# Quantum optimal control theory for electron dynamics

### Alberto Castro

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Institute for Biocomputation and Physics of Complex Systems (BIFI) of
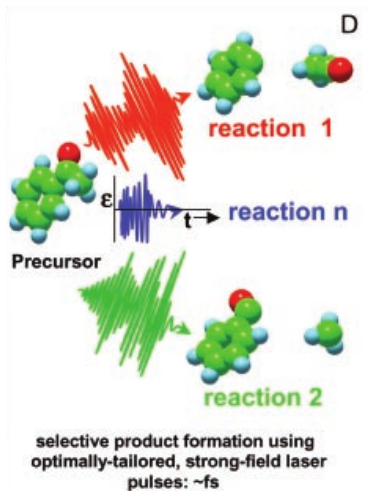the University of Zaragoza (Spain)

10th Benasque TDDFT School, Benasque (Spain),
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Instituto Universitario de Investigación
**Biocomputación y Física
de Sistemas Complejos**
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▶ C. P. Koch et al., "Quantum Optimal Control in Quantum Technologies. Strategic Report on Current Status, Visions and Goals for Research in Europe", EPJ Quantum Technology 9, 19 (2022).

▶ Q. Ansel et al., "Introduction to theoretical and experimental aspects of quantum optimal control", Journal of Physics B: Atomic, Molecular and Optical Physics 57, 133001 (2024).

▶ U. Boscain et al., "Introduction to the Pontryagin Maximum Principle for Quantum Optimal Control", PRX Quantum 2, 030203 (2021)

▶ C. Brif et al., "Control of quantum phenomena: past, present and future", New J. Phys. 12, 075008 (2010).

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# Basic idea, in a cartoon



[R. J. Levis *et al*, Science **292**, 709 (2001)]

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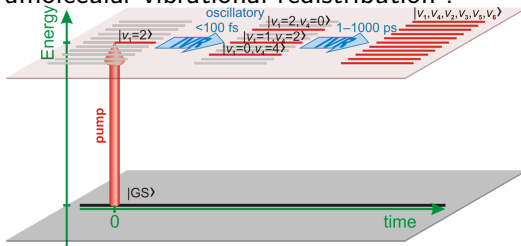### Pioneering schemes
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# Mono-chromatic lasers

▶ Lasers (coherent, monochromatic, intense light) promised to deliver precise control of quantum systems

▶ Initially, the first attempts to control molecules (i.e. "photo-selective chemistry") were based on tuning the laser frequency to specific bonds

▶ Those attempts were seldom successful, due to "intramolecular vibrational redistribution".



▶ Analogous problems will appear in other quantum control attempts, beyond molecular photo-chemistry.

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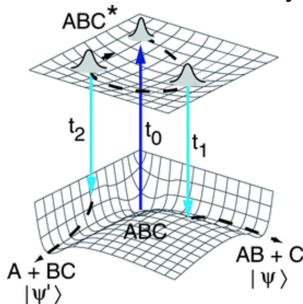
# Interferences, and the "two pathway" scheeme

[P. Brumer and M. Shapiro, Chem. Phys. Lett. **126**, 541 (1986)]

- ▶ Use of two monochromatic lasers with commensurate frequencies for creating quantum interference between two reaction pathways.
- ▶ By tuning the phase difference between the two laser fields, it is possible to control the branching ratios of molecular reactions.
- ▶ It produces modest results, perhaps a modulation of 50% in branching rations of chemical reactions.

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# Pump and dump

[D. J. Tannor and S. A. Rice J. Chem. Phys. **83**, 5013 (1985)]



▶ Limitations: knowledge of the potential energy surfaces,
  competing processes.

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# Adaptive feedback control

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**Adaptive feedback control**
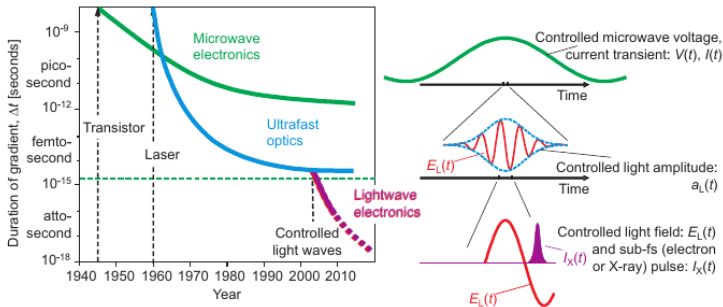
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### Teaching Lasers to Control Molecules

Richard S. Judson[a]

*Center for Computational Engineering, Sandia National Laboratories, Livermore, California 94551-0969*

Herschel Rabitz

*Department of Chemistry, Princeton University, Princeton, New Jersey 08544*
(Received 26 August 1991)

We simulate a method to teach a laser pulse sequences to excite specified molecular states. We use a learning procedure to direct the production of pulses based on "fitness" information provided by a laboratory measurement device. Over a series of pulses the algorithm learns an optimal sequence. The experimental apparatus, which consists of a laser, a sample of molecules, and a measurement device, acts as an analog computer that solves Schrödinger's equation *exactly*, in real time. We simulate an apparatus that learns to excite specified rotational states in a diatomic molecule.

