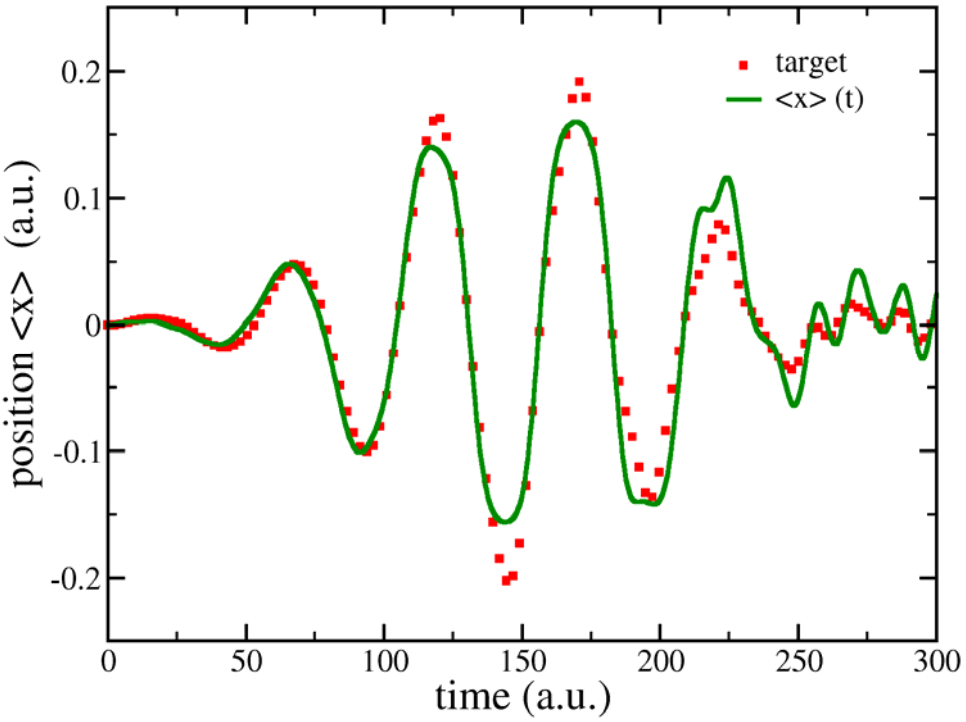
with <u>given</u> trajectory $r_0(t)$.

Algorithm maximizes the density along the path $r_0(t)$:

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

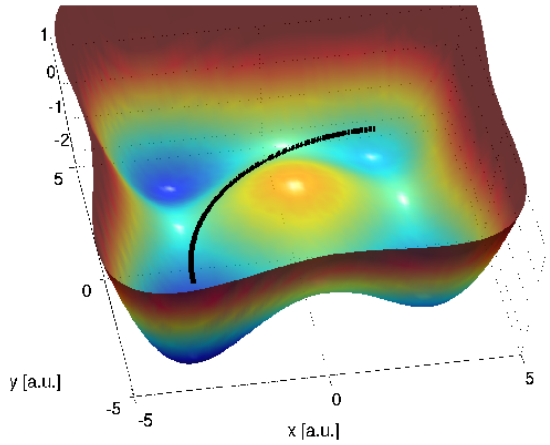
J. Werschnik and E.K.U.G., in: Physical Chemistry of Interfaces and Nanomaterials V, M. Spitler and F. Willig, eds, Proc. SPIE 6325, 63250Q(1-13) (ISBN: 9780819464040, doi: 10.1117/12.680065); also on arXiv:0707.1874

