Optimal control and quantum dynamics

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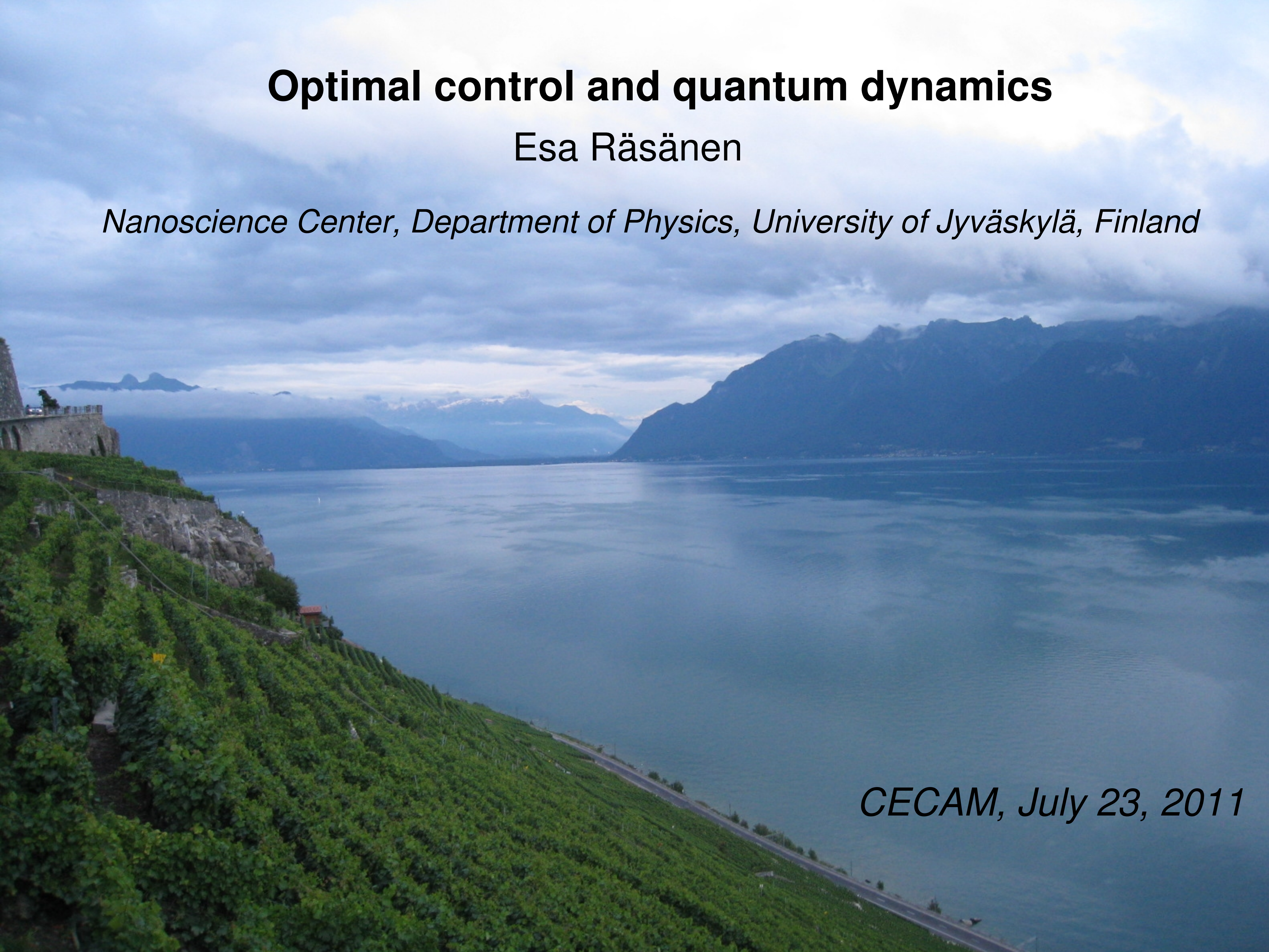
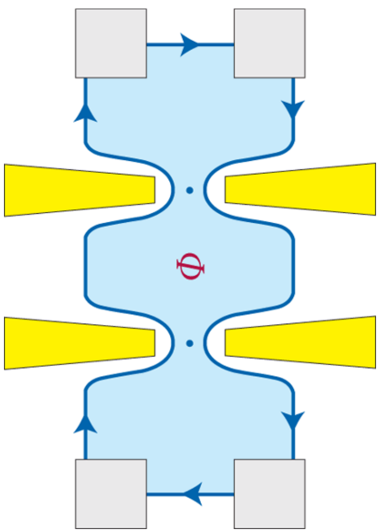


Outline

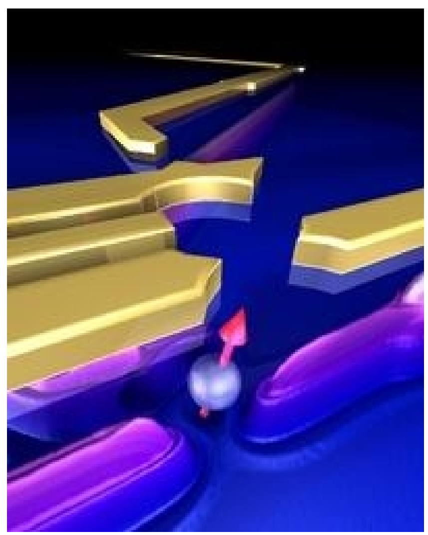
- Some motivation
- TDDFT I - Side remark: “Initial-state dependence”
- Optimal control theory (OCT) and applications
  - Control of excitations
  - Control of 1-electron ionization
  - Control of 2-electron ionization (OCT & TDDFT)

Long-term objectives

electromagnetic control of low-dimensional systems

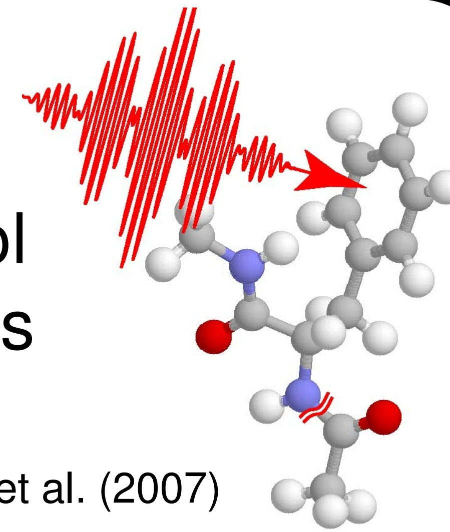


Goldman (2007)



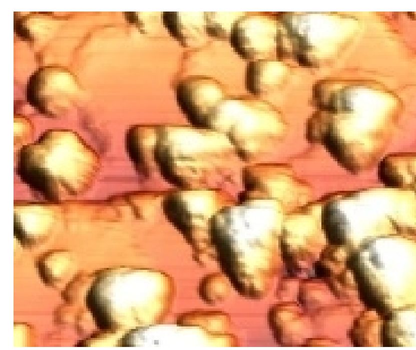
Delft Qubit Project

laser-control of molecules



Laarmann et al. (2007)