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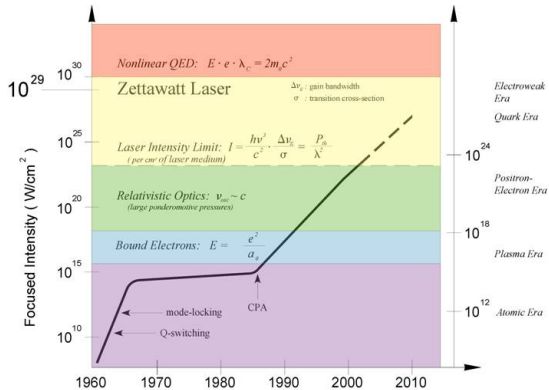Alberto Castro

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# The learning loop
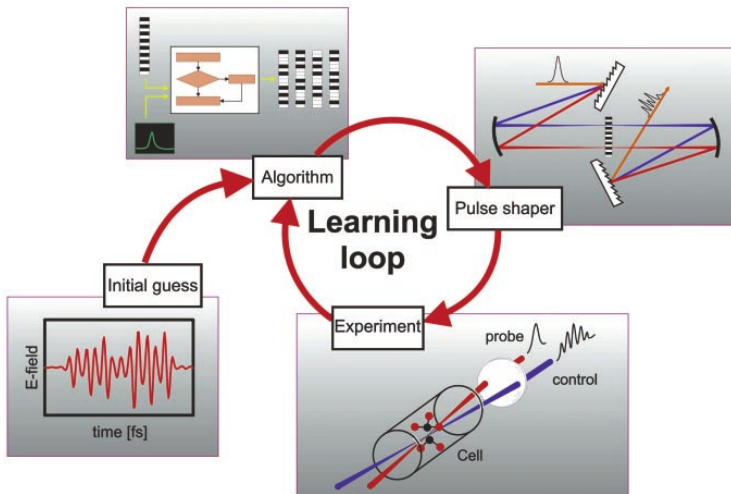


[H. Rabitz *et al*, Science **288**, 824 (2000)]

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# Laser technology: The road to atto-second physics



[Krausz & Ivanov, Rev. Mod. Phys. **81**, 169 (2009)]

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# Laser technology: increase in intensities

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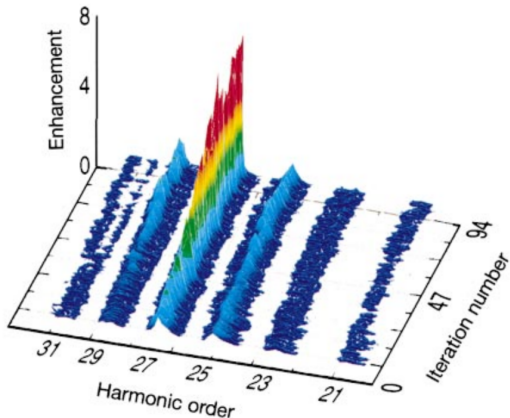experiments
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# Examples of AFC experiments: Photo-dissociation reactions in molecules
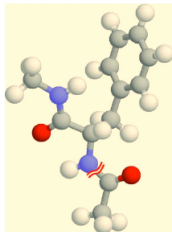


FIG. 1. (Color online) Optimal tailoring of intense femtosecond light can be used to preferentially break peptide bonds, such as the indicated N1–C3 bond in the amino acid complex Ac-Phe-NHMe.
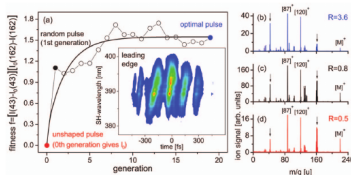
["Coherent control of bond breaking in amino acid complexes with tailored femtosecond pulses", Laarmann et al, J. Chem. Phys. **127**, 201101 (2007)]

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# Examples of AFC experiments: High harmonic generation



["Shaped-pulse optimization of coherent emission of high-harmonic soft X-rays", R. Bartels, Nature **406**, 164 (2000)]

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# Examples of AFC experiments: other

▶ Multi-photon ionization of atoms.

▶ Electronic excitation in molecules (fluorescence is used as the probe to build the merit function).

▶ Molecular alignment.

▶ Photo-induced electron transfer between molecules

▶ Photo-isomerization of molecules.

▶ etc.

