From the femto- to the atto-second time scale: analysis and control of the electronic motion with time-dependent density-functional theory

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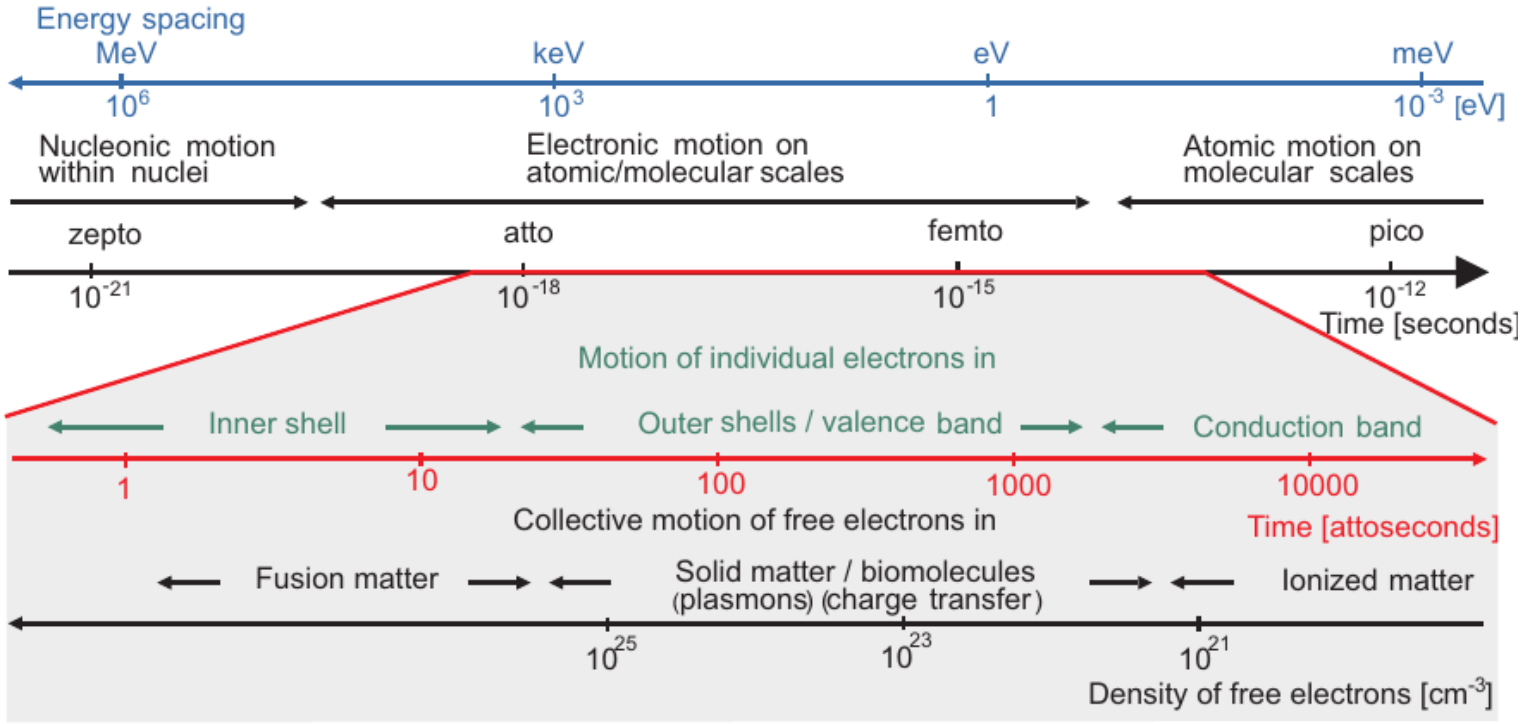
Universidad Zaragoza

Electronic time-scale

The atto-second is the natural time scale of electrons in atoms and molecules. Atto-second physics allows to observe, manipulate, and control electrons in real time.



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

Collaborators

- Jorge Bugadosky
- Hardy Gross
- Jan Werschnik
- Kevin Krieger
- Esa Räsänen
- Angel Rubio
- Umberto de Giovanninni
- Jessica Walkenhorst
- Ilya Tokatly

Outline

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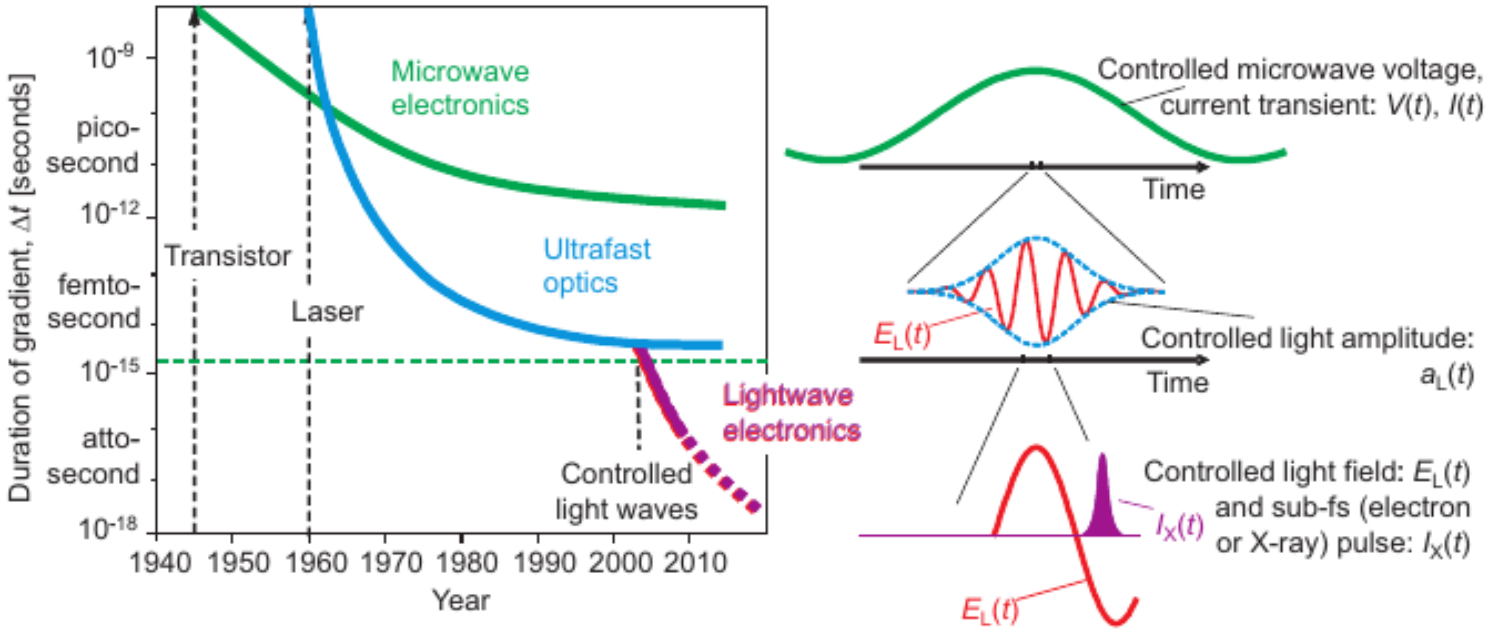
The road to atto-second physics