4th generation solar cells



Wagner (2009)

TDDFT: Initial-state dependence

Reminder: we propagate individual particles exposed to

$$v_{\mathrm{KS}}(\mathbf{r},t) = \underbrace{v_{\mathrm{ext}}(\mathbf{r},t)}_{\textit{system}} + \underbrace{v_{\mathrm{H}}(\mathbf{r},t)}_{\textit{classicism}} + \underbrace{v_{\mathrm{xc}}(\mathbf{r},t)}_{\textit{all the trouble!}}$$

$$v_{\mathrm{xc}}(\mathbf{r},t) = v_{\mathrm{xc}}[n(\mathbf{r};t_0,\ldots,t),\Phi_0,\Psi_0](\mathbf{r},t)$$

density at previous times

initial KS wave function

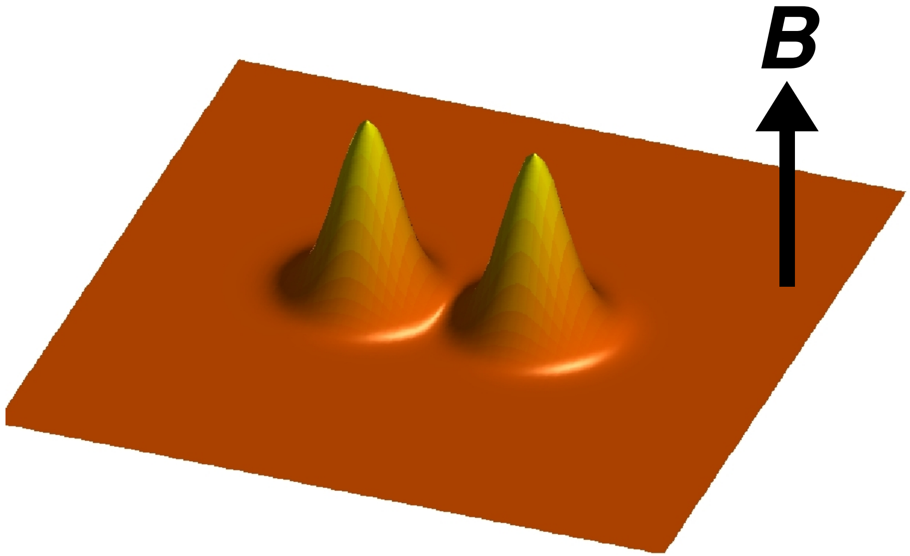
initial many-body wave function

N. T. Maitra and K. Burke, Phys. Rev. A **63**, 042501 (2001)

Example: Two 2D Gaussian wave packets in magnetic field

$$\psi_\pm(x,y) = \frac{1}{a\sqrt{\pi}} \exp\left[-\frac{(x \pm a)^2 + y^2}{2a^2}\right] \exp[\pm i x/a]$$

- initially at rest
- interaction effects at t > 0:
  => repulsion
  => Lorentz force
  => “flower-like” motion



- initial wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+(\mathbf{r}_1) & \psi_+(\mathbf{r}_2) \\ \psi_-(\mathbf{r}_1) & \psi_-(\mathbf{r}_2) \end{vmatrix}$$

- initial density

$$\rho(x,y) = \frac{2e^{1-\frac{x^2+y^2}{a^2}}\left[-\cos(2y/a) + e^2\cosh(2x/a)\right]}{\pi a^2(e^4 - 1)}$$

Quiz

1. How to construct the initial Kohn-Sham orbitals?

(a) orthonormalize the wave-packet orbitals and use them
(b) simply use the wave packets as initial Kohn-Sham orbitals
(c) take the square root of the exact density (divided by two)
(d) they cannot be properly constructed in this case

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(a) no
(b) yes - one other choice
(c) yes - infinitely many choices

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Harriman construction

J. E. Harriman, Phys. Rev. A **24**, 680 (1980):

“For any nonnegative, normalized density an arbitrary number of orthonormal orbitals can be constructed with squares which sum to the given density.”

Harriman orbitals: $$\varphi_i(x,y) = \sqrt{\frac{\rho(x,y)}{N}}\exp\left[ikf(x)\right]$$

with any set of $k = 0,\ \pm 1,\ \pm 2, \ldots$

and with $$f(x) = \frac{2\pi}{N}\int_{-\infty}^{x} dx' \int_{-\infty}^{\infty} dy\,\rho(x',y)$$

It is straightforward to show that

(1) $$\sum_{i=1}^{N} |\varphi_i(x,y)|^2 = \rho(x,y)$$

(2) $$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\,dy\,\varphi_{k'}^{*}(x,y)\,\varphi_k(x,y) = \delta_{kk'}$$

Time-propagation (animation follows...)