Control of time-dependent density of hydrogen atom in laser pulse

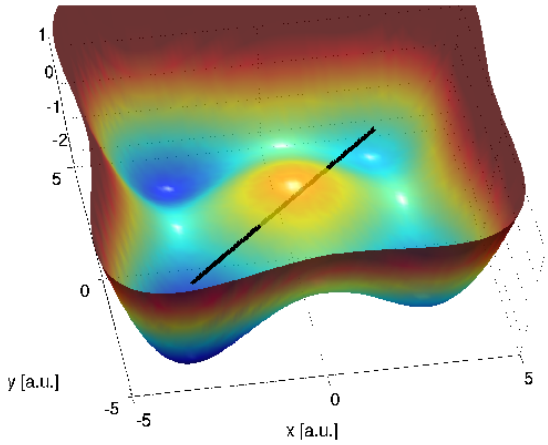


Control of charge transfer along selected pathways

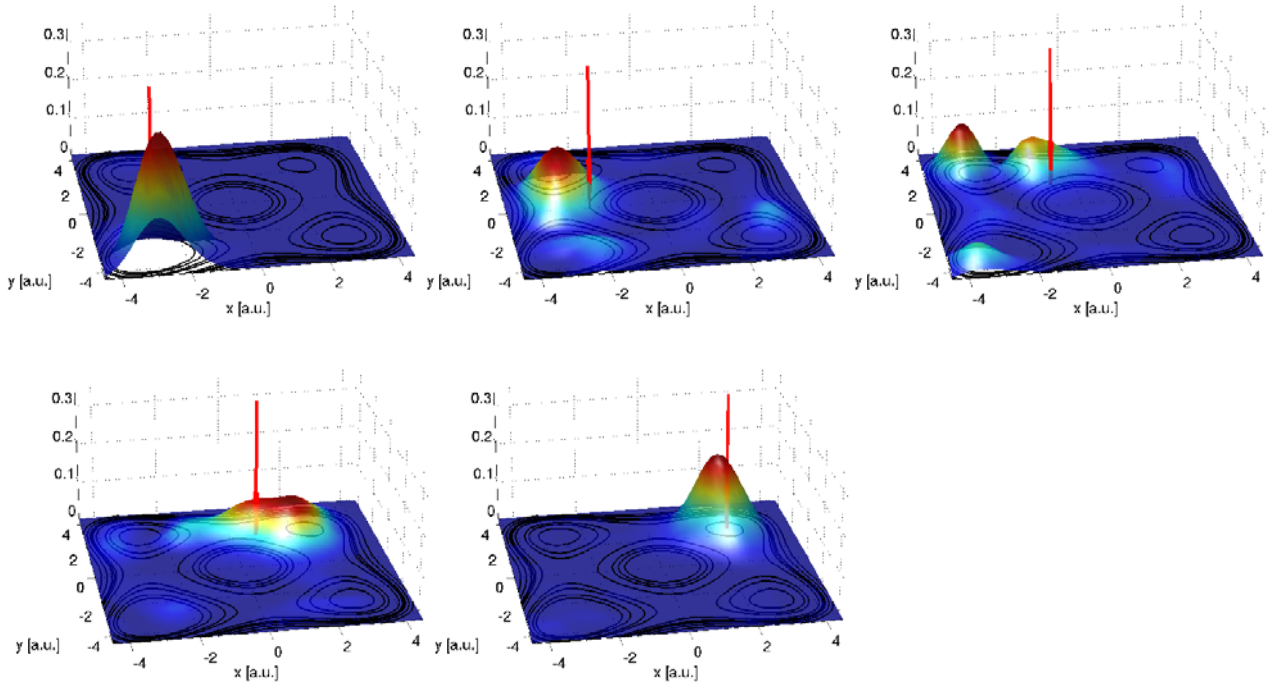
