Quantum optimal control theory for electron dynamics

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Control of quantum phenomena: past, present and future

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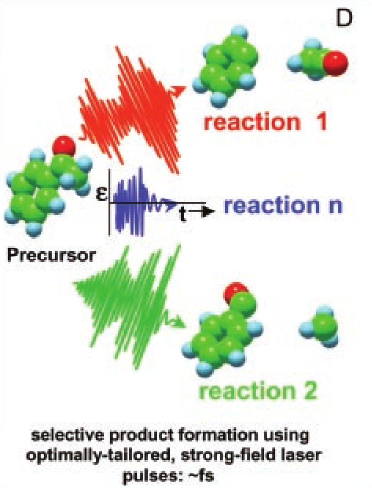
New Journal of Physics **12** (2010) 075008 (68pp)

Basic idea, in a cartoon



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

Outline

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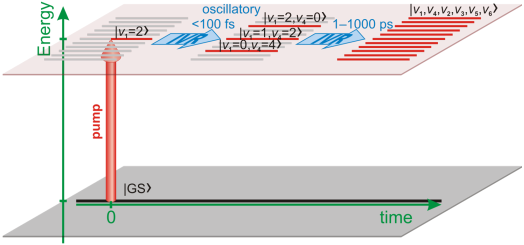
Mono-chromatic lasers

- 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.

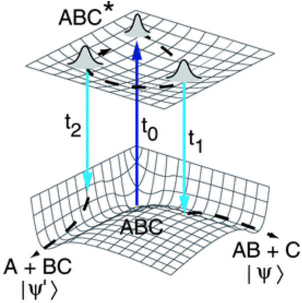
Interferences, and the "two pathway" scheeme

[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.

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.

Outline

Adaptive feedback control

VOLUME 68, NUMBER 10 PHYSICAL REVIEW LETTERS 9 MARCH 1992

Teaching Lasers to Control Molecules

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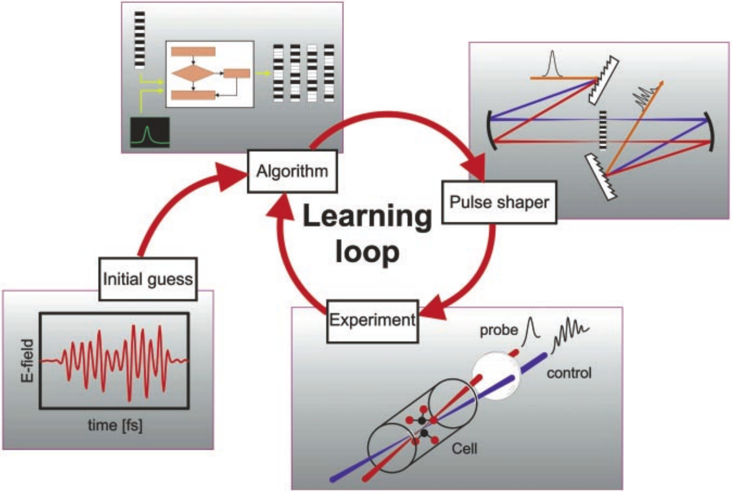
(Received 26 August 1991)

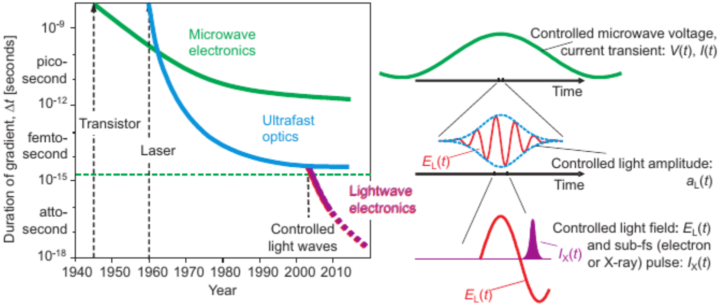
We simulate a method to teach a laser pulse sequences to excite specified molecular states. We use a learning procedure to direct the production of pulses based on "fitness" information provided by a laboratory measurement device. Over a series of pulses the algorithm learns an optimal sequence. The 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.