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# What makes experimental "control" possible

- ▶ Existence of laser sources, since the 1960's.
- ▶ *Femto*-second laser sources, which allow for fast processes (avoiding decoherence), and extending the band-width.
- ▶ High-intensities.
- ▶ Laser *shapers*.
- ▶ Learning-loops algorithms.

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# Optimal control theory

Typical formulation of a (general) optimal control problem:

▶ Dynamical system:

$$
\begin{aligned}
\dot{x}(t) &= f(x(t), u(t), t) \\
x(0) &= x_0
\end{aligned}
$$

Typically, $u = u(t)$. But it can be a set of parameters whatsoever.

▶ Minimize the cost functional:

$$
F[x, u] = F^{\text{terminal}}[x(T), u] + \int_0^T \mathrm{d}t \; L(x(t), u(t))
$$

▶ Since $u \to x[u]$, it amounts to minimizing

$$
G[u] = F[x[u], u]
$$

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# Essential theoretical results

▶ Pontryagin's minimum principle (1956)
  [V.G. Boltyanskii, R.V. Gamkrelidze, and L.S. Pontryagin,
  "Towards a theory of optimal processes", (Russian), Reports Acad.
  Sci. USSR **110**, 1 (1956)]
  It provides a *necessary* condition for the minimum – in
  practice, typically, an expression for $\nabla G[u]$ so that the
  equation $\nabla G[u] = 0$ can be posed.

▶ Hamilton-Jacobi-Bellman equation (1954)
  (Theory of "dynamic programming", Richard Bellman)
  [R.E Bellman, "Dynamic Programming and a new formalism in the
  calculus of variations" Proc. Nat. Acad. Sci. **40**, 231 (1954)]

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# Essential theoretical results

▶ Simpler approaches: *direct* or *gradient-less* algorithms.
  They only require a means to compute $G[u]$ (i.e. a
  method to propagate the dynamical equation and
  compute the resulting cost or target functional).

▶ The most fashionable, the families of *evolutionary* or
  *genetic* algorithms.

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# Pontryagin's minimum principle

If we define the "Hamiltonian"

$$H(\lambda(t), x(t), u(t), t) = \lambda^\dagger(t) f(x(t), u(t), t) + L(x(t), u(t))$$

where $\lambda$ is the "costate", an object of the same kind of $x$,

1. The optimal control $u^0$, trajectory $x^0$ and costate $\lambda^0$ minimize $H$ at all times:

$$H(\lambda^0(t), x^0(t), u^0(t), t) \le H(\lambda^0(t), x^0(t), u(t), t)$$

If there are not differentiability problems,

$$\frac{\partial H}{\partial u}(\lambda^0(t), x^0(t), u^0(t), t) = 0 \,.$$

2. The optimal costate verifies:

$$\dot{\lambda}^{0\dagger}(t) = \lambda^{0\dagger}(t) \frac{\delta f}{\delta x}(x^0(t), u^0(t)) + \frac{\delta L}{\delta x}(x^0(t), u^0(t))$$

$$\lambda^{0\dagger}(T) = \frac{\delta}{\delta x} F^{\text{terminal}}[x^0(T), u^0(T)]$$

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# Quantum optimal control theory

$$\hat{H} = \hat{H}[u_1, \ldots, u_M; t]$$

$$i\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \hat{H}[u; t]|\Psi(t)\rangle$$
$$|\Psi(t_0)\rangle = |\Psi_0\rangle$$

$$\Psi(t_0) \longrightarrow \Psi[u](t) \longrightarrow \Psi[u](T)$$

Maximize a quantity

$$F = F[\Psi[u](t)]\,,$$

that depends on the system evolution, or final state, or both.

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# Main equations: computation of the gradient

$$F[\Psi, u] = J_1[\Psi(T)] + J_2[u]$$

$$G[u] = F[\Psi[u], u]$$

$$\frac{\partial G}{\partial u_m} = \frac{\partial J_2}{\partial u_m} + 2\mathrm{Im} \int_0^T \mathrm{d}t \langle \chi(t)| \frac{\partial \hat{H}}{\partial u_m} |\Psi(t)\rangle \,,$$

where the "costate" $\chi$ verifies:

$$i\frac{\mathrm{d}}{\mathrm{d}t}|\chi(t)\rangle = \hat{H}(t)|\chi(t)\rangle \,,$$

$$|\chi(T)\rangle = \frac{\delta}{\delta\Psi^*(T)} F[\Psi(T)]$$

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where the "costate" $\chi$ verifies:

$$i \frac{\mathrm{d}}{\mathrm{d}t} |\chi(t)\rangle = \hat{H}(t) |\chi(t)\rangle \,,$$

$$|\chi(T)\rangle = \frac{\delta}{\delta \Psi^*(T)} F[\Psi(T)]$$

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# Derivation

The following derivation is based on:

A. Castro and I. V. Tokatly, "Quantum optimal control theory in the linear response formalism" PRA **84**, 033410 (2011)

It is not the standard one, but is based on linear response theory, and therefore more appropriate for a TDDFT school.