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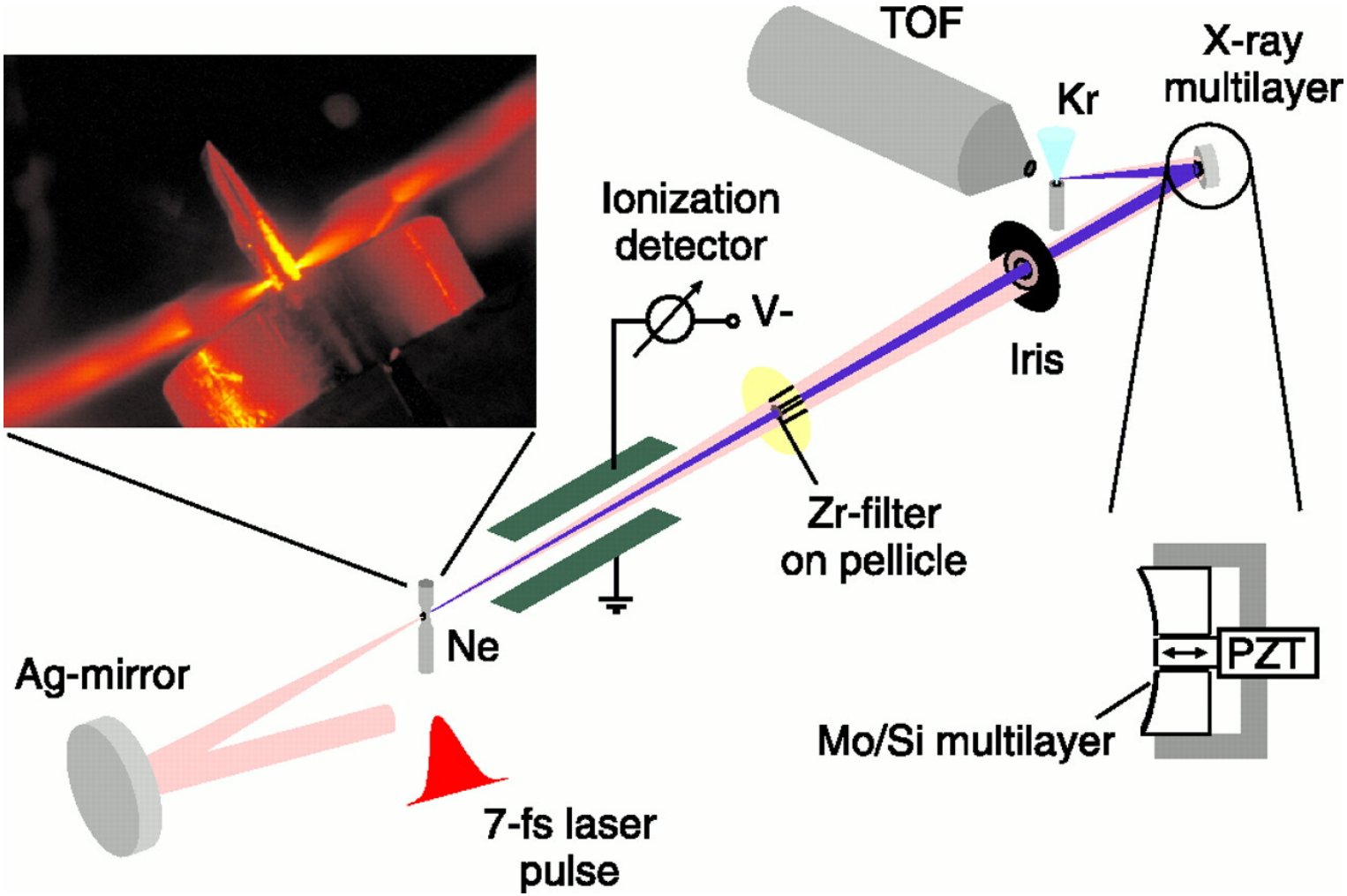
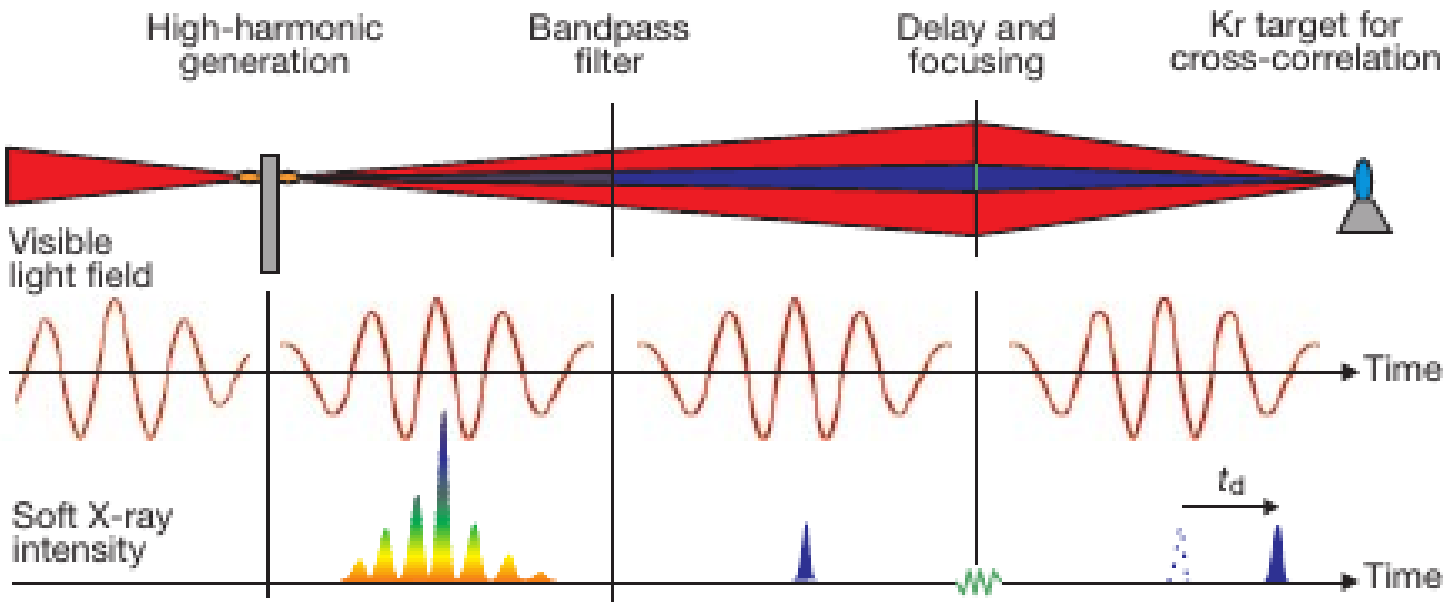
Some initial break-throughs



"X-ray pulses approaching the attosecond frontier", Drescher *et al.* Science **291**, 1923 (2001).

First generation of isolated "almost" atto-second pulses.

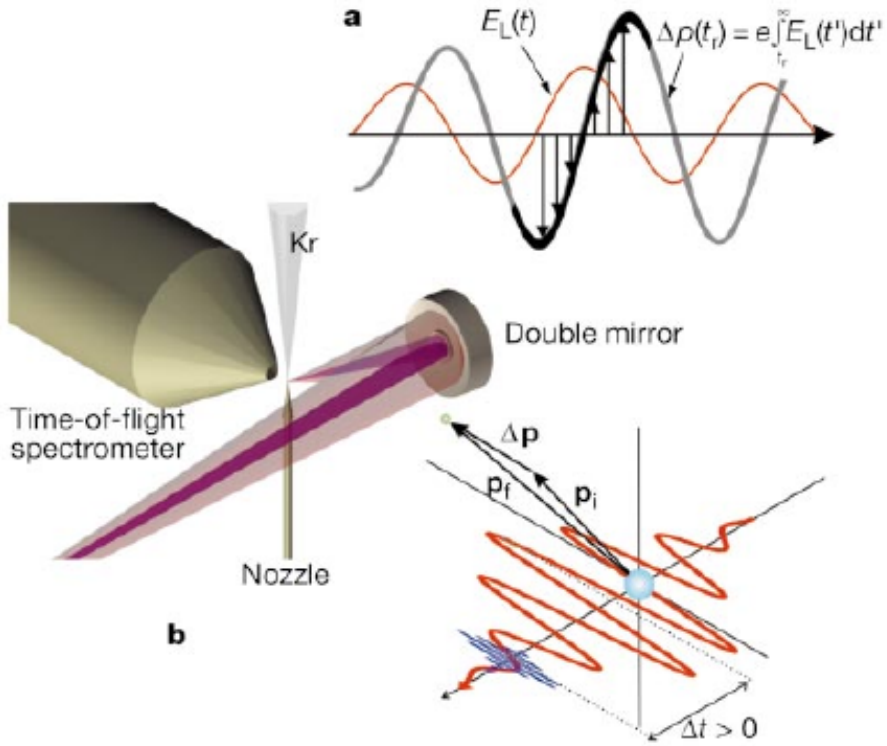
Some initial break-throughs



"Attosecond metrology", Hentschel *et al*, *Nature* **214**, 509 (2001).

Trace of electronic dynamics with at time resolution of 150 as.

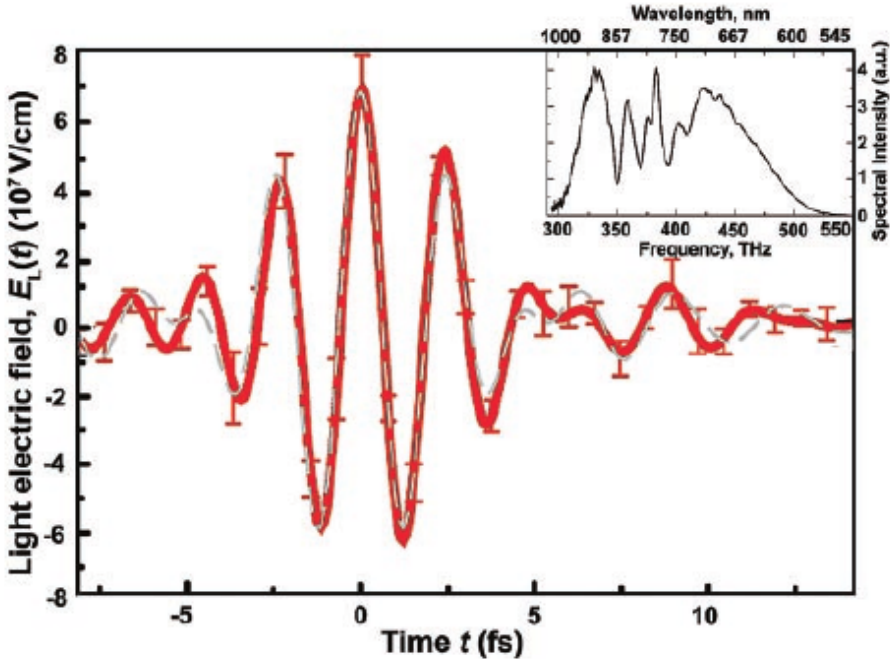
Some initial break-throughs



"Time resolved atomic inner-shell spectroscopy", Drescher *et al*, *Nature* **419**, 803 (2002).

Measurement of the relaxation dynamics time-constants of core excited atoms with atto-second resolution by means of a pump-probe scheme based on a 7 fs 750 nm pulse and a sub-femtosecond soft X-ray pulse.

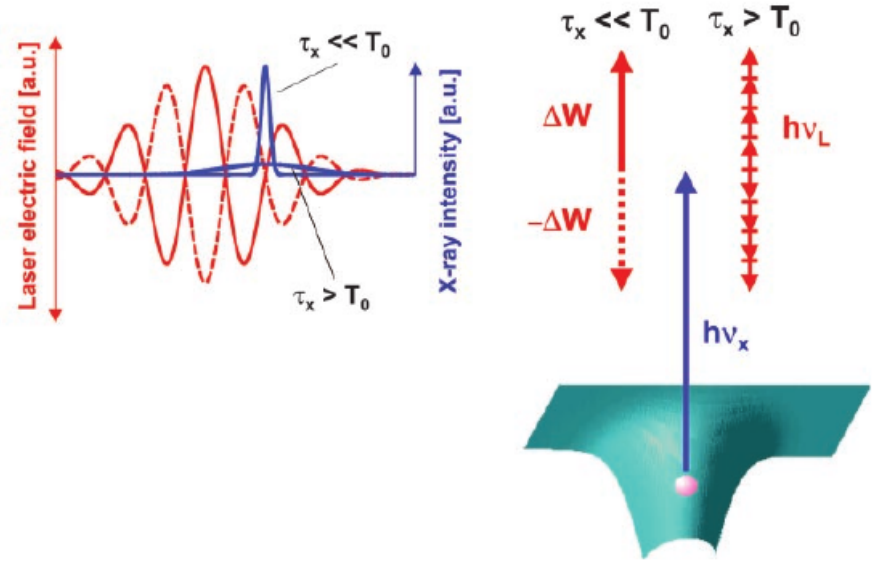
Some initial break-throughs



"Direct measurement of light waves", Goulielmakis *et al*, *Science* **305**, 1267 (2004).

Full characterization of a visible femto-second pulse by making use of 250 as. electron bursts.

Some initial break-throughs



"Steering atto-second electron wave packets with light", Kienberger *et al*, *Science* **297**, 1144 (2004).

Control over the velocity of photo-electrons generated by sub-femtosecond XUV pulses, by making use of a synchronized longer femtoseconf pulse.

Outline

Pump-probe spectroscopy on the atto-second time-scale with TDDFT

Pump-probe spectroscopy with weak probes can be considered as a generalized out-of equilibrium response theory:

$$\hat{H}(t) = \mathcal{H} + \varepsilon(t)\hat{V} + f(t)\hat{V}$$

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

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

$$\delta A(t) = \int_0^T \mathrm{d}\tau\ f(\tau)\chi_{\hat{A},\hat{V}}[\varepsilon](t,\tau)$$

$$\chi_{\hat{A},\hat{V}}(t,\tau) = -i\theta(t-\tau)\mathrm{Tr}\{\hat{\rho}(t_0)\left[\hat{A}_H[\varepsilon](t), \hat{V}_H[\varepsilon](\tau)\right]\}$$

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Pump-probe spectroscopy on the atto-second time-scale with TDDFT

- TDDFT:

$$n(\vec{r},t) \Leftrightarrow v(\vec{r},t) \quad \rightarrow \quad \Psi(t)$$

[Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)]

- Kohn-Sham substitution: we work with a proxy system of non-interacting electrons whose density is by construction identical to that of the real system:

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

Observables

- Dipole moment (for, e.g., absorption spectroscopy):

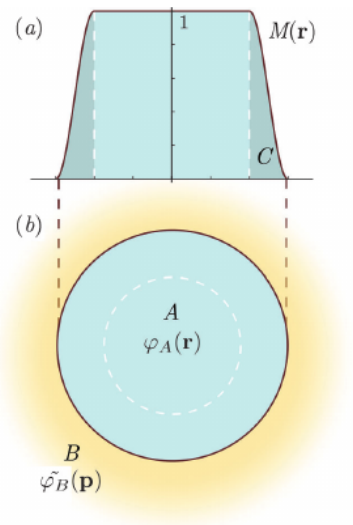
$$\langle \Psi(t)|\hat{\vec{D}}|\Psi(t)\rangle = \int \mathrm{d}^3 r \; n(\vec{r},t)\vec{r}$$

- High-harmonic generation

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

- Photo-electron spectroscopy

$$P(\vec{p}) \approx \lim_{t\to\infty} \sum_{occ} |\tilde{\varphi}_i^B(\vec{r},t)|^2$$



Attosecond Transient Absorption Spectroscopy

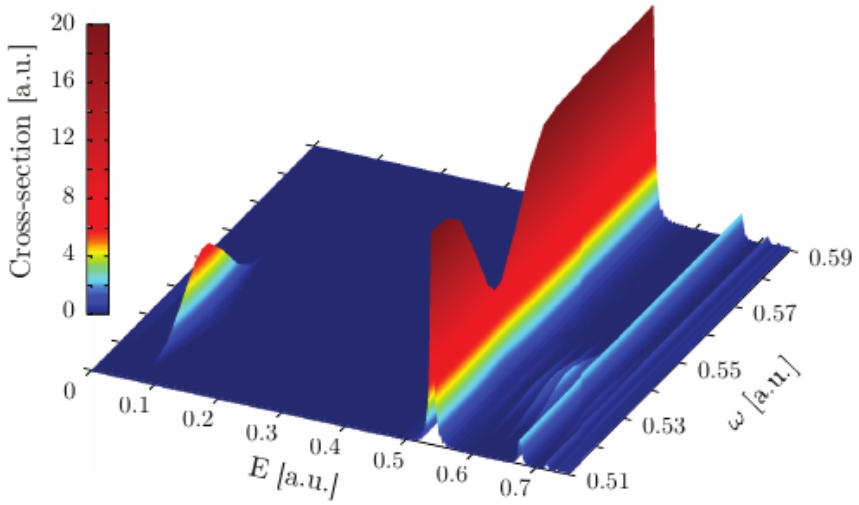


FIG. 2. Out of equilibrium absorption spectrum as function of the pump laser frequency for one-dimensional Helium. The system is driven out of equilibrium by 45 cycle $\sin^2$ envelope laser pulses of intensity $I = 5.26 \times 10^{11}$ W/cm^2, at different carrier frequencies and then probed right after. Maximal response is observed for frequencies close to the first optical transition $\omega = 0.533$ a.u..

"Simulating Pump-Probe Photoelectron and Absorption Spectroscopy on the Attosecond Timescale with Time-Dependent Density Functional Theory",

U. de Giovannini, G. Brunetto, AC, J. Walkenhorst, and A. Rubio ChemPhysChem 14, *1363*

(2013)

Attosecond Time Resolved Photo-electron Spectroscopy

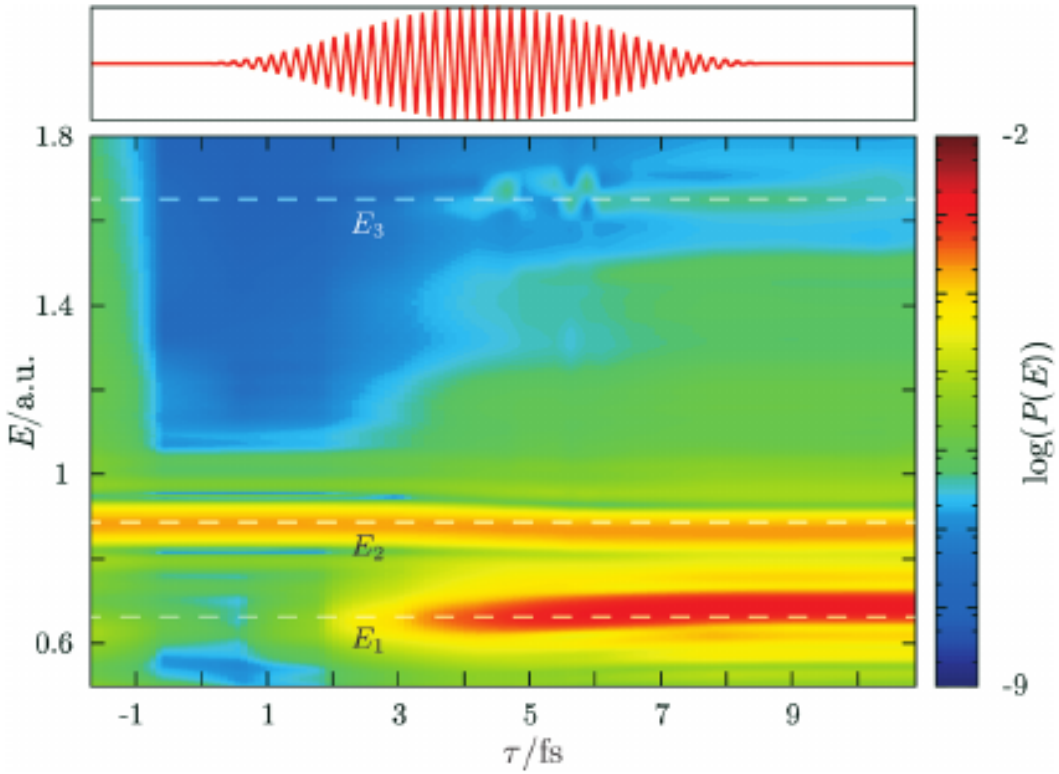


Figure 7. Helium transient photoelectron spectrum on a logarithmic scale. The pump laser (upper panel) is the same as that given in Figure 5 and the probe is a 40 cycle trapezoidal laser pulse with an 8 cycle ramp, $\omega_p = 1.8$ a.u., $I = 5.4 \times 10^9$ W cm^{-2} aligned with the pump pulse.

U. de Giovannini, G. Brunetto, AC, J. Walkenhorst, and A. Rubio ChemPhysChem 14, *1363 (2013)*

Outline

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.
  - Our choices:
    - The *simplex* algorithm [J.A. Nelder and R. Mead, Computer Journal **7**, 308 (1965)], and
    - the NEWUOA algorithm [M. J. D. Powell, IMA J. Numer. Anal. **28**, 649 (2008)].

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:

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

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

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Application to Hamiltonian systems

$$\begin{aligned} \dot{q}_i(t) &= \frac{\partial H}{\partial p_i}(q(t), p(t), u, t)\,, \\ \dot{p}_i(t) &= -\frac{\partial H}{\partial q_i}(q(t), p(t), u, t)\,. \end{aligned}$$

In condensed vector notation:

$$\begin{aligned} \dot{\mathbf{q}} &= \frac{\partial H}{\partial \mathbf{p}}\,, \\ \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{q}}\,. \end{aligned}$$

In this case, x is the vector $[\mathbf{q}, \mathbf{p}]^\dagger$.
The cost (or target) functional can be, for example, any expression in the form:

$$F[\mathbf{q}, \mathbf{p}, u] = J_1[\mathbf{q}(T), \mathbf{p}(T)] + J_2[u]\,.$$

Application to Hamiltonian systems

$$\frac{\partial G}{\partial u_m} = \frac{\partial J_2}{\partial u_m} - \int_0^T \mathrm{d}t\ \tilde{\mathbf{p}}(t) \cdot \frac{\partial}{\partial u_m}\frac{\partial H}{\partial \mathbf{p}}(\mathbf{q}(t),\mathbf{p}(t),u,t) + \int_0^T \mathrm{d}t\ \tilde{\mathbf{q}}(t) \cdot \frac{\partial}{\partial u_m}\frac{\partial H}{\partial \mathbf{q}}(\mathbf{q}(t),\mathbf{p}(t),u,t)$$

The "costate" $[\tilde{\mathbf{q}},\tilde{\mathbf{p}}]^\dagger$ is itself a Hamiltonian system, determined by the quadratic Hamiltonian:

$$\tilde{H}(\tilde{q},\tilde{p},q,p,u,t) = \frac{1}{2}\tilde{\mathbf{q}}^t\mathbf{H}^{qq}(q,p,u,t)\tilde{\mathbf{q}} + \frac{1}{2}\tilde{\mathbf{q}}^t\mathbf{H}^{qp}(q,p,u,t)\tilde{\mathbf{p}} + \frac{1}{2}\tilde{\mathbf{q}}^t\mathbf{H}^{pq}(q,p,u,t)\tilde{\mathbf{p}} + \frac{1}{2}\tilde{\mathbf{q}}^t\mathbf{H}^{pp}(q,p,u,t)\tilde{\mathbf{p}}\,.$$

Application to Hamiltonian systems

The matrices $\mathbf{H}^{xy}$ are defined as:

$$
\begin{aligned}
H_{ij}^{qq} &= \frac{\partial^2 H}{\partial q_i \partial q_j}(q,p,u,t) \\
H_{ij}^{qp} &= \frac{\partial^2 H}{\partial q_i \partial p_j}(q,p,u,t) \\
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Quantum optimal control theory

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

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

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

Maximize a quantity

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

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

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Is there anything new about QOCT?

Quantum mechanics as a particular case of Hamiltonian systems:

$$|\Psi\rangle = \sum_k c_k |\Psi_k\rangle$$

$$c_k = q_k + i p_k \rightarrow (q_k, p_k) \in \mathbb{R}^{2n}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle \quad \equiv \quad \begin{aligned} \dot{\mathbf{q}} &= \frac{\partial H}{\partial \mathbf{p}}, \\ \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{q}}. \end{aligned}$$

where

$$H(q,p,t) := \langle \Psi(q,p)|\hat{H}(t)|\Psi(q,p)\rangle$$

is a quadratic expression in $\mathbf{q}, \mathbf{p}$, i.e. a "generalized harmonic oscillator system".

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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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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:

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

QOCT + TDDFT

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

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

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

$$\begin{aligned}
\dot{\underline{\varphi}}[u](t) &= -i\underline{\underline{\hat{H}}}[n(t), u, t]\underline{\varphi}[u](t)\,, \\
\underline{\varphi}_u(0) &= \underline{\varphi}_0\,, \\
\dot{\underline{\lambda}}[u](t) &= -i\left[\underline{\underline{\hat{H}}}[n(t), u, t] + \underline{\underline{\hat{K}}}[\underline{\varphi}[u](t)]\right]\underline{\lambda}[u](t)\,, \\
\underline{\lambda}[u](T) &= \frac{\delta F}{\delta \underline{\varphi}^*}[\underline{\varphi}[u](T), u]\,.
\end{aligned}$$

QOCT + TDDFT

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

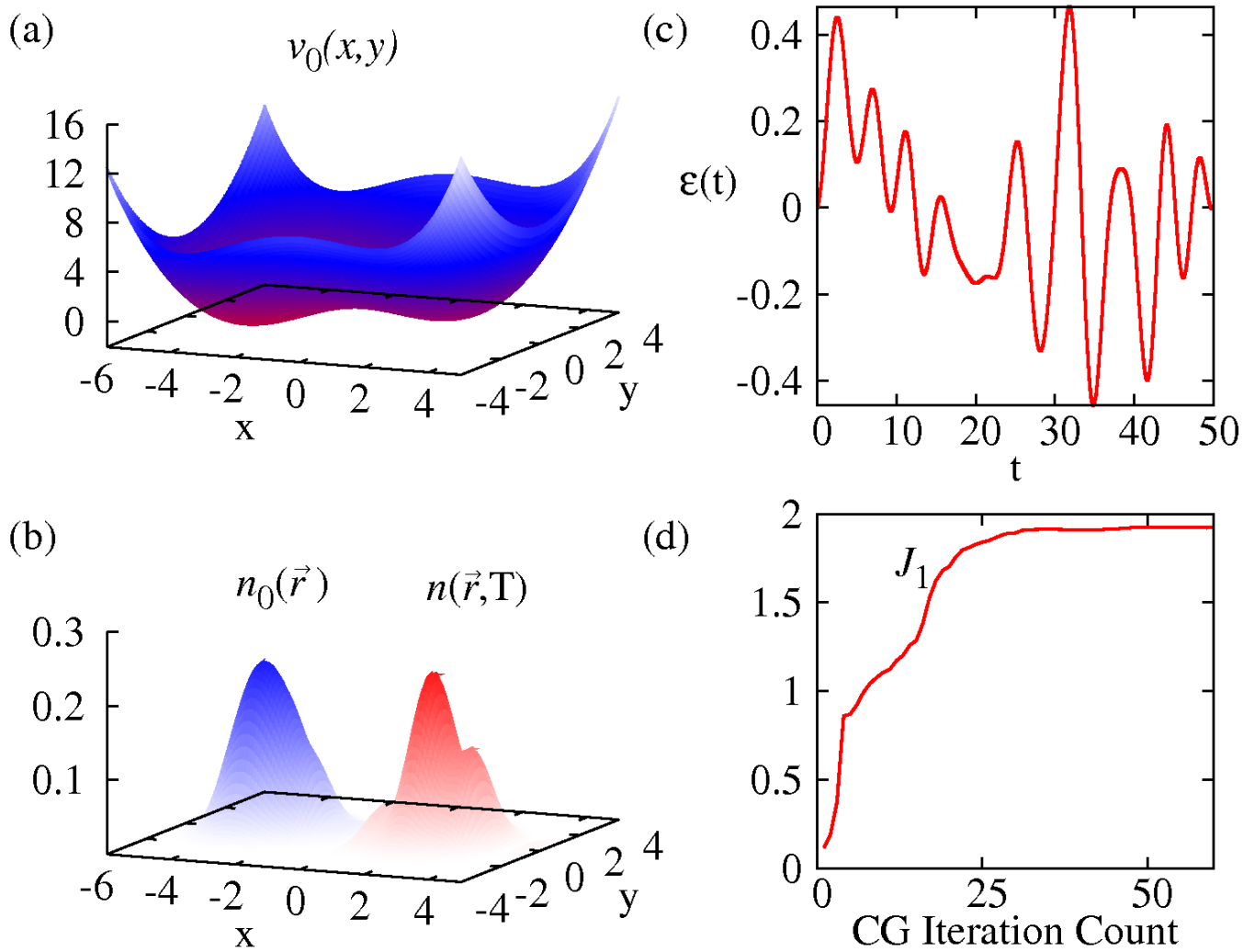
$$\dot{\lambda}_i[u](t) = -i\hat{H}^{\dagger}[n[u](t), u, t]\lambda_i[u](t) - i\sum_{j=1}^{N} \hat{K}_{ij}[\underline{\varphi}[u](t)]\lambda_j[u](t)$$

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

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

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

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

QOCT + TDDFT

Most important theoretical difficulty: many targets are easily formulated in terms of states (or projectors), e.g.:

$$F[\Psi(T)] = |\langle \Psi_I | \Psi(T) \rangle|^2$$

However, those states are the true many-body states, and we only have access to the time-dependent density, and to the Kohn-Sham orbitals.

Femtosecond laser pulse shaping for enhanced ionization

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

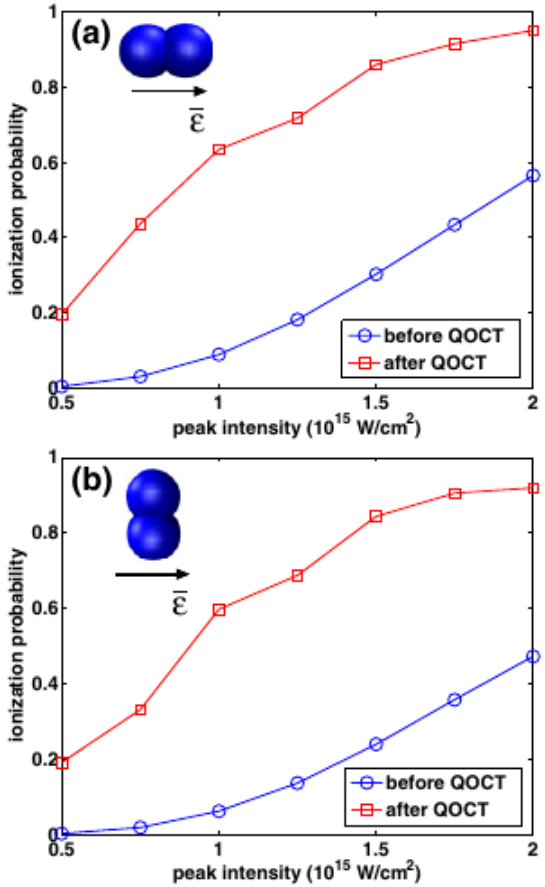


Fig. 1: (Color online) Ionization probability for the initial pulse (circles) and for the optimized pulse (squares) as a function of the peak intensity of the initial pulse. The polarization of the pulse is (a) parallel and (b) perpendicular to the molecule.

- 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

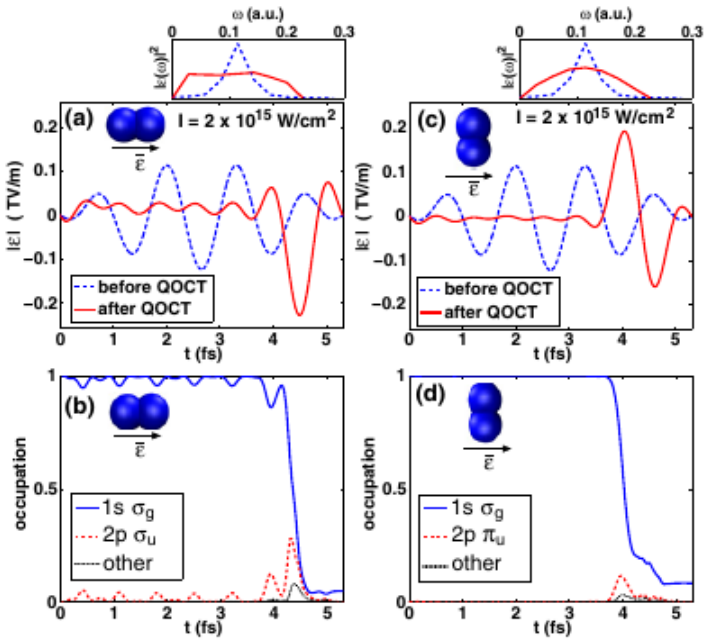


Fig. 2: (Color online) (a) Initial and optimized pulses (parallel polarization) and their power spectra (in arbitrary units) and (b) the occupation of selected single-electron states in the optimized ionization process, when $I = 2 \times 10^{15}\,\mathrm{W/cm^2}$. (c), (d) Same as (a), (b) but for perpendicular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

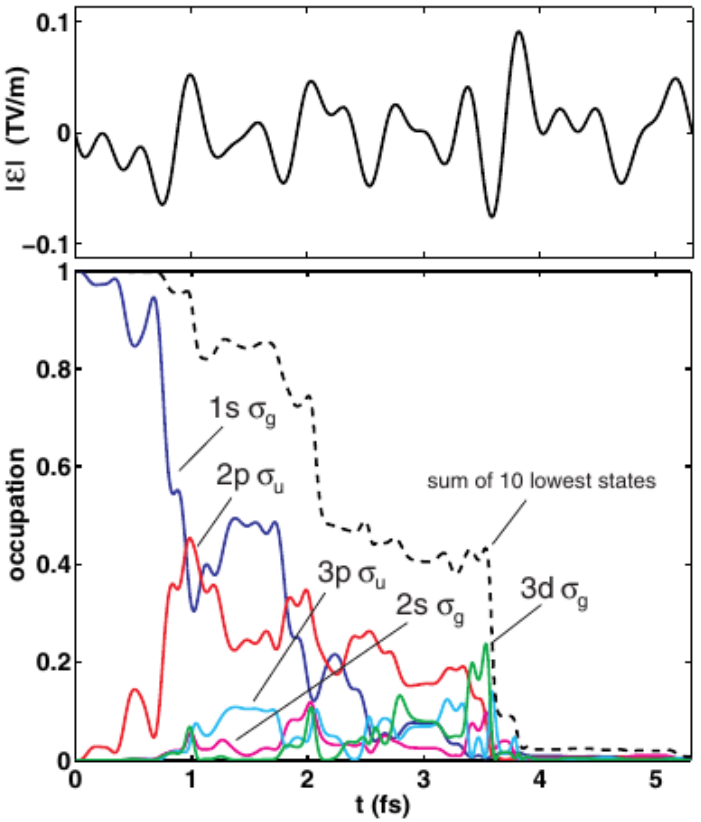


Fig. 4: (Color online) Upper panel: optimized laser pulse for the ionization when the cutoff frequency is $4\,\omega_0$ (see text) and the intensity is fixed to 0.5×10^{15} W/cm^2. Lower panel: occupation of a few lowest states during the pulse interaction.

- 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)]

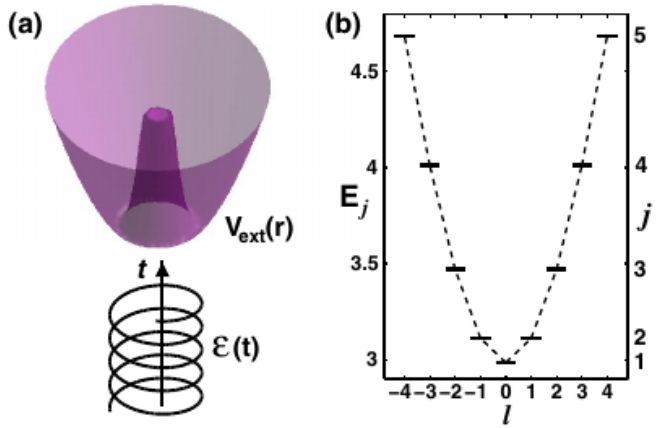


FIG. 1 (color online). (a) Shape of the external confining potential for a quantum ring and an example of a circularly polarized laser field. (b) Energy-level spectrum of a quantum ring. The transitions are allowed along the dashed line so that $\Delta l = \pm 1$.

- 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

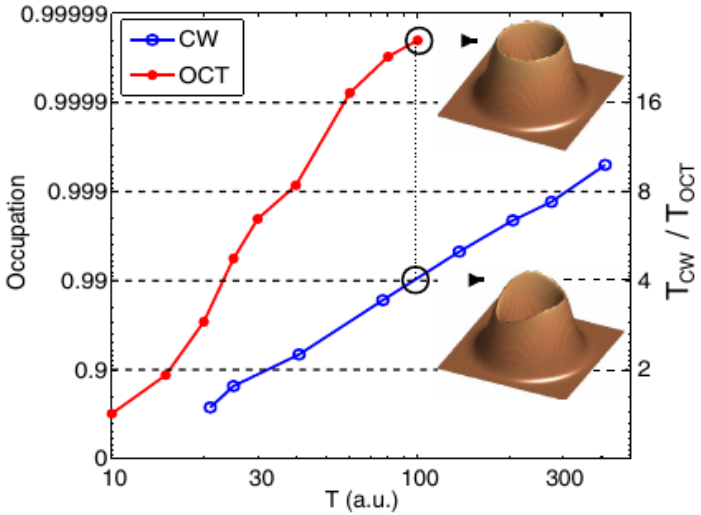


FIG. 3 (color online). Maximum occupation of the target state in transition $|1\rangle \rightarrow |2\rangle$ as a function of the pulse length. The open (blue) circles correspond to continuous waves and the filled (red) circles to the optimal-control result. The insets show the densities $|\Psi(T =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

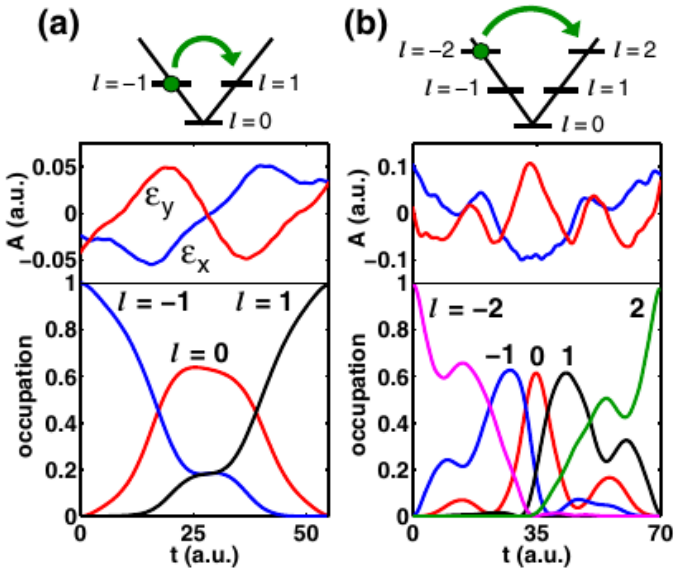
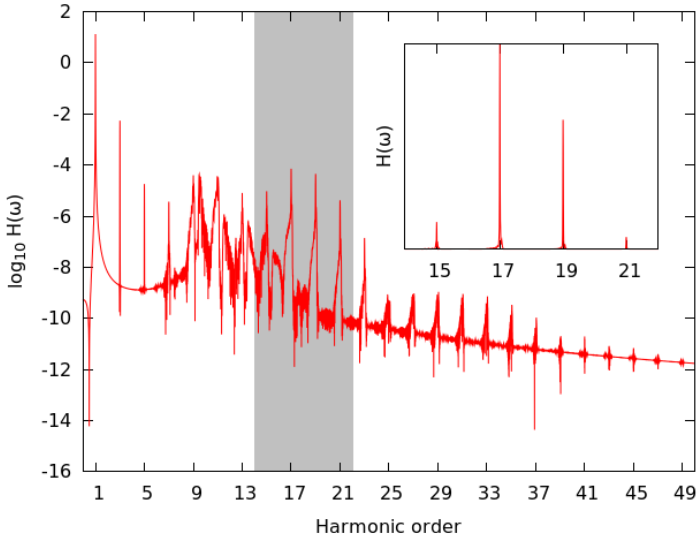


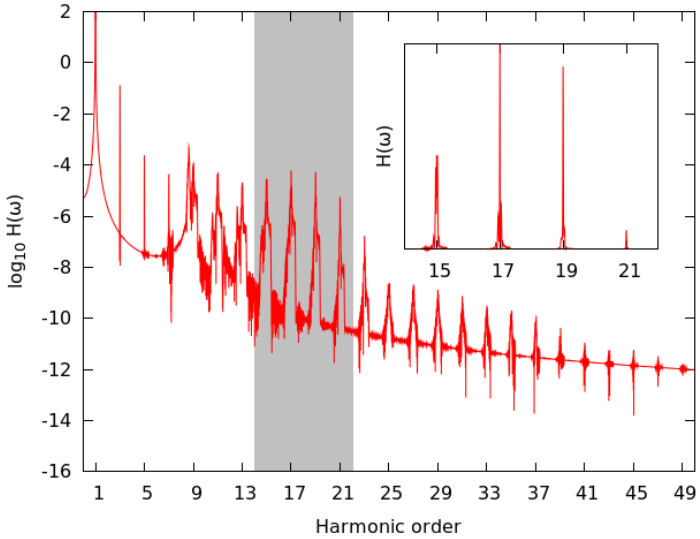
FIG. 4 (color online). Schematic picture of transitions from $l = -1$ to $l = 1$ (a) and from $l = -2$ to $l = 2$ (b) (upper panel), optimized fields for these transitions (middle panel), and the occupations of the states (lower panel).

Optimal laser control of the harmonic generation

He atom, EXX:



He atom, EXX, frozen H+xc:



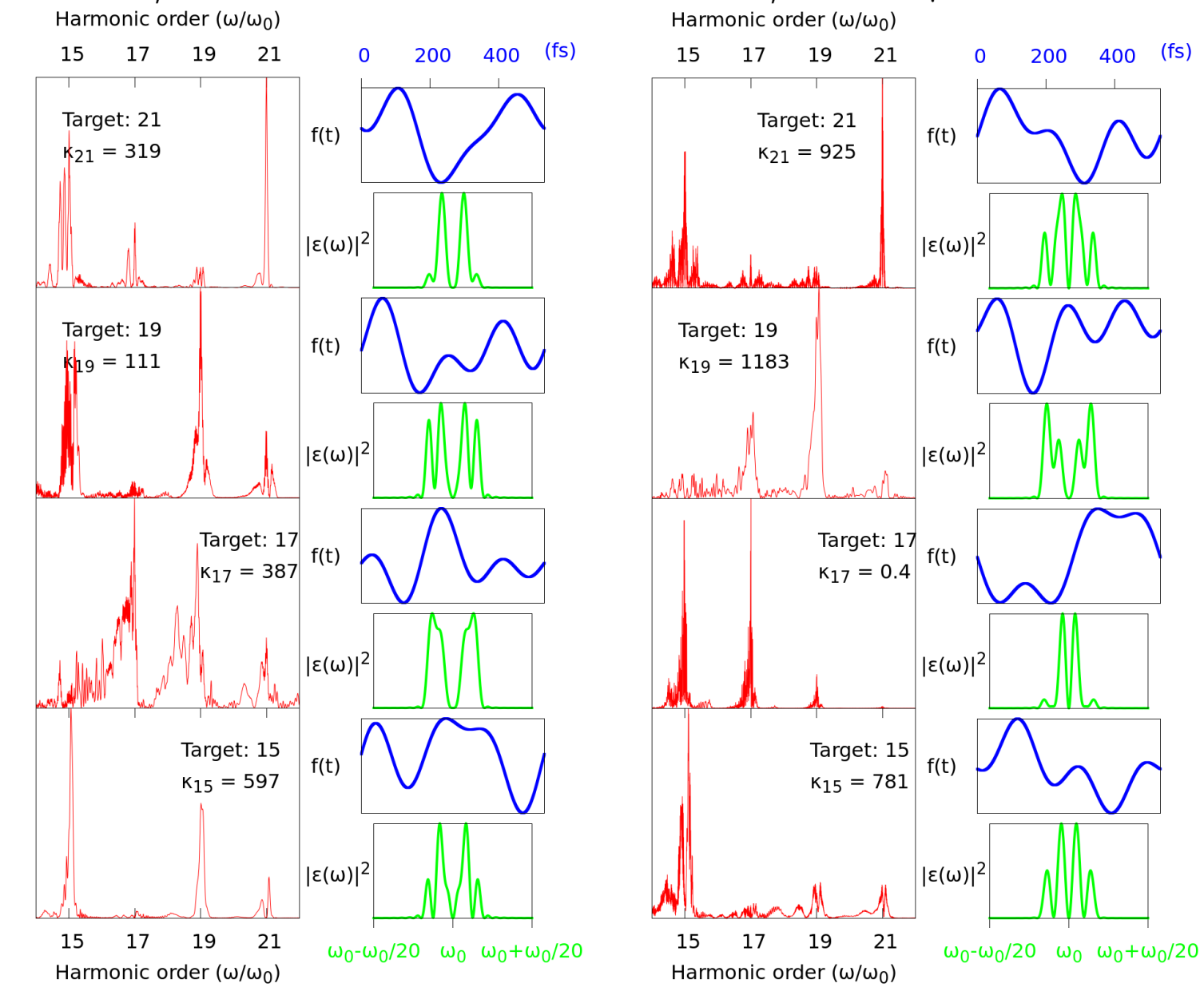
- Target: selective enhancement or quenching of harmonics:

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

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

- 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



Optimal laser control of the harmonic generation: Cut-off extension

$$\begin{aligned} F[\varphi] &= \int \mathrm{d}\omega \alpha(\omega) H[\varphi](\omega) \\ &= \int \mathrm{d}\omega \alpha(\omega) |\vec{f}[\varphi](\omega)|^2 \,, \end{aligned}$$

$$\vec{f}(t) = \int \mathrm{d}^3 r \; n(\vec{r},t) \nabla v(\vec{r}) + N\varepsilon(t)\vec{\pi} \,.$$

The functional derivative of F, needed for the propagation of the co-state, is:

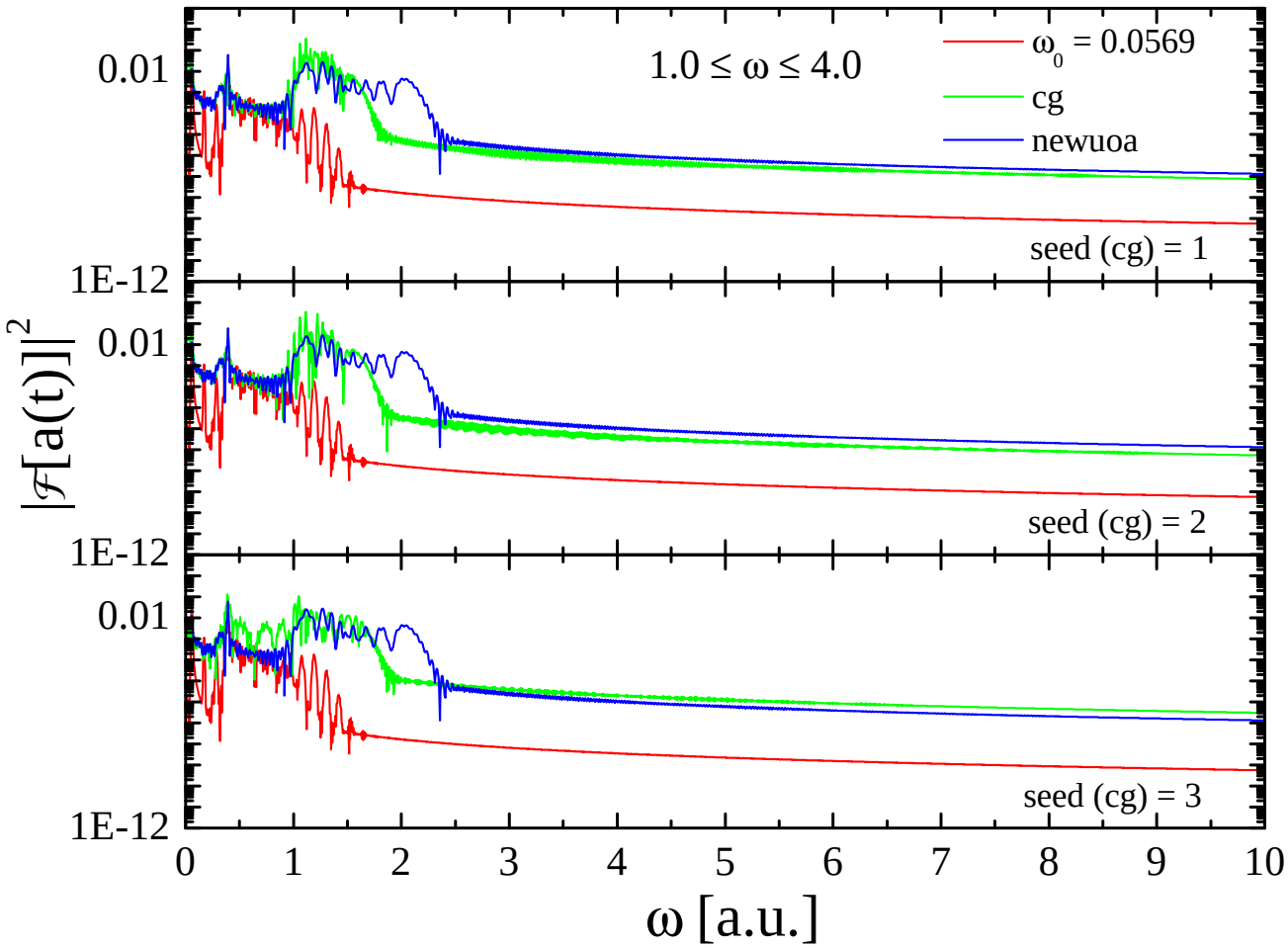
$$\frac{\delta F}{\delta \varphi^*(\vec{r},t)} = \vec{g}[\varphi](t) \cdot \nabla v(\vec{r}) \; \varphi(\vec{r},t) \,,$$

where

$$\vec{g}[\varphi](t) = 2\mu \int \mathrm{d}\omega \; \alpha(\omega) \mathrm{Re}\left[\vec{f}[\varphi](\omega) e^{-i\omega t}\right] \,.$$

Optimal laser control of the harmonic generation: Cut-off extension

$$\alpha(\omega) = \mathrm{step}(\omega - \omega_c)$$



Optimization Schemes for Selective Molecular Cleavage with Tailored Ultrashort Laser Pulses

Coupled electron-ion model: Ehrenfest dynamics:

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

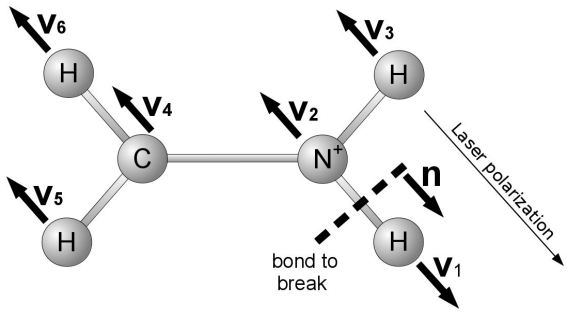
$$\begin{aligned}
\dot{q}_a(t) &= \frac{\partial H_{\rm clas}}{\partial p_a}[q(t),p(t),u,t] \\
&\quad + \langle\Psi(t)|\frac{\partial \hat{H}_{\rm quantum}}{\partial p_a}[q(t),p(t),u,t]|\Psi(t)\rangle \\
\dot{p}_a(t) &= -\frac{\partial \hat{H}_{\rm clas}}{\partial q_a}[q(t),p(t),u,t] \\
&\quad - \langle\Psi(t)|\frac{\partial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

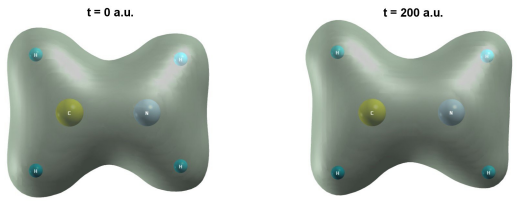
Optimization Schemes for Selective Molecular Cleavage with Tailored Ultrashort Laser Pulses

Several options:

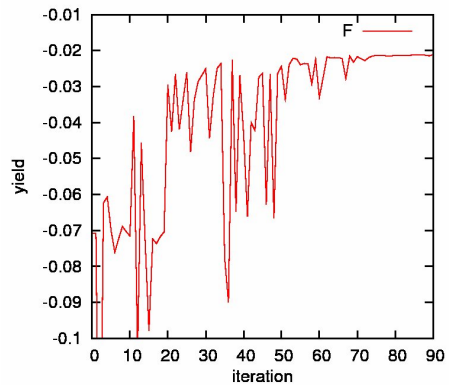
- Assume the dynamical system is the electronic system only: the ions are clamped during the action of the laser pulse. One can then use the usual QOCT. Valid only for very short pulses.
- The dynamical system is the Ehrenfest sytem:
  - Use a *direct*, or *gradient-less* optimization scheme. No need to develop new theory, since the only operation required is the forward propagation of the Ehrenfest system.
  - Full use of the QOCT equations, that require the gradient.

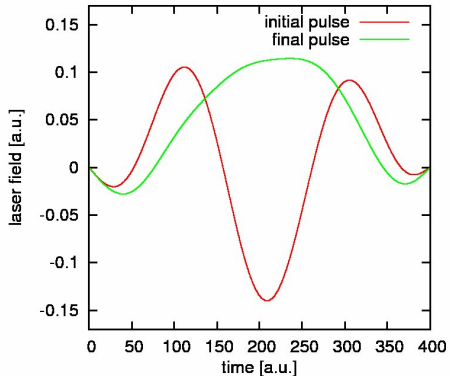
Optimization Schemes for Selective Molecular Cleavage with Tailored Ultrashort Laser Pulses

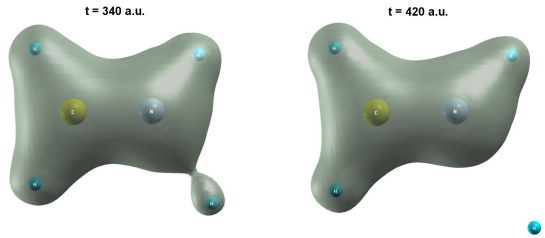




$$F = \mathbf{n} \cdot (\mathbf{v}_1 - \mathbf{v}_2) - 10 \sum_{i=1}^{6} |\mathbf{v}_i - \mathbf{v}_2|$$







[K. Krieger, AC, and E. K. U. Gross, Chem. Phys. **391**, 50 (2011)]

Ultrafast photo-dissociation of the Hydrogen molecule

- During the laser irradiation, the nuclei do not have time to move, but the electrons are shaked, and communicate a sudden dissociative momentum to the nuclei.
- Hybrid quantum-classical model (Ehrenfest model): definition of the targets in terms of the classical forces on the nuclei:

$$\vec{P}_\alpha = \int_0^T \mathrm{d}t \; \vec{F}_\alpha(t) \,,$$

$$\vec{F}_\alpha = \vec{F}_\alpha[n(t)] = -\int \mathrm{d}^3 r \; n(\vec{r},t) \vec{\nabla}_\alpha v_0(\vec{r},\{\vec{R}_\alpha\}) \,.$$

- Therefore

$$\vec{P}_\alpha[n] = \int_0^T \mathrm{d}t \int \mathrm{d}^3 r \; n(\vec{r},t) \vec{\nabla}_\alpha v_0(\vec{r},\{\vec{R}_\alpha\}) \,.$$

Definition of the target

- The target is then defined in terms of a function of these momenta:

$$F[\underline{\varphi}] = \tilde{F}[n] = T(\underline{P}[n]) \,,$$

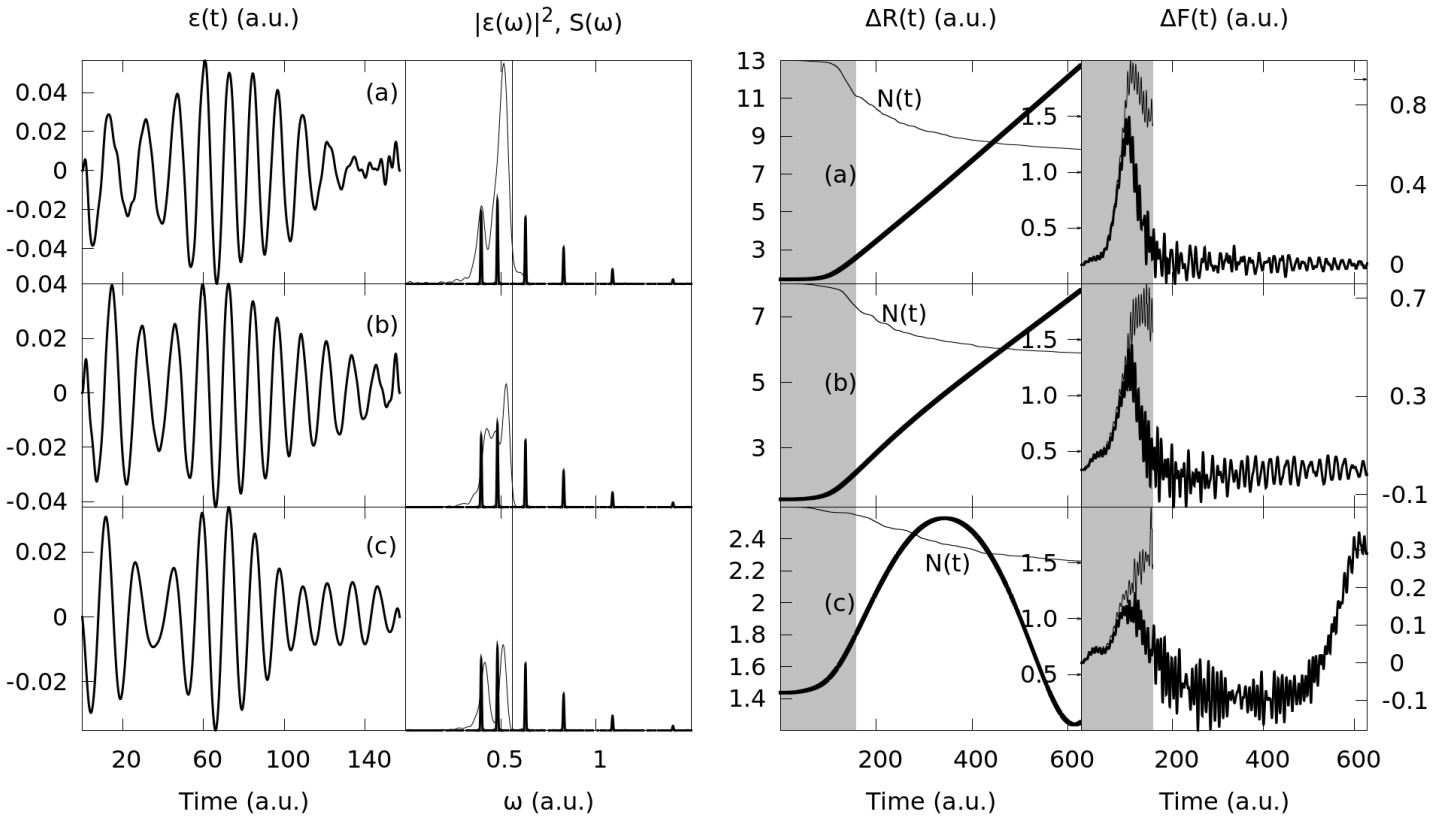
for example:

$$\tilde{F}[n] = P_{1x}[n] - P_{2x}[n] \,.$$

- The remaining ingredient in order to compute the gradient is the functional derivative:

$$\frac{\delta F[\underline{\varphi}]}{\delta \varphi_i^*(\vec{r},t)} = \sum_{\alpha=1}^{K} \sum_{\mu=x,y,z} 2 \frac{\partial T}{\partial P_{\alpha\mu}}(\underline{p}[n]) \frac{\partial v_0(\vec{r};\vec{R})}{\partial R_{\alpha\mu}} \varphi_i(\vec{r},t) \,.$$

Results



[AC, ChemPhysChem **14**, 1488 (2013)]

QOCT+TDDFT+Ehrenfest

[AC and E. K. U. Gross, "Optimal control theory for quantum-classical systems: Ehrenfest Molecular Dynamics based on TDDFT" arXiv:1308.4162]

$$
\begin{aligned}
\dot{q}_a(t) &= \frac{\partial H_{\rm clas}}{\partial p_a}[q(t),p(t),u,t] \\
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\end{aligned}
$$

$$
G[u] = F[q[u],p[u],\underline{\varphi}[u],u]
$$

Outline

Summary

- TDDFT can be used to study ultra-fast pump-probe spectroscopy (TAS and TRPES). The treatment must be non-perturbative (explicitly time-dependent).
- QOCT and TDDFT can be successfully merged in a numerically tractable way. The targets must be formulated in terms of the density, in order to be consistent with TDDFT. This is not always possible.
- Very fast photo-dissociation can be tackled in a *static* manner: by optimizing the electron system only, and placing the system in a state that leads to photo-dissociation after the pulse.
- However, a general treatment would require the construction of a QOCT+TDDFT+Ehrenfest methodology.

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Laser control

Rederivation in the language of linear response

(A) Generalized, out of equilibrium linear response:

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

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

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

$$\delta A(t) = \int_0^T \mathrm{d}\tau\ f(\tau)\chi_{\hat{A},\hat{V}}(t,\tau)$$

$$\chi_{\hat{A},\hat{V}}(t,\tau) = -i\theta(t-\tau)\mathrm{Tr}\{\hat{\rho}(t_0)\left[\hat{A}_H(t), \hat{V}_H(\tau)\right]\}$$

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

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

$$\delta A(t) = \int_0^T \mathrm{d}\tau\ f(\tau)\chi_{\hat{A},\hat{V}}(t,\tau)$$

$$\chi_{\hat{A},\hat{V}}(t,\tau) = -i\theta(t-\tau)\mathrm{Tr}\{\hat{\rho}(t_0)\left[\hat{A}_H(t), \hat{V}_H(\tau)\right]\}$$

Rederivation in the language of linear response

(A) Generalized, out of equilibrium linear response:

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

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

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

$$\delta A(t) = \int_0^T \mathrm{d}\tau\ f(\tau)\chi_{\hat{A},\hat{V}}(t,\tau)$$

$$\chi_{\hat{A},\hat{V}}(t,\tau) = -i\theta(t-\tau)\mathrm{Tr}\{\hat{\rho}(t_0)\left[\hat{A}_H(t), \hat{V}_H(\tau)\right]\}$$

Rederivation in the language of linear response

(A) Corollarium: QOCT equations

$$\begin{aligned}\hat{H}[u_1,\ldots,u_m+\delta u_m,\ldots;t] &= \hat{H}[u;t]+\delta u\frac{\partial \hat{H}}{\partial u_m}[u;t] \\ &\quad \hat{H}_0(t) \quad +f(t)\hat{V}\end{aligned}$$

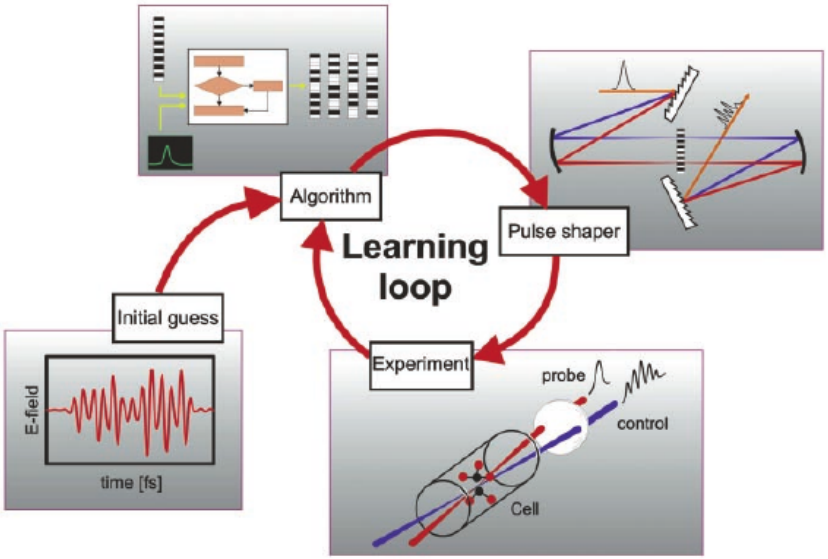
Assuming $\hat{H}[u]=\hat{\mathcal{H}}+\varepsilon(u,t)$,

$$\frac{\partial G}{\partial u_m}=\frac{\partial J_2}{\partial u_m}+\int_0^T \mathrm{d}t\ \frac{\partial \varepsilon}{\partial u_m}\chi_{\hat{A},\hat{V}}(T,t)$$

[AC and I. Tokatly, Phys. Rev. A **84**, 033410 (2011)]

Laser control

Adaptive feedback control:



"Whither the future of controlling quantum phenomena?", Rabitz *et al*, *Science* **288**, 824 (2000).

Laser control

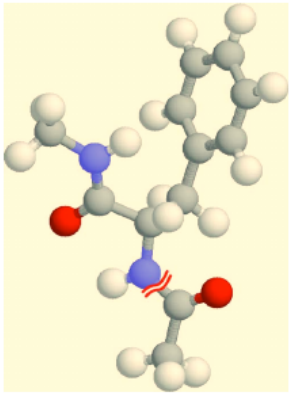