The learning loop



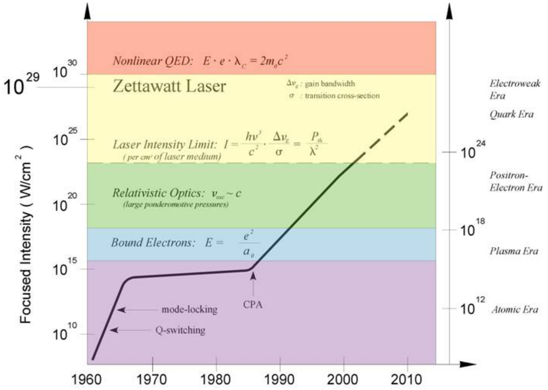
[H. Rabitz *et al*, Science **288**, 824 (2000)]

Laser technology: The road to atto-second physics



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

Laser technology: increase in intensities



Examples of AFC experiments: Photo-dissociation reactions in molecules

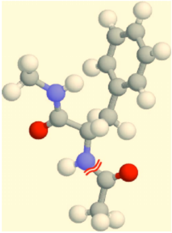
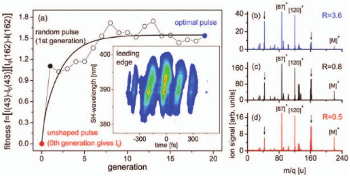
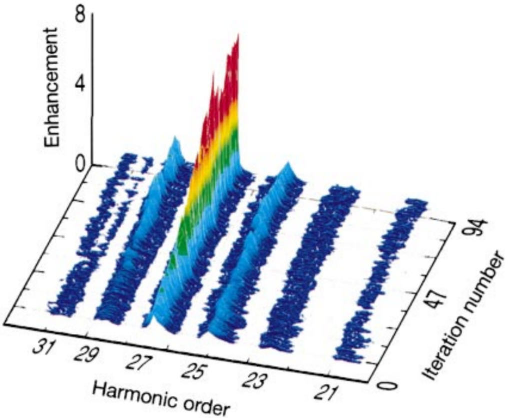


FIG. 1. (Color online) Optimal tailoring of intense femtosecond light can be used to preferentially break peptide bonds, such as the indicated N1–C3 bond in the amino acid complex Ac-Phe-NHMe.



["Coherent control of bond breaking in amino acid complexes with tailored femtosecond pulses", Laarmann et al, J. Chem. Phys. **127**, 201101 (2007)]

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)]

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.

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.

Outline

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"Classical" 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

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

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)]

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.

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 λ is the "costate", an object of the same kind of x, the following holds:

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

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

2. The costate verifies the following equation of motion:

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

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

Quantum optimal control theory

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

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

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

Maximize a quantity

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

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

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" χ 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

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:

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

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:

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

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

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.

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:

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

where u is a real parameter that determine the precise shape of the real function ϵ.

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:

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

These are the “QOCT equations”.

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:

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

Derivation

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

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

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

Continuous control function

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

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

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

This is a linear-quadratic problem whose solution verifies:

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

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.

Femtosecond laser pulse shaping for enhanced ionization

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

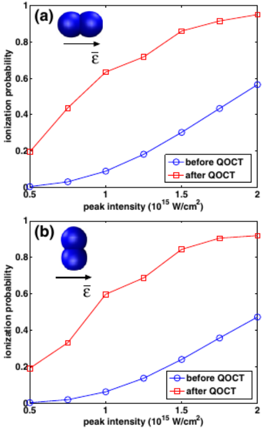

Fig. 1: (Color online) Ionization probability for the initial pulse (circles) and for the optimized pulse (squares) as a function of the peak intensity of the initial pulse. The polarization of the pulse is (a) parallel and (b) perpendicular to the molecule.

- 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.

Femtosecond laser pulse shaping for enhanced ionization

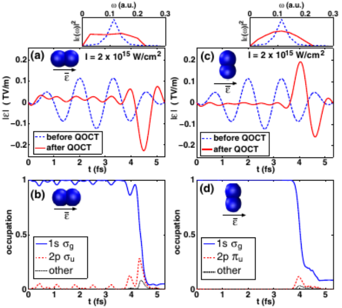

Fig. 2: (Color online) (a) Initial and optimized pulses (parallel polarization) and their power spectra (in arbitrary units) and (b) the occupation of selected single-electron states in the optimized ionization process, when $I = 2 \times 10^{15}$ W/cm^2. (c), (d) Same as (a), (b) but for perpendicular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

Femtosecond laser pulse shaping for enhanced ionization

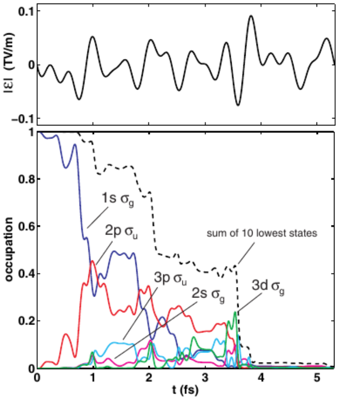

Fig. 4: (Color online) Upper panel: optimized laser pulse for the ionization when the cutoff frequency is $4\,\omega_0$ (see text) and the intensity is fixed to 0.5×10^{15} W/cm^2. Lower panel: occupation of a few lowest states during the pulse interaction.