Trajectory 1



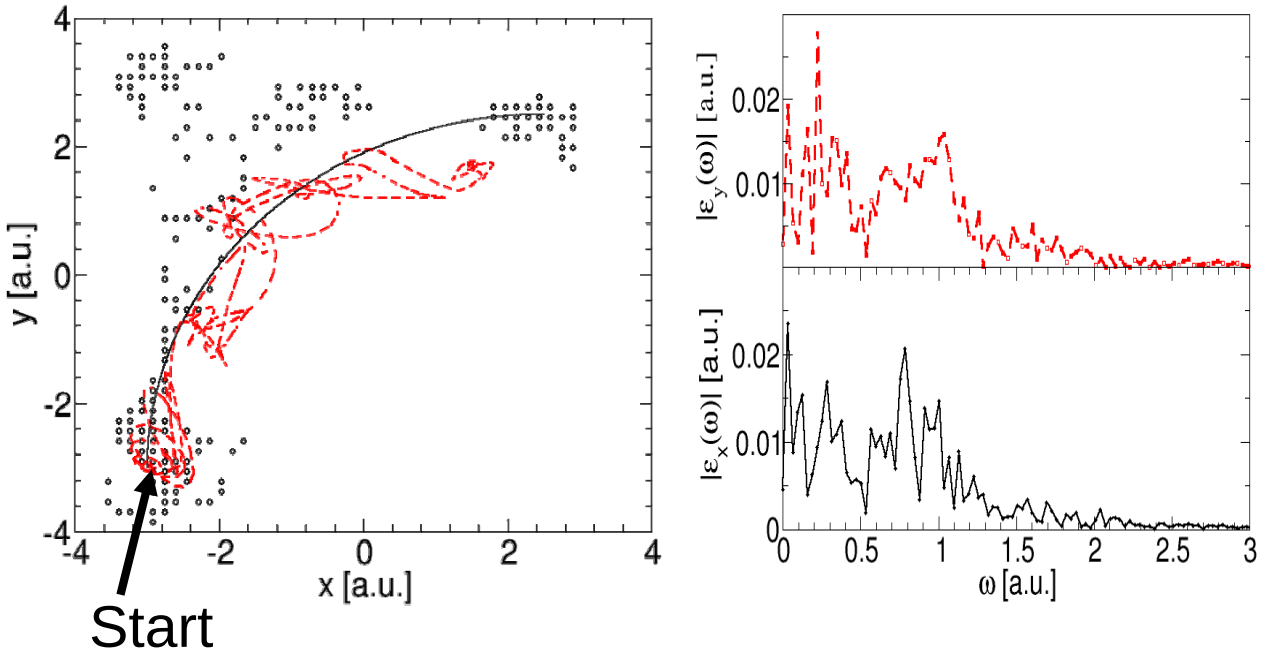
Trajectory 2



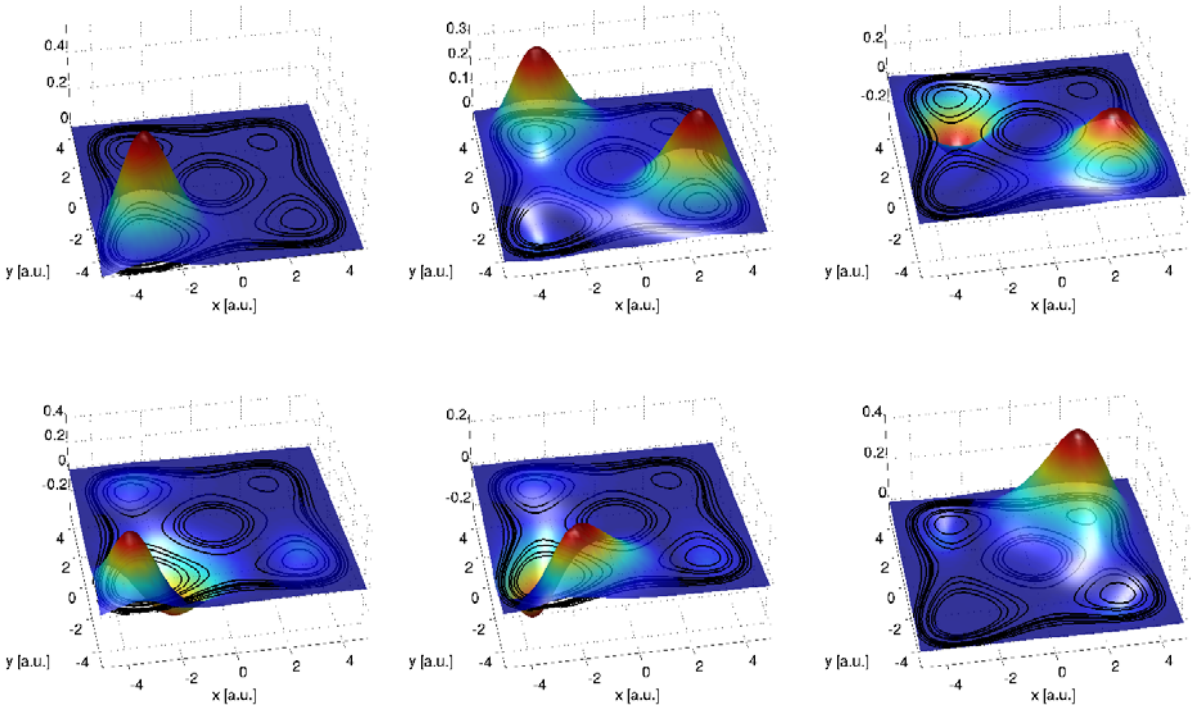
Time-evolution of wavepacket with the optimal laser pulse for trajectory 1