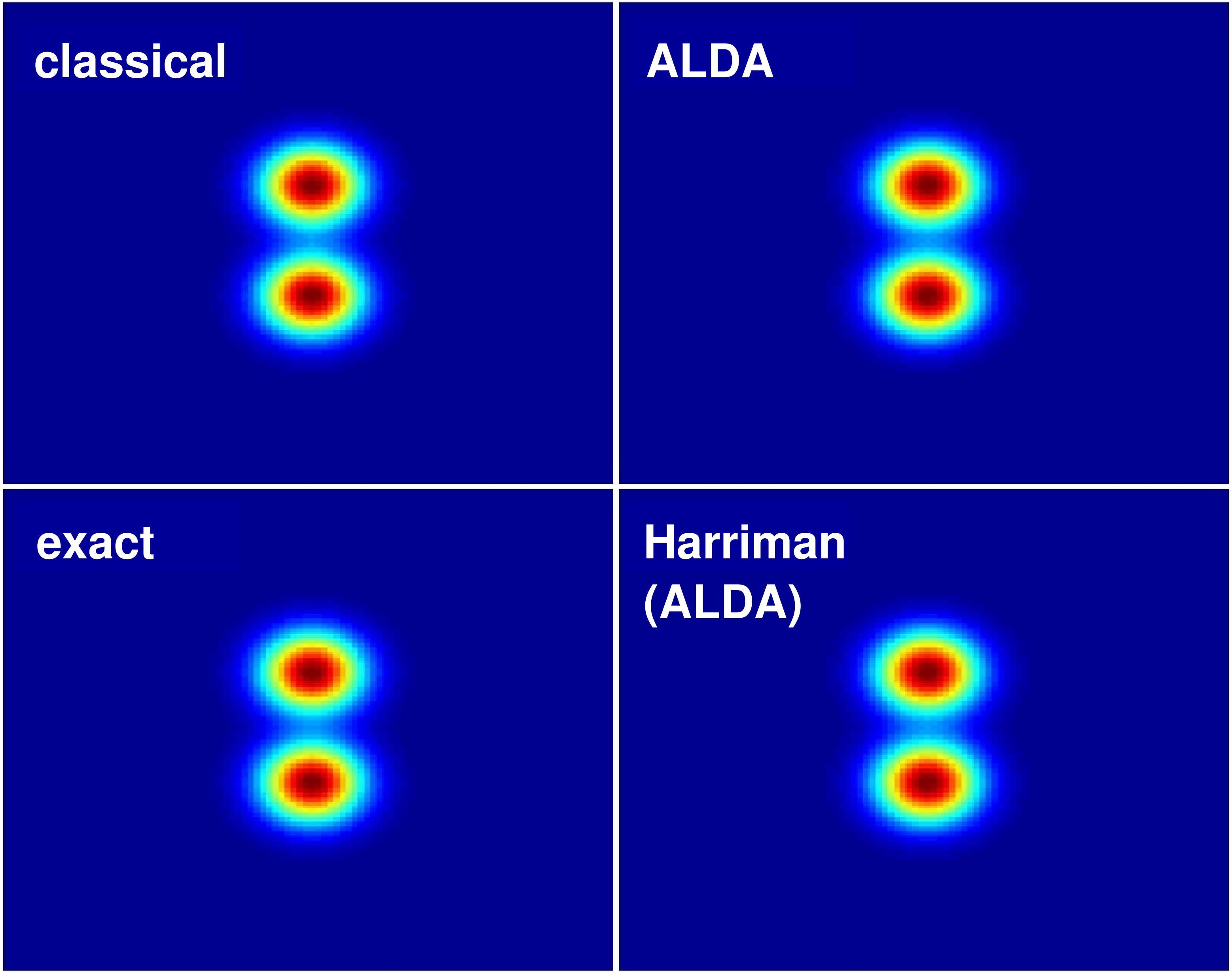
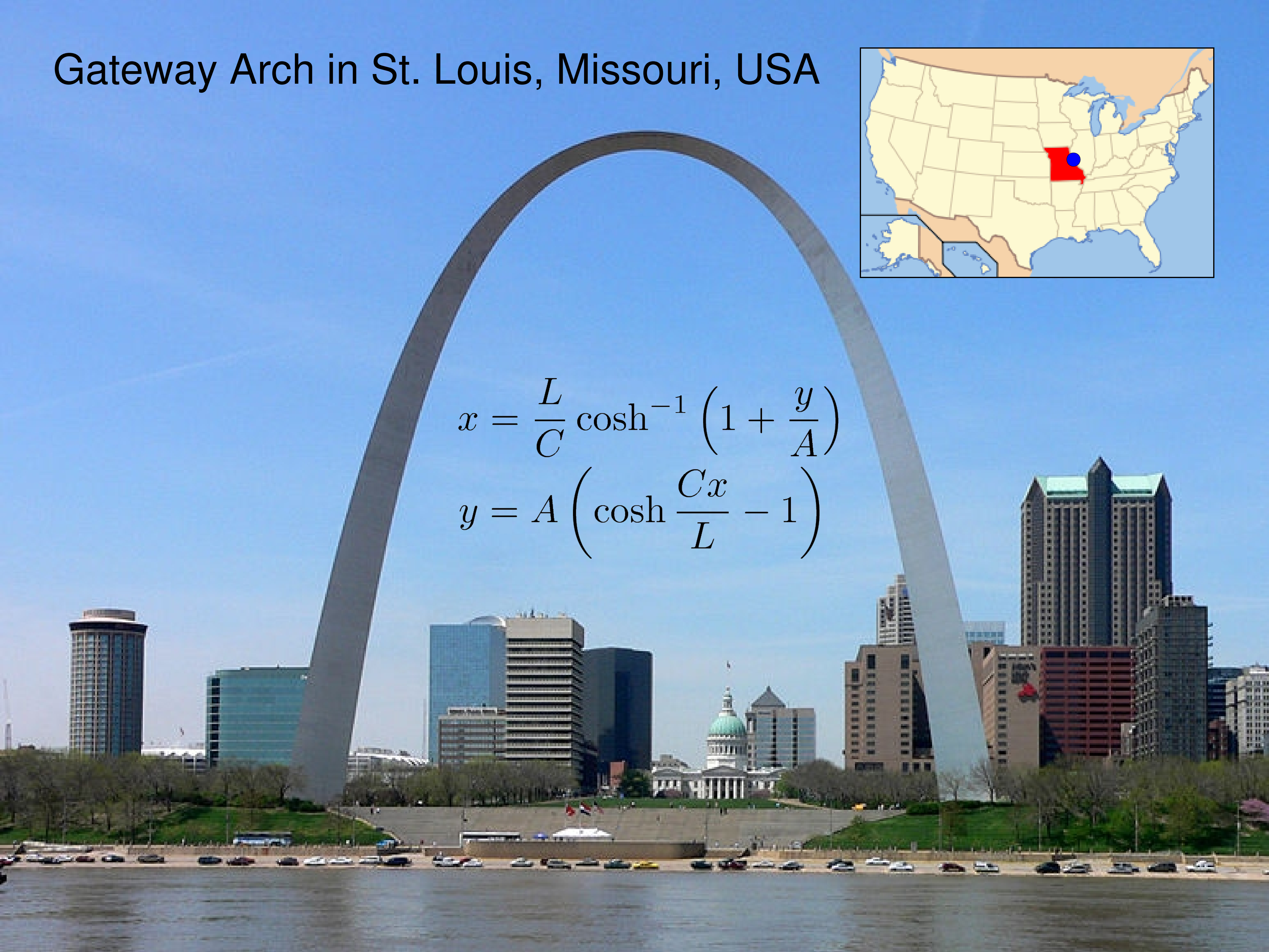


Fig: Initial density for the time-propagation with different methods.