- Higher cut-off frequency implies more complicated structure for the optimal pulse.
- Ionization is not a direct ground-state to continuum step.

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)]

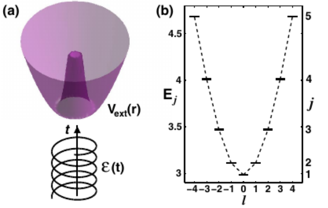

FIG. 1 (color online). (a) Shape of the external confining potential for a quantum ring and an example of a circularly polarized laser field. (b) Energy-level spectrum of a quantum ring. The transitions are allowed along the dashed line so that $\Delta l = \pm 1$.

- 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).

Optimal Control of Quantum Rings by Teraherz Laser Pulses

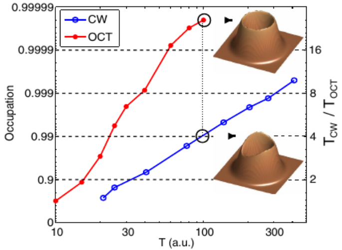

FIG. 3 (color online). Maximum occupation of the target state in transition $|1\rangle \rightarrow |2\rangle$ as a function of the pulse length. The open (blue) circles correspond to continuous waves and the filled (red) circles to the optimal-control result. The insets show the densities $|\Psi(T =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

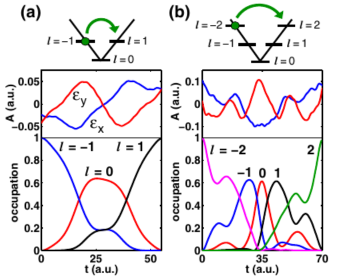

FIG. 4 (color online). Schematic picture of transitions from $l = -1$ to $l = 1$ (a) and from $l = -2$ to $l = 2$ (b) (upper panel), optimized fields for these transitions (middle panel), and the occupations of the states (lower panel).

Outline

TDDFT in a nutshell

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

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

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

$$\begin{aligned} i\frac{\partial\varphi_i}{\partial t}(\vec{r},t) &= \left[-\frac{1}{2}\nabla^2\varphi_i(\vec{r},t) + v_{\rm Hartree}[n](\vec{r},t) + v_{\rm xc}[n](\vec{r},t) + v_{\rm ext}(\vec{r},t;u)\right]\varphi_i(\vec{r},t \\ n(\vec{r},t) &= \sum_{i=1}^{N} 2|\varphi_i(\vec{r},t)|^2\,. \end{aligned}$$

- 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.

QOCT + TDDFT

PRL **109,** 153603 (2012) PHYSICAL REVIEW LETTERS week ending 12 OCTOBER 2012

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

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(Received 14 September 2010; revised manuscript received 16 February 2012; published 12 October 2012)

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.

QOCT + TDDFT

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

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

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QOCT + TDDFT

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

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

QOCT + TDDFT

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

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

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

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

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

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

QOCT + TDDFT

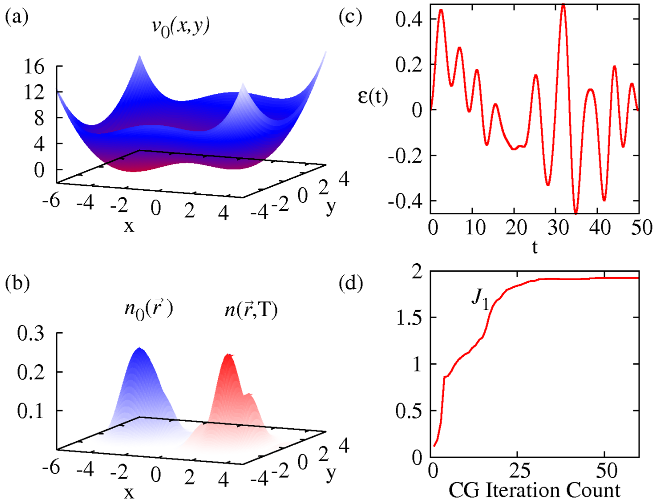
$$\underline{\dot{\lambda}}[u](t) = -i\left[\underline{\underline{\hat{H}}}^{\dagger}[n[u](t), u, t] + \underline{\underline{\hat{K}}}[\underline{\varphi}[u](t)]\right]\underline{\lambda}[u](t)\,,$$

