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

- Laser-control of molecules
  - Laarmann et al. (2007)

- Electromagnetic control of low-dimensional systems
  - Goldman (2007)
  - Delft Qubit Project

- 4th generation solar cells
  - Wagner (2009)
TDDFT: Initial-state dependence

Reminder: we propagate individual particles exposed to

\[ \nu_{KS}(\mathbf{r}, t) = \nu_{ext}(\mathbf{r}, t) + \nu_H(\mathbf{r}, t) + \nu_{xc}(\mathbf{r}, t) \]

system classicism all the trouble!

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

density at previous times

initial KS wave function

initial many-body wave function

Example: Two 2D Gaussian wave packets in magnetic field

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

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

- initial wave function

\[ \Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+(r_1) & \psi_+(r_2) \\ \psi_-(r_1) & \psi_-(r_2) \end{vmatrix} \]

- initial density

\[ \rho(x, y) = \frac{2e^{1 - \frac{x^2+y^2}{a^2}}}{\pi a^2(e^4 - 1)} \left[ - \cos(2y/a) + e^2 \cosh(2x/a) \right] \]
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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2. Are there alternative choices for orthonormal orbitals that give the exact initial density?

(a) no
(b) yes - one other choice
(c) yes - infinitely many choices
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2. Are there alternative choices for orthonormal orbitals that give the exact initial density?
   (a) no
   (b) yes - one other choice
   (c) yes - infinitely many choices => Harriman construction
Harriman construction


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

Harriman orbitals:

$$\varphi_i(x, y) = \sqrt{\frac{\rho(x, y)}{N}} \exp[i k f(x)]$$

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

Quantum optimal control theory (OCT)

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

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

**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**

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

here \( \hat{O} \) is a projection operator

**field constraint**

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

(with fixed fluence)

**fulfillment of the TD-SE**

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

- Forward propagation for $|\Psi(t)\rangle$
  \[ i \frac{d}{dt} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle, \quad |\Psi(0)\rangle = |\Psi_{\text{initial}}\rangle \]

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

Application 1: Control of current in a quantum ring

Experiments:

Model:
Coherent spin-switch / single-qubit gate

Application 2: Enhancing ionization through pulse shaping

Optimize this!

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:

\[ \int_0^{T} dt \, f(t) = 0 \quad \Rightarrow \quad f_0 = 0 \]

Endpoints:

\[ f(0) = f(T) = 0 \quad \Rightarrow \quad \sum_{n=1}^{N} f_n = 0 \]

Cutoff frequency:

\[ \omega_{\text{max}} = 2 \omega_0 \]

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:

\[ F_0 = \int_0^{T} f^2(t) \, dt = \text{const.} \]
Effect of pulse optimization

(a) parallel polarization

(b) perpendicular polarization

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.*

Ionization yield in different approximations

End of laser pulse

- Exact
- Ind
- OEP
- LDA

$\text{density [a.u.]}$

$t [\text{a.u.}]$
Approximate optimized laser pulses applied to exact 1D H2

Ionization yield

Laser pulses

End of laser pulse

- Density [a.u.]
- t [a.u.]

- e [a.u.]
- t [a.u.]

- Exact
- Ind
- LDA
- OEP

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

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!)

Summary

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OCTOPUS code
(real-space & real-time DFT/TDDFT)
freely available at: www.tddft.org
Thank you