Gateway Arch in St. Louis, Missouri, USA

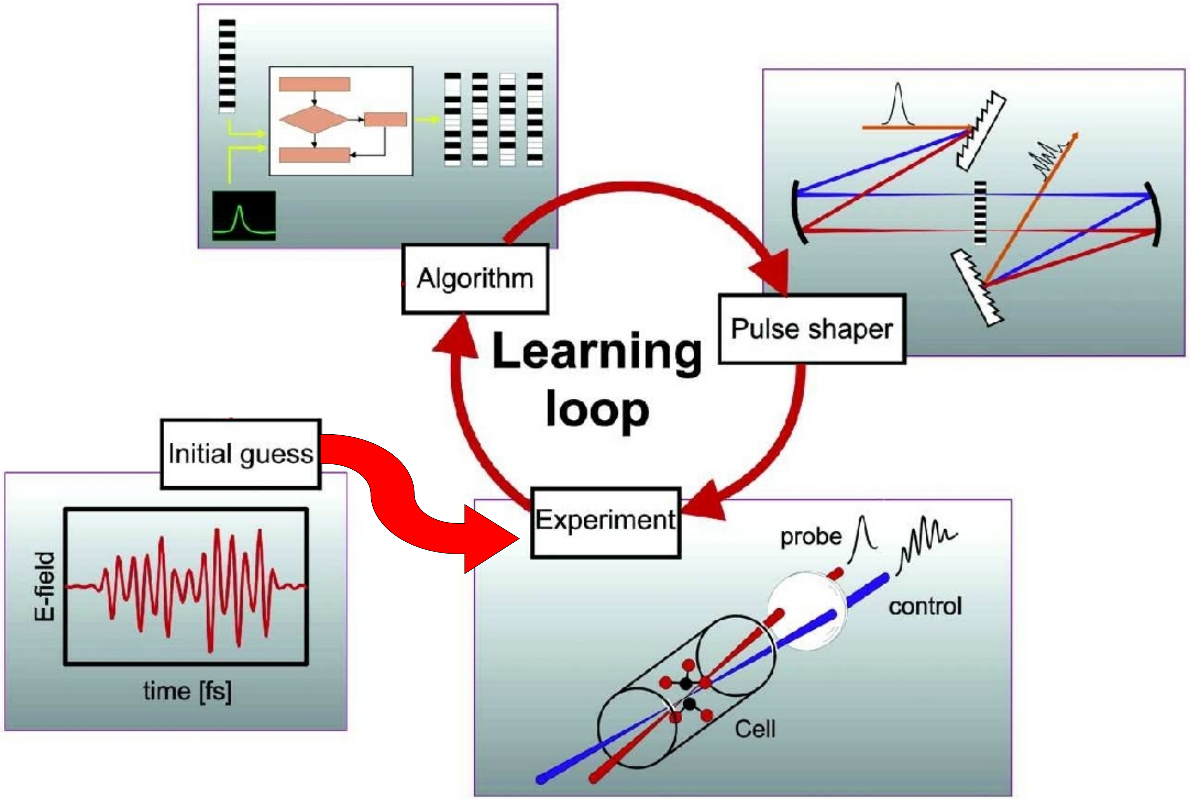


$$x = \frac{L}{C} \cosh^{-1}\left(1 + \frac{y}{A}\right)$$

$$y = A\left(\cosh \frac{Cx}{L} - 1\right)$$

Optimal control: Overview

- Classical control since 1697
- General goals: (i) control of chemical reactions (e.g. molecular design), (ii) coherent control of spin/charge operations (qubits)
- “Traditional” control in chemistry: Learning-loop experiments



from H. Rabiz et al., Science **288**, 824 (2000)

Quantum optimal control theory (OCT)

Key question: What is the external time-dependent field that drives the system into a predefined goal?

$$i\frac{d}{dt}\big|\Psi(t)\big\rangle = \hat{H}\big[\epsilon_k(t)\big]\big|\Psi(t)\big\rangle$$

control functions

- Usually the control function is an electric field (laser pulse)

$$\hat{H}(t) = \hat{H}_0 + \epsilon(t)\,\hat{D}$$

- Most commonly the objective is the transition probability to a target state

Formulation of OCT

- Find the extremal points of the functional

$$J[\Psi,\chi,\epsilon] = J_1[\Psi] + J_2[\epsilon] + J_3[\Psi,\chi,\epsilon]$$

target functional ***field constraint*** ***fulfillment of the TD-SE***

$$J_1[\Psi] = \langle \Psi(T)|\hat{O}|\Psi(T)\rangle = |\langle \Psi(T)|\Psi_{\mathrm{target}}\rangle|^2$$

here $\hat{O}$ is a projection operator

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

$$J_3[\Psi,\chi,\epsilon] = -2\,\mathrm{Im} \left[\int_0^T dt\, \langle \chi(t)| i\frac{d}{dt} - \hat{H}(t)|\Psi(t)\rangle \right]$$

Control equations

- Forward propagation for $|\Psi(t)\rangle$

$$i\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle, \quad |\Psi(0)\rangle = |\Psi_{\mathrm{initial}}\rangle$$

- Backward propagation for $|\chi(t)\rangle$

$$i\frac{d}{dt}|\chi(t)\rangle = \hat{H}(t)|\chi(t)\rangle, \quad |\chi(T)\rangle = \hat{O}|\Psi(T)\rangle$$

- Solution field:

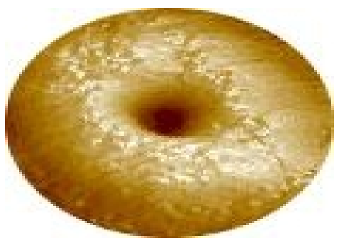
$$\epsilon(t) = -\frac{1}{\alpha}\,\mathrm{Im}\,\left[\langle\chi(t)|\mu|\Psi(t)\rangle\right] \quad \text{with} \quad \int_0^T dt\,\epsilon^2(t) = E_0$$

These self-consistent equations are solved iteratively (various algorithms).

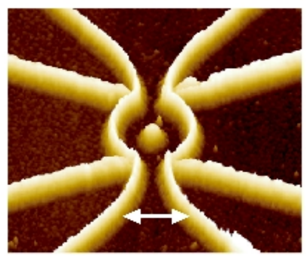
For a review, see J. Werschnik and E.K.U. Gross, J. Phys. B: At. Mol. Opt. Phys. **40**, R175-R211 (2007).

Application 1: Control of current in a quantum ring

Experiments:

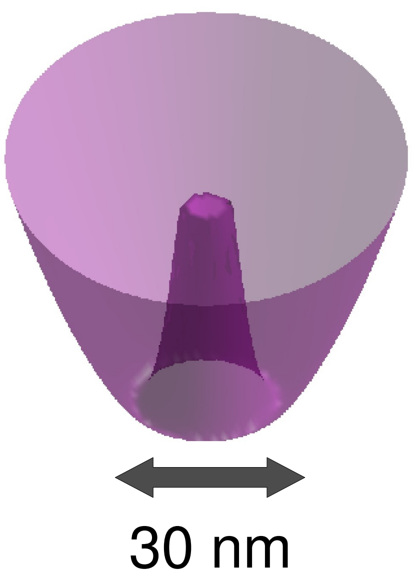


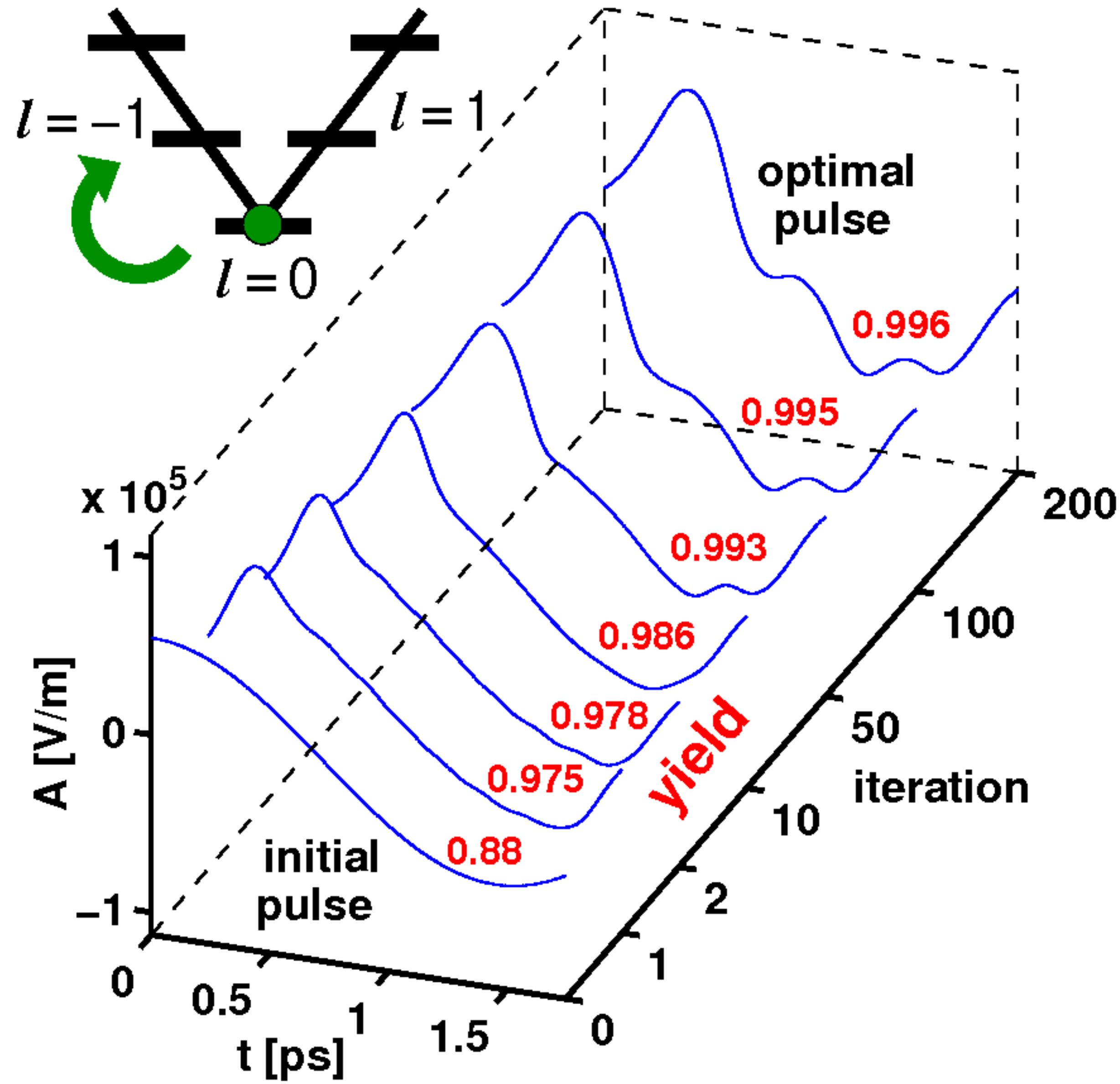
Lorke *et al.* (2000)



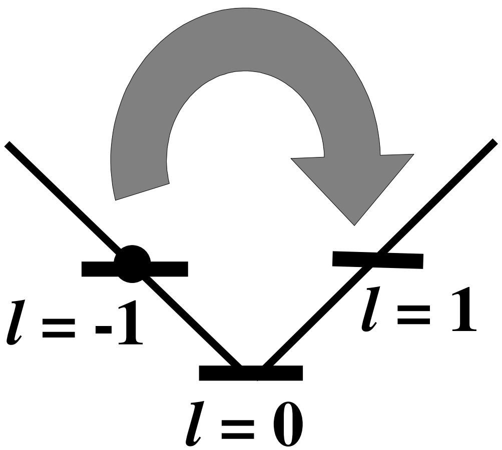
Ihn *et al.* (2001)

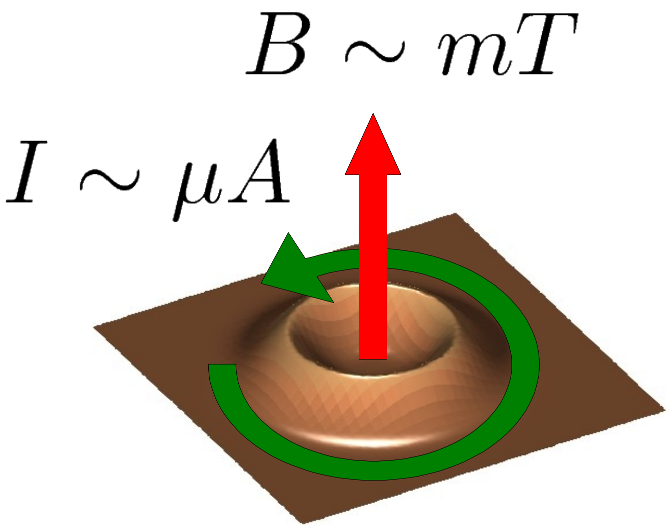
Model:

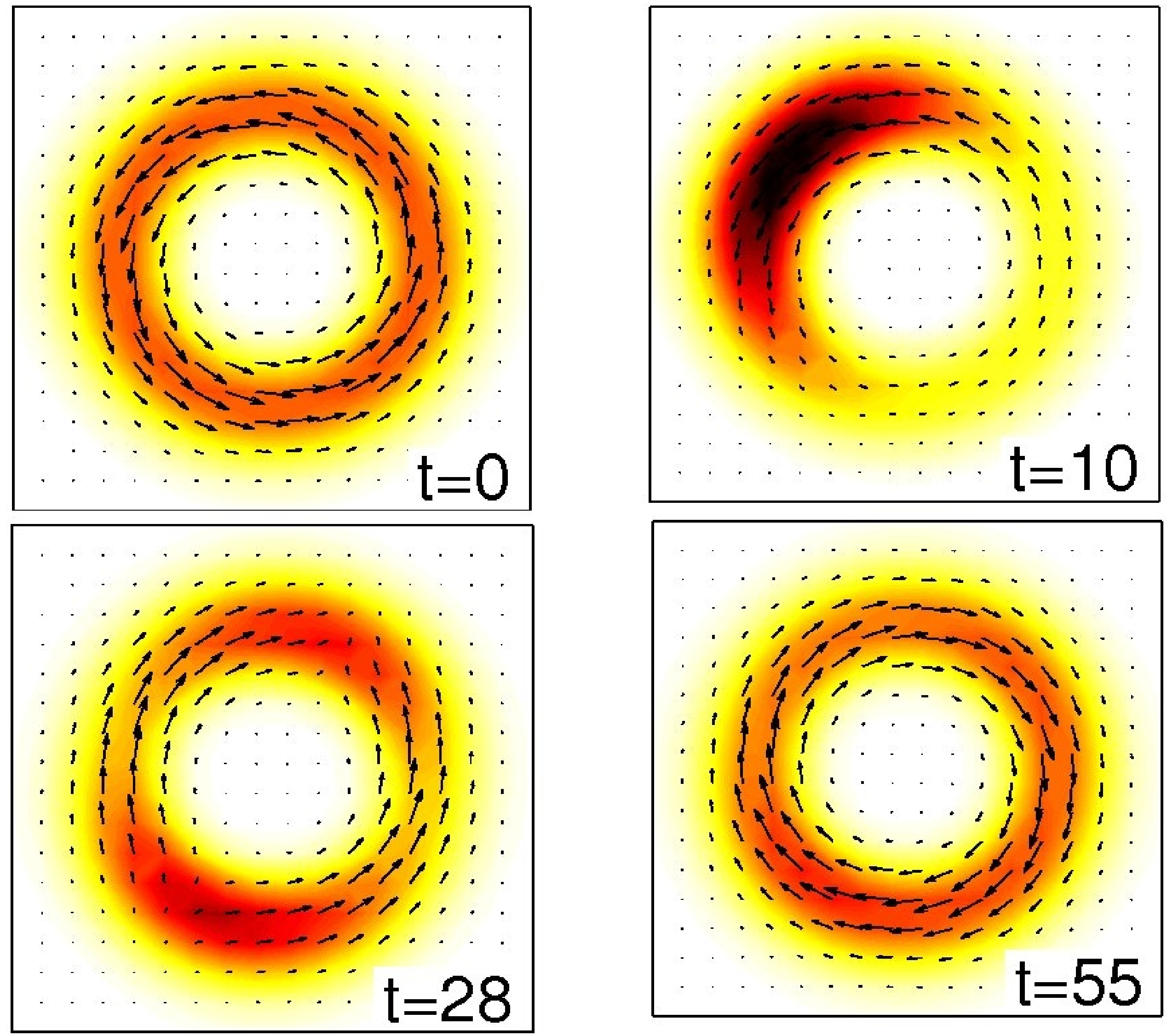




Coherent spin-switch / single-qubit gate



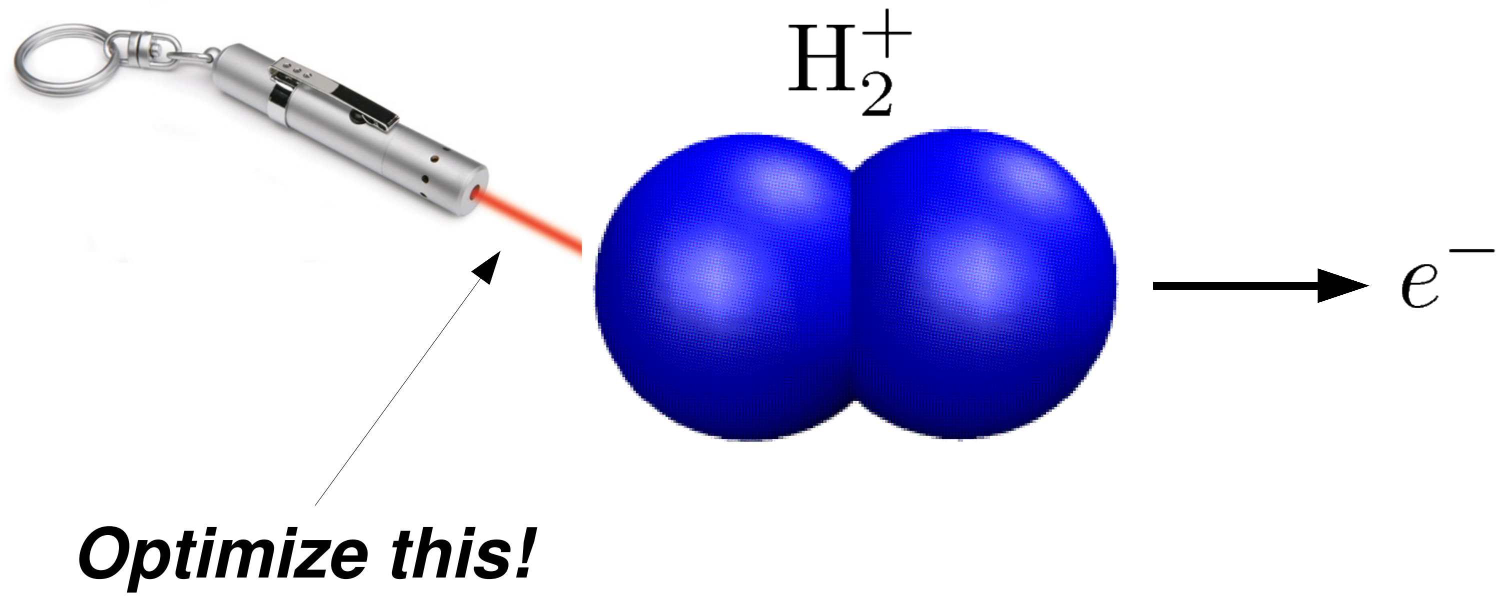




"single-qubit gate"

E.R., A. Castro, J. Werschnik, A. Rubio, and E.K.U. Gross, Phys. Rev. Lett. **98**, 157404 (2007)

Application 2: Enhancing ionization through pulse shaping



Target operator: $$\hat{O} = \hat{1} - \sum_{i}^{\text{bound}} |\varphi_i\rangle\langle\varphi_i|$$