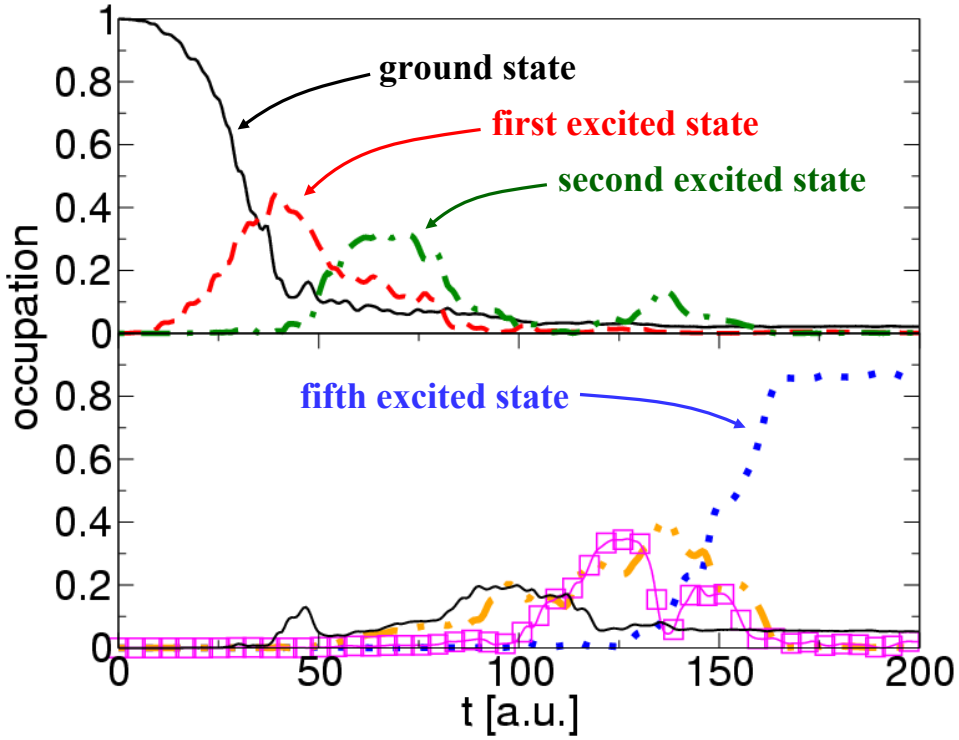
Trajectory 1: Results



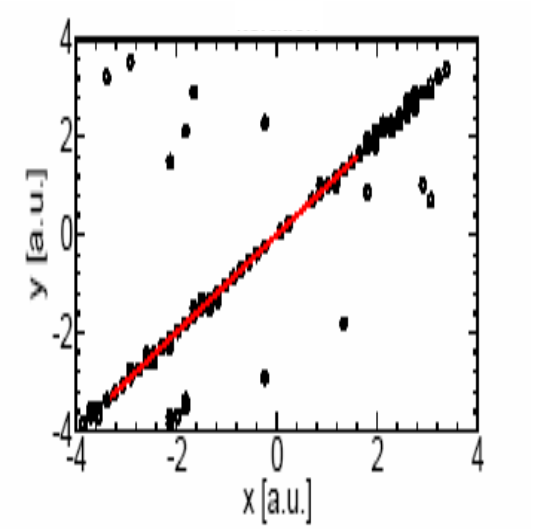
Lowest six eigenstates

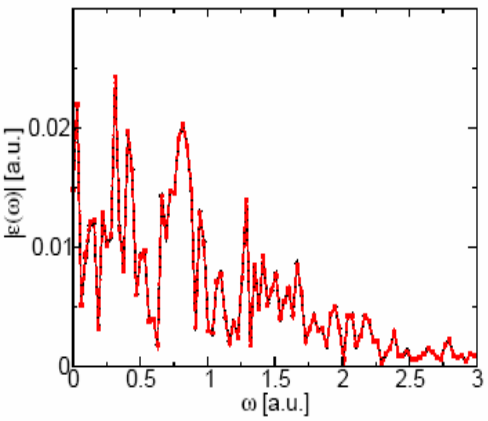


Populations of eigenstates



Trajectory 2






Thanks !