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## Derivation

**1** A system is governed by the Hamiltonian
$\hat{H}(t) = \hat{H}_0(t) + f(t)\hat{V}$, so that its evolution is given by:

$$i\frac{\partial}{\partial t}\hat{\rho}(t) = \left[\hat{H}(t), \hat{\rho}(t)\right],$$

Show that, to first order in $f$, the change in the value of the
expectation value of some observable $\hat{A}$ due to the presence of the
*perturbation* $f(t)\hat{V}$ is given by:

$$\delta A(t) = \langle\hat{A}\rangle(t) - \langle\hat{A}\rangle_{f=0}(t) = \int_{-\infty}^{\infty}\mathrm{d}t' \, f(t')\chi_{\hat{A},\hat{V}}(t,t'),$$

where the *linear response function* is given by:

$$\chi_{\hat{A},\hat{V}}(t,t') = -i\theta(t-t')\mathrm{Tr}\{\hat{\rho}(t_0)\left[\hat{A}_H(t), \hat{V}_H(t')\right]\}.$$

$\hat{X}_H(t) = \hat{U}(t_0,t)\hat{X}\hat{U}(t,t_0)$ is the Heisenberg representation of $\hat{X}$,
where $\hat{U}(t,t_0)$ is the evolution operator in the absence of the
perturbation.

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## Derivation
### Hints:

1. Expand $\hat{\rho}(t)$ in a power series in $f$:

$$\hat{\rho}(t) = \sum_{n=0}^{\infty} \hat{\rho}_n(t),$$

where $\hat{\rho}_0$ is the unperturbed solution, $\hat{\rho}_1$ is linear in $f$, etc.

2. Find the differential equations that verify $\hat{\rho}_0$ and $\hat{\rho}_1$, and verify that they are equivalent to the integral equations:

$$\hat{\rho}_0(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}(t_0, t),$$
$$\hat{\rho}_1(t) = -\mathrm{i}\int_{t_0}^{t} \mathrm{d}t'\; \hat{U}(t, t')\left[f(t')\hat{V}, \hat{\rho}_0(t')\right]\hat{U}(t', t),$$

3. To first order in $f$,

$$\delta A(t) = \mathrm{Tr}\{\hat{\rho}_1(t)\hat{A}\}.$$

Substituting $\hat{\rho}_1(t)$, after some algebra one arrives to the final result.

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## Derivation

**2** A system is governed by the Hamiltonian
$\hat{H}[u](t) = \hat{\mathcal{H}} + \epsilon[u](t)\hat{V}$, so that its evolution is given by:

$$i\frac{\partial}{\partial t}\hat{\rho}[u](t) = \left[\hat{H}[u](t), \hat{\rho}[u](t)\right], \hat{\rho}[u](t_0) = \hat{\rho}_{\mathrm{init}},$$

where $u$ is a real parameter that determine the precise shape of
the real function $\epsilon$.

Given the function $G[u] = \mathrm{Tr}\{\hat{\rho}[u](t_f)\hat{A}\}$ (the expectation value
of some observable $\hat{A}$ at some final time $t_f$), show that:

$$\frac{\partial G}{\partial u}[u] = -i \int_{t_0}^{t_f} \mathrm{d}\tau \, \frac{\partial \epsilon}{\partial u}[u](\tau)\mathrm{Tr}\{\hat{\rho}[u](\tau)\left[\hat{A}[u](\tau), \hat{V}\right]\}.$$

where $\hat{A}[u]$ is defined as:

$$\frac{\partial}{\partial t}\hat{A}[u](t) = -i\left[\hat{H}[u](t), \hat{A}[u](t)\right],$$
$$\hat{A}[u](t_f) = \hat{A}.$$

These are the "QOCT equations".

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## Derivation
### Hints:

1. Obviously, $\frac{\partial G}{\partial u}[u] = \lim_{\Delta u \to 0} \Delta u^{-1}(G[u + \Delta u] - G[u])$.

2. Note that $G[u]$ corresponds to the propagation of the system with the Hamiltonian $\hat{H}[u](t)$, whereas $G[u + \Delta u]$ corresponds to the propagation of the system with:

$$\hat{H}[u + \Delta u](t) = \hat{H}[u](t) + \Delta u \frac{\partial \epsilon}{\partial u}[u]\hat{V}.$$

3. Now we can use directly the LRT result of the previous problem, by making the identifications,

$$\hat{H}_0(t) = \hat{H}[u](t), \quad f(t) = \Delta u \frac{\partial \epsilon}{\partial u}[u](t).$$

and we arrive at:

$$\frac{\partial G}{\partial u}[u] = \int_{t_0}^{\infty} \mathrm{d}\tau \, \frac{\partial \epsilon}{\partial u}[u](\tau)\chi_{\hat{A},\hat{V}}(t_f, \tau).$$

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## Derivation

**3** Show that, for pure systems $(\hat{\rho}[u](t) = |\Psi[u](t)\rangle\langle\Psi[u](t)|)$, the previous result is:

$$\frac{\partial G}{\partial u}[u] = 2\mathrm{Im}\int_{t_0}^{t_f}\mathrm{d}\tau\,\frac{\partial\epsilon}{\partial u}[u](\tau)\langle\chi[u](\tau)|\hat{V}|\Psi[u](\tau)\rangle\,.$$

$$\begin{aligned}\frac{\partial}{\partial t}|\chi(t)\rangle &= -i\hat{H}[u](t)|\chi(t)\rangle\,,\\ |\chi(t_f)\rangle &= \hat{A}|\Psi[u](t_f)\rangle\,,\end{aligned}$$

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# Formulation in terms of (unparametrized) control functions

$$\hat{H}(t) = \hat{H}_0 + u(t)\hat{V}$$

$$F[\Psi, u] = J_1[\Psi(T)] + \alpha \int_0^T \, \mathrm{d}t \, u^2(t)$$

$$G[u] = F[\Psi[u], u]$$

This is a linear-quadratic problem whose solution verifies:

$$\frac{\delta G}{\delta u(t)} = 2\alpha u(t) + \mathrm{Im}\langle \chi(t)|\hat{V}|\Psi(t)\rangle = 0$$

Some of the most succesful algorithms originally developed for QOCT (Krotov, Rabitz) assume this form. Cannot be used for more general target definitions, especially if one wishes to add constraints to the form of $u$.

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# Femtosecond laser pulse shaping for enhanced ionization

[AC, E. Räsänen, A. Rubio, and E. K. U. Gross, EPL **87**, 53001 (2009)]
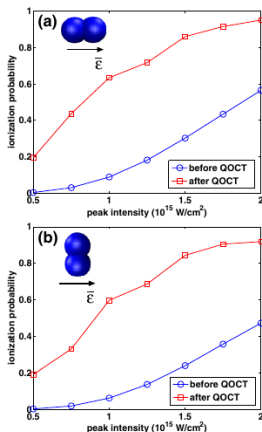


Fig. 1: (Color online) Ionization probability for the initial pulse (circles) and for the optimized pulse (squares) as a function of the peak intensity of the initial pulse. The polarization of the pulse is (a) parallel and (b) perpendicular to the molecule.

▶ Target: Maximal ionization of $H_2^+$ molecule (clamped nuclei).

▶ $F[\Psi(T)] = \langle \Psi(T)|\Psi(T)\rangle - \sum_{\text{bound}} |\langle \Psi|\Psi_I\rangle|^2$

▶ Use of absorbing boundary conditions

▶ Use of *direct* optimization algorithm.

▶ Expansion of control field into a Fourier series $\Rightarrow$ automatic existence of a frequency constraint.

▶ Further constraints: total length (5fs) and total fluence.

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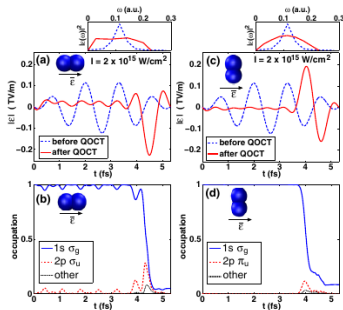


Fig. 2: (Color online) (a) Initial and optimized pulses (parallel polarization) and their power spectra (in arbitrary units) and (b) the occupation of selected single-electron states in the optimized ionization process, when $I = 2 \times 10^{15}$ W/cm$^2$. (c), (d) Same as (a), (b) but for perpendicular polarization.

▶ Using a stringent frequency cut-off, the optimization attempts to build a peak with maximum intensity. With short, intense pulses, most ionization occurs during the maximum.

▶ With parallel orientation, zero carrier envelope phase (half-cycle pulse), and $\pi/2$ with perpendicular orientation.

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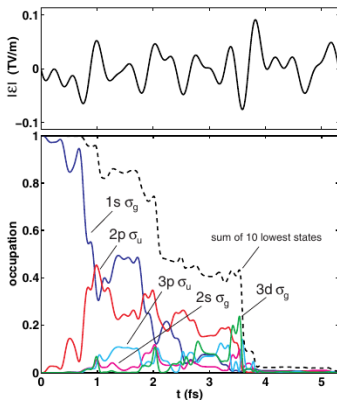


Fig. 4: (Color online) Upper panel: optimized laser pulse for the ionization when the cutoff frequency is $4\omega_0$ (see text) and the intensity is fixed to $0.5 \times 10^{15}$ W/cm$^2$. Lower panel: occupation of a few lowest states during the pulse interaction.

- ▶ Higher cut-off frequency implies more complicated structure for the optimal pulse.

- ▶ Ionization is not a direct ground-state to continuum step.

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# Optimal Control of Quantum Rings by Teraherz Laser Pulses

[E. Räsänen, AC, J. Werschnik, A. Rubio, and E. K. U. Gross, Phys. Rev. Lett. **98**, 157404 (2007)]
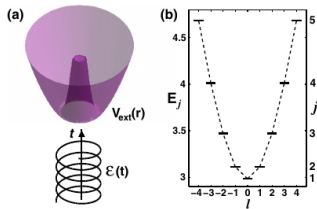


FIG. 1 (color online). (a) Shape of the external confining potential for a quantum ring and an example of a circularly polarized laser field. (b) Energy-level spectrum of a quantum ring. The transitions are allowed along the dashed line so that $\Delta l = \pm 1$.

▶ Electron trapped in a ring edged into a 2D semiconductor heterostructure (2D electron gas).

▶ Levels are coupled in a consecutive fashion, ordered by angular momentum.

▶ Use of a two-component laser pulse.

▶ The target is the population of any of the levels, from any of the other levels (precise control over the electronic current).

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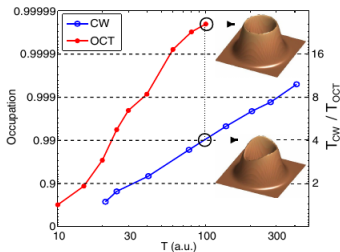


FIG. 3 (color online). Maximum occupation of the target state in transition $|1\rangle \rightarrow |2\rangle$ as a function of the pulse length. The open (blue) circles correspond to continuous waves and the filled (red) circles to the optimal-control result. The insets show the densities $|\Psi(T=100)|^2$ when the corresponding achieved occupations are 0.99 and 0.9998 for these pulse types, respectively.
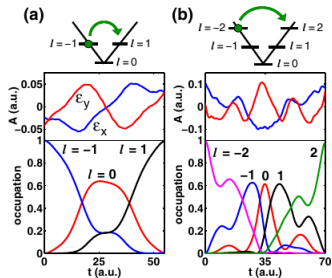


FIG. 4 (color online). Schematic picture of transitions from $l = -1$ to $l = 1$ (a) and from $l = -2$ to $l = 2$ (b) (upper panel), optimized fields for these transitions (middle panel), and the occupations of the states (lower panel).

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# TDDFT in a nutshell

▶ Propagating the many-electron Schrödinger equation is a computationally demanding task.

$$i\frac{\partial}{\partial t}\Psi(x_1, \ldots, x_N; t) = \hat{H}(t)\Psi(x_1, \ldots, x_N; t).$$

▶ Time-dependent density-functional theory substitutes it by the set of "time-dependent Kohn-Sham equations":

$$i\frac{\partial\varphi_i}{\partial t}(\vec{r}, t) = \left[-\frac{1}{2}\nabla^2\varphi_i(\vec{r}, t) + v_{\mathrm{Hartree}}[n](\vec{r}, t) + v_{\mathrm{xc}}[n](\vec{r}, t) + v_{\mathrm{ext}}(\vec{r}, t; u)\right]\varphi_i(\vec{r}, t)$$

$$n(\vec{r}, t) = \sum_{i=1}^{N} 2|\varphi_i(\vec{r}, t)|^2.$$

▶ These are the equations of a non-interacting system of electrons, whose time-dependent density is identical to the real one.

▶ All observables are functionals of the time-dependent one-electron density $n$, even if sometimes the functional definition is unknown.

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# QOCT + TDDFT

### Controlling the Dynamics of Many-Electron Systems from First Principles: A Combination of Optimal Control and Time-Dependent Density-Functional Theory

A. Castro,[1] J. Werschnik,[2] and E. K. U. Gross[3]

[1]ARAID Foundation–Institute for Biocomputation and Physics of Complex Systems (BIFI)
and Zaragoza Scientific Center for Advanced Modeling (ZCAM), University of Zaragoza, E-50018 Zaragoza, Spain
[2]Jenoptik Optical Systems GmbH, Jena, Germany
[3]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

*Also in:*

*AC and E. K. U. Gross, "Quantum Optimal Control", in "Fundamentals of Time-Dependent Density Functional Theory", edited by M.A.L. Marques, N. Maitra, F. Nogueira, E.K.U Gross. and Angel Rubio (Springer, Berlin, 2012), pages 265-276.*

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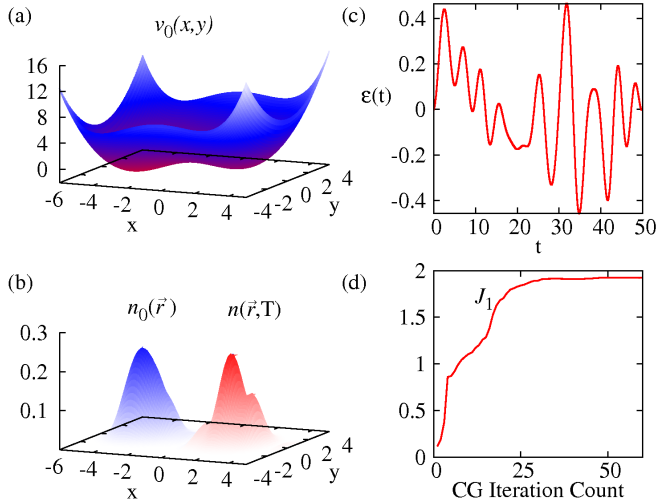dynamics

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# QOCT + TDDFT

▶ We have a system of $N$ electrons, driven by an external potential $v_{\mathrm{ext}}(\vec{r}, t, u)$.

▶ The time-dependent density is therefore determined by $u$:

$$u \longrightarrow n[u](\vec{r}, t) = \langle \Psi[u](t)|\hat{n}(\vec{r})|\Psi[u](t)\rangle$$

▶ The objective is to maximize some function $G$ of the *control parameters* $u$, defined in terms of a functional of the density:

$$G[u] = \tilde{F}[n[u], u].$$

▶ Since the definition is given in terms of the density, everything can be reformulated for the Kohn-Sham system, and the optimization will be equivalent. Since we use the Kohn-Sham substitution, we may use the Kohn-Sham orbitals instead:

$$F[\varphi[u], u] \equiv \tilde{F}[n[u], u], \quad n[u](\vec{r}, t) = \sum |\varphi_i[u](\vec{r}, t)|^2.$$

# QOCT + TDDFT

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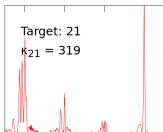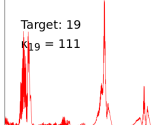QOCT for hybrid
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$$F[\underline{\varphi}[u], u] \equiv \tilde{F}[n[u], u], \quad n[u](\vec{r}, t) = \sum |\varphi_i[u](\vec{r}, t)|^2.$$

# QOCT + TDDFT

Optimal control theory equations for TDDFT (terminal target only):

$$\nabla_u G[u] = \nabla_u F[\underline{\varphi}[u], u] +$$

$$2\mathrm{Im}\left[\sum_{i=1}^{N}\int_0^T \mathrm{d}t \,\langle\lambda_i[u](t)|\nabla_u \hat{H}[n[u](t), u, t]|\varphi_i[u](t)\rangle\right]$$

$$\dot{\underline{\varphi}}[u](t) = -i\underline{\hat{H}}[n(t), u, t]\underline{\varphi}[u](t)\,,$$

$$\underline{\varphi}_u(0) = \underline{\varphi}_0\,,$$

$$\dot{\underline{\lambda}}[u](t) = -i\left[\underline{\hat{H}}[n(t), u, t] + \underline{\hat{K}}[\underline{\varphi}[u](t)]\right]\underline{\lambda}[u](t)\,,$$

$$\underline{\lambda}[u](T) = \frac{\delta F}{\delta \underline{\varphi}^*}[\underline{\varphi}[u](T), u]\,.$$

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$$\dot{\underline{\lambda}}[u](t) = -i\left[\underline{\underline{\hat{H}}}^{\dagger}[n[u](t), u, t] + \underline{\underline{\hat{K}}}[\varphi[u](t)]\right]\underline{\lambda}[u](t)\,,$$

$$\dot{\lambda}_i[u](t) = -i\hat{H}^{\dagger}[n[u](t), u, t]\lambda_i[u](t) - i\sum_{j=1}^{N}\hat{K}_{ij}[\varphi[u](t)]\lambda_j[u](t)$$

$$\langle\vec{r}|\hat{K}_{ij}[\varphi[u](t)]|\lambda_j[u](t)\rangle =$$

$$-2i\varphi_i[u](\vec{r}, t)\mathrm{Im}\left[\int\mathrm{d}^3r'\,\lambda_j[u]^*(\vec{r}', t)f_{\mathrm{Hxc}}[n[u](t)](\vec{r}, \vec{r}')\varphi_j[u](\vec{r}', t)\right]$$

$$f_{\mathrm{Hxc}}[n[u](t)](\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|} + f_{\mathrm{xc}}[n[u](t)](\vec{r}, \vec{r}')$$

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# Optimal laser control of the harmonic generation

He atom, EXX:
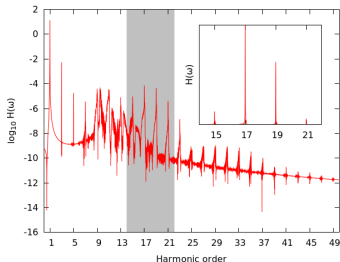


He atom, EXX, frozen H+xc:
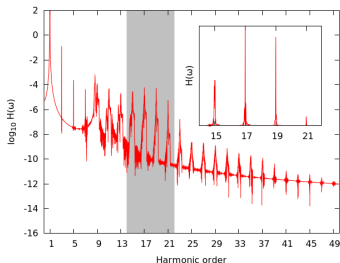


▶ Target: selective
enhancement or quenching of
harmonics:

$$F[\varphi] = \sum_k \alpha_k \max_{\omega \approx k\omega_0} \{\log_{10} H[\varphi](\omega)\}$$

$$H(\omega) = |\int_0^T \mathrm{d}t \, \frac{\mathrm{d}^2}{\mathrm{d}t^2} \langle \hat{\bar{\mu}} \rangle(t) e^{-\mathrm{i}\omega t}|^2$$

▶ Time-dependent target, it
depends on the full evolution
of the system.

▶ "TDDFT-friendly" target: it
only depends on the
time-dependent density.

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# The Ehrenfest model for molecular dynamics

$$\hat{H}[q, p, u, t] = H_{\text{clas}}[q, p, u, t]\hat{I} + \hat{H}_{\text{quantum}}[q, p, u, t].$$

$$
\begin{aligned}
\dot{q}_a(t) &= \frac{\partial H_{\text{clas}}}{\partial p_a}[q(t), p(t), u, t] \\
&\quad + \langle\Psi(t)|\frac{\partial \hat{H}_{\text{quantum}}}{\partial p_a}[q(t), p(t), u, t]|\Psi(t)\rangle \\
\dot{p}_a(t) &= -\frac{\partial \hat{H}_{\text{clas}}}{\partial q_a}[q(t), p(t), u, t] \\
&\quad - \langle\Psi(t)|\frac{\partial \hat{H}_{\text{quantum}}}{\partial q_a}[q(t), p(t), u, t]|\Psi(t)\rangle \\
\dot{\Psi}(x, t) &= -\mathrm{i}\hat{H}_{\text{quantum}}[q(t), p(t), u, t]\Psi(x, t),
\end{aligned}
$$

# Ehrenfest + TDDFT + QOCT

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## Optimal control theory for quantum-classical systems: Ehrenfest molecular dynamics based on time-dependent density-functional theory

**A Castro**[1] **and E K U Gross**[2]

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[2] Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
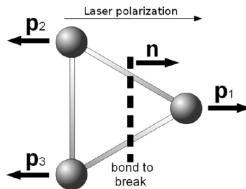
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# Selective photo-dissociation: $H_3^+$

$F[n, q, p] = (\vec{p}_1(T) - \vec{p}_2(T))^2 + (\vec{p}_1(T) - \vec{p}_3(T))^2 - (\vec{p}_2(T) - \vec{p}_3(T))^2$

$T_{\text{laser}} \approx 7$ fs

$I_{\text{peak}} \approx 1.8 \ 10^{13} \text{W/cm}^2$

$E_{\text{cutoff}} = 2.0$ a.u.   (100 degrees of freedom)

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# How fast can we (Coulomb) explode a metal cluster

▶ Coulomb explosion: fast strong ionization, followed by fast disintegration of the system.

▶ It can be helped with resonantly enhanced multi-photon ionization: tuning of the laser pulse to some excitation (the surface plasmon in the case of a cluster)

▶ But:

  ▶ As the electrons disappear, the resonance frequency blue-shifts.
  ▶ As the nuclei separate, the resonance frequency red-shifts.

▶ The topic was explored with the EMD-TDDFT model:

### Impact of Ionic Motion on Ionization of Metal Clusters under Intense Laser Pulses

E. Suraud[1] and P. G. Reinhard[2]

[1]Laboratoire Physique Quantique, Université P. Sabatier, 118 Route de Narbonne, 31062 Toulouse, cedex, France
[2]Institut für Theoretische Physik, Universität Erlangen, Staudtstrasse 7, D-91058 Erlangen, Germany
(Received 28 October 1999)

We discuss the impact of ionic motion on ionization of metal clusters subject to intense laser pulses in a microscopic approach. We show that for long enough pulses, ionic expansion can drive the system into resonance with the electronic plasmon resonance, which leads to a strongly enhanced ionization.

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# How fast can we (Coulomb) explode a cluster

$F[n, q, p] = - \int d^3r \; n(\vec{r}, T)$    $T_{\text{laser}} \approx 16$ fs

$I_{\text{peak}} \approx 1.0 \; 10^{12} \text{W/cm}^2$    $E_{\text{cutoff}} = 0.5$ a.u.