Pulse constraints

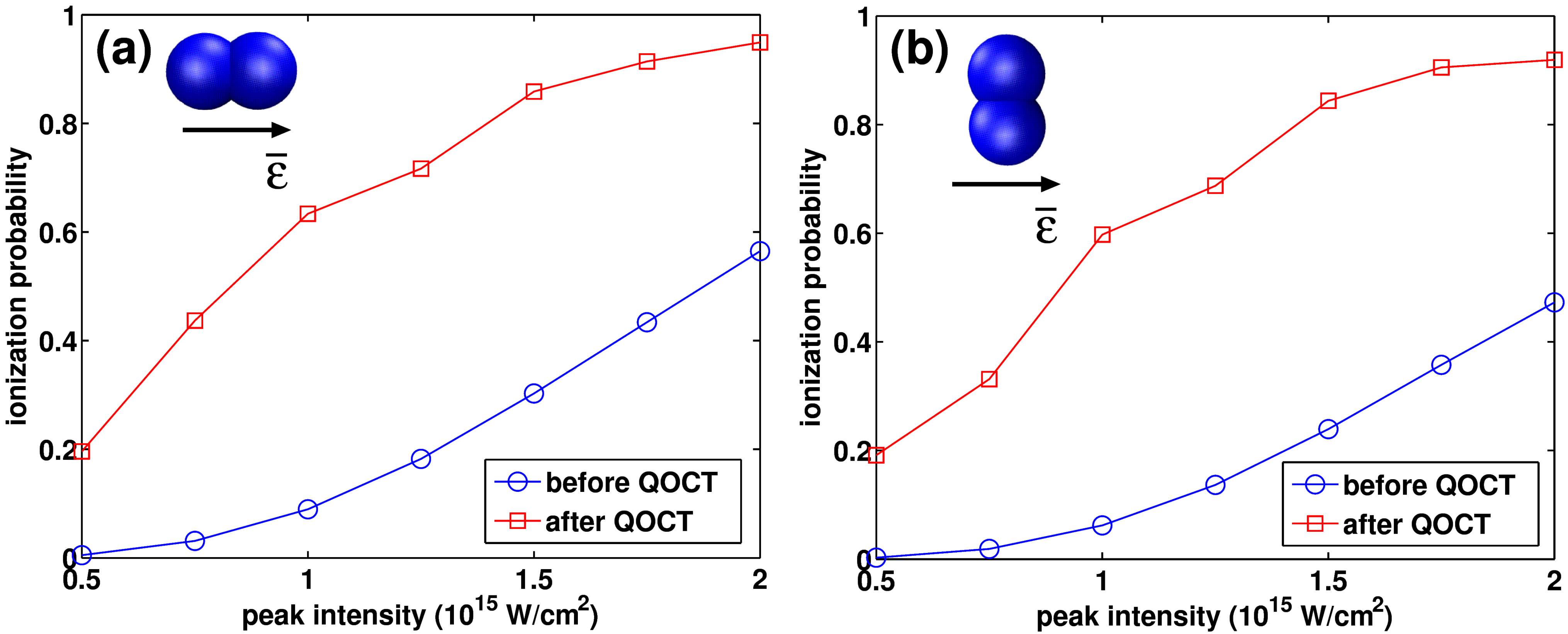
- Representation in the basis

$$f(t) = f_0 + \sum_{n=1}^{N} \left[f_n \sqrt{\frac{2}{T}} \cos(\omega_n t) + g_n \sqrt{\frac{2}{T}} \sin(\omega_n t) \right]$$

- Sum-rule constraint: $\int_0^T \mathrm{d}t\, f(t) = 0 \;\Rightarrow\; f_0 = 0$
- Endpoints: $f(0) = f(T) = 0 \;\Rightarrow\; \sum_{n=1}^{N} f_n = 0$
- Cutoff frequency: $\omega_{\mathrm{max}} = 2\,\omega_0$

  where the *initial* frequency (before optimization) is $\omega_0 = 0.114 \text{ a.u.}$
  -- a typical value for frequency-doubled Ti:S lasers with $\lambda = 400 \text{ nm}$
- Pulse length: eight cycles corresponding to $T \approx 5.3 \text{ ns}$
- Pulse strength (fluence) fixed: $F_0 = \int_0^T f^2(t)\, \mathrm{d}t = \text{const.}$

Effect of pulse optimization



(a) parallel polarization **(b) perpendicular polarization**

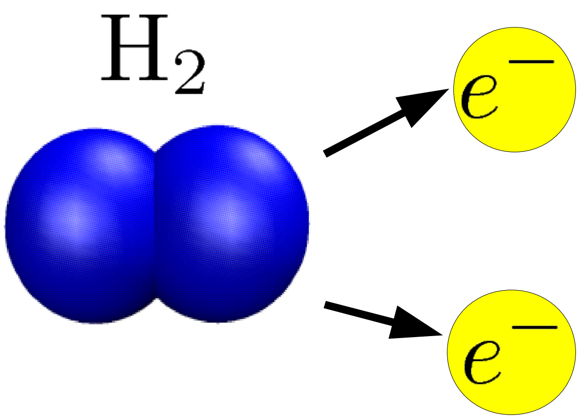
A. Castro, E. R., A. Rubio, and E.K.U. Gross, Europhys. Lett. **87**, 53001 (2009)

Application 3: Enhancing ionization in a two-particle system

1D model with soft-Coulomb interaction

=> exactly solvable (on a 2D grid - x and y as electron coordinates)

=> in TDDFT with 1D-LDA

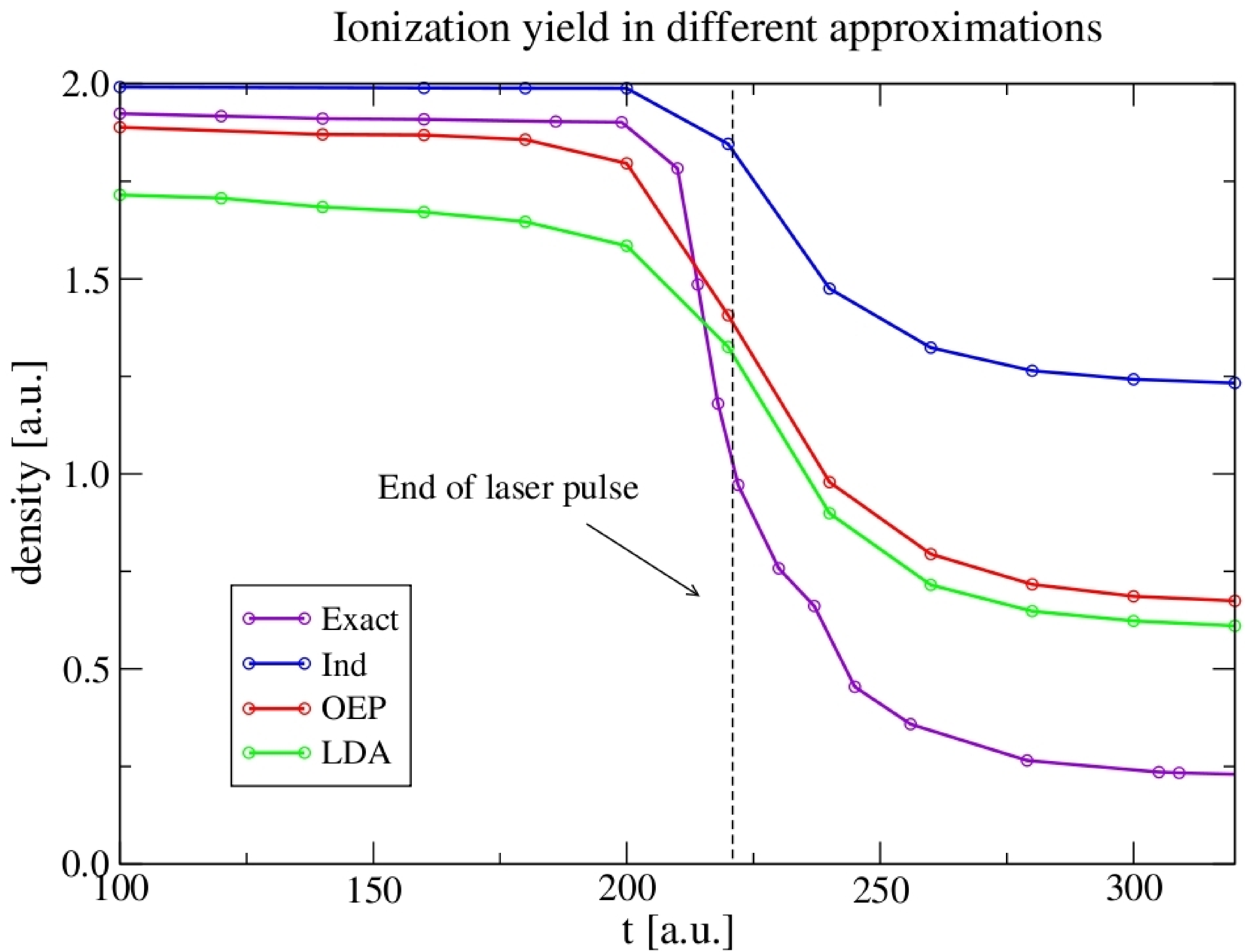


$$V(x,y) = -\frac{1}{\sqrt{(x+d/2)^2+1}} - \frac{1}{\sqrt{(x-d/2)^2+1}} - \frac{1}{\sqrt{(y+d/2)^2+1}} - \frac{1}{\sqrt{(y-d/2)^2+1}} + \frac{1}{\sqrt{(x-y)^2+1}}$$