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

$$\langle\vec{r}|\hat{K}_{ij}[\underline{\varphi}[u](t)]|\lambda_j[u](t)\rangle =$$
$$-2i\varphi_i[u](\vec{r},t)\mathrm{Im}\left[\int \mathrm{d}^3r'\lambda_j[u]^*(\vec{r}',t) f_{\mathrm{Hxc}}[n[u](t)](\vec{r},\vec{r}')\varphi_j[u](\vec{r}',t)\right]$$

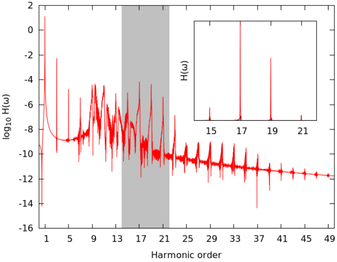
$$f_{\mathrm{Hxc}}[n[u](t)](\vec{r},\vec{r}') = \frac{1}{|\vec{r}-\vec{r}'|} + f_{\mathrm{xc}}[n[u](t)](\vec{r},\vec{r}')$$

QOCT + TDDFT

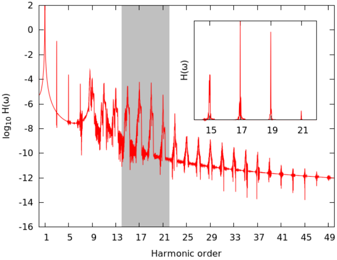

(a)
$v_0(x,y)$
16
12
8
4
0
-6 -4 -2 0 2 4
x
-4 -2 0 2 4
y
(c)
ε(t)
0.4
0.2
0
-0.2
-0.4
0 10 20 30 40 50
t
(b)
$n_0(\vec{r})$
$n(\vec{r},T)$
0.3
0.2
0.1
(d)
J_1
2
1.5
1
0.5
0
0 25 50
CG Iteration Count

Optimal laser control of the harmonic generation

He atom, EXX:



He atom, EXX, frozen H+xc:



- Target: selective enhancement or quenching of harmonics:

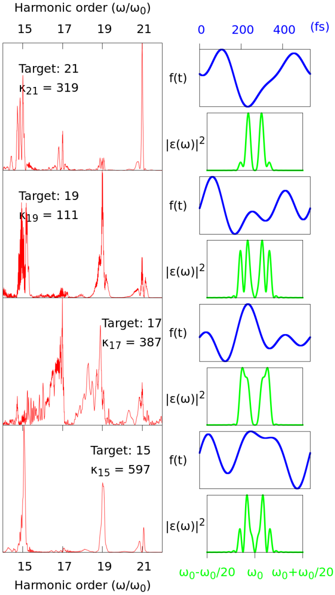
$$F[\varphi] = \sum_k \alpha_k \max_{\omega\approx k\omega_0} \{\log_{10} H[\varphi](\omega)\}$$

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

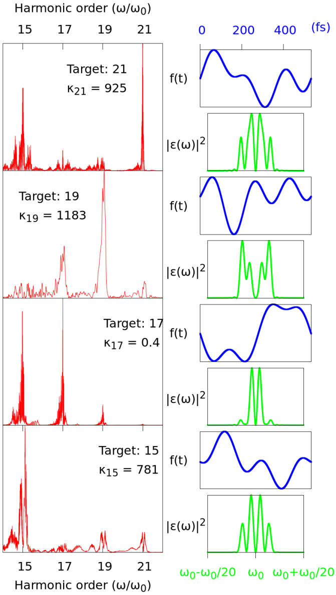
- Time-dependent target, it depends on the full evolution of the system.
- "TDDFT-friendly" target: it only depends on the time-dependent density.

Optimal laser control of the harmonic generation

He atom, EXX:



He atom, froze H+xc



Outline

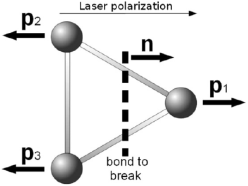
The Ehrenfest model for molecular dynamics

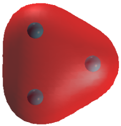
$$\hat{H}[q,p,u,t] = H_{\rm clas}[q,p,u,t]\hat{I} + \hat{H}_{\rm quantum}[q,p,u,t]\,.$$

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

Selective photo-dissociation: H_3^+

$F[n,q,p] = (\vec{p}_1(T) - \vec{p}_2(T))^2 + (\vec{p}_1(T) - \vec{p}_3(T))^2 - (\vec{p}_2(T) - \vec{p}_3(T))^2$
$T_{\rm laser} \approx 7$ fs
$I_{\rm peak} \approx 1.8 \;\; 10^{13} {\rm W/cm}^2$
$E_{\rm cutoff} = 2.0$ a.u. (100 degrees of freedom)





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

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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.

How fast can we (Coulomb) explode a cluster

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

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