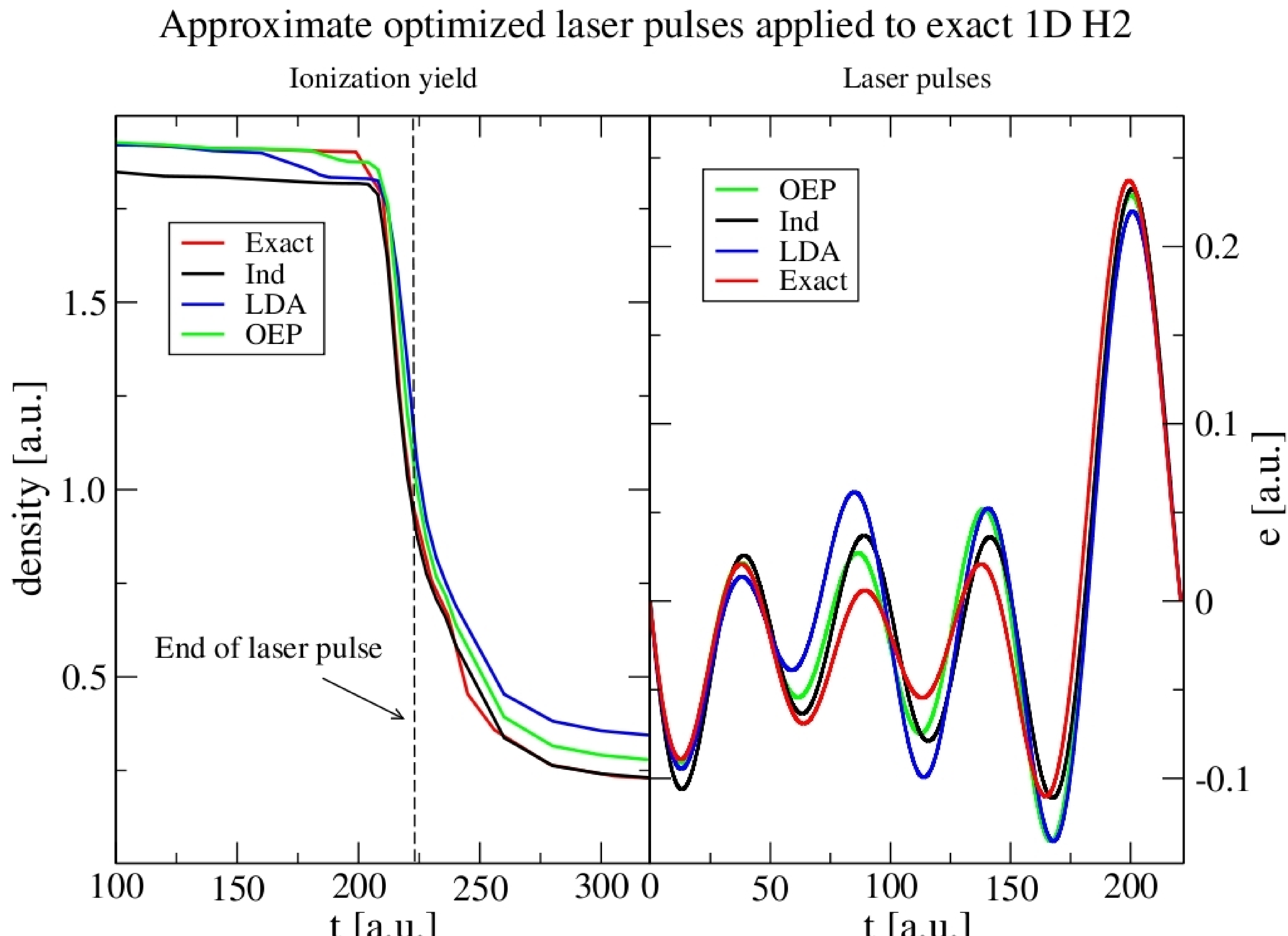
Main idea:

Use the density (outside the molecule) as the target for ionization within TDDFT-OCT. Compare the result with the exact case.

For formal "marriage" of OCT and TDDFT, see
A. Castro, J. Werschnik, and E.K.U. Gross, arXiv:1009.2241



Ionization yield in different approximations
density [a.u.]
t [a.u.]
2.0
1.5
1.0
0.5
0.0
100
150
200
250
300
End of laser pulse
Exact
Ind
OEP
LDA



Approximate optimized laser pulses applied to exact 1D H2
Ionization yield
Laser pulses
Exact
Ind
LDA
OEP
End of laser pulse
density [a.u.]
t [a.u.]
1.5
1.0
0.5
100
150
200
250
300
OEP
Ind
LDA
Exact
e [a.u.]
0.2
0.1
0
-0.1
0
50
100
150
200

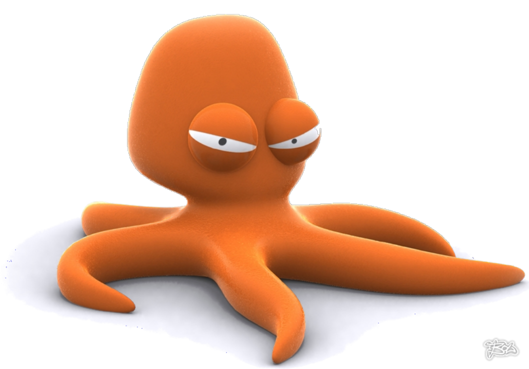
Summary

- Optimal control theory (OCT) is a powerful tool to achieve quantum mechanical targets via optimization of the external field.

ionization *charge & spin* *HHG* *current* *dissociation*

- Ionization of small molecules can be remarkably enhanced by pulse shaping. A density target can be used to describe many-electron ionization, and optimization within ALDA produces pulses that work well in a real system (exact solution / experiment!)

Thanks to: Ville Kotimäki, Tobias Kramer, Alberto Castro, Jan Werschnik, Maria Hellgren, Angel Rubio, E.K.U. Gross



OCTOPUS code
(real-space & real-time DFT/TDDFT)
freely available at: `www.tddft.org`
A. Castro *et al.*, Phys. Stat. Sol. (b) **243,** 2465 (2006)

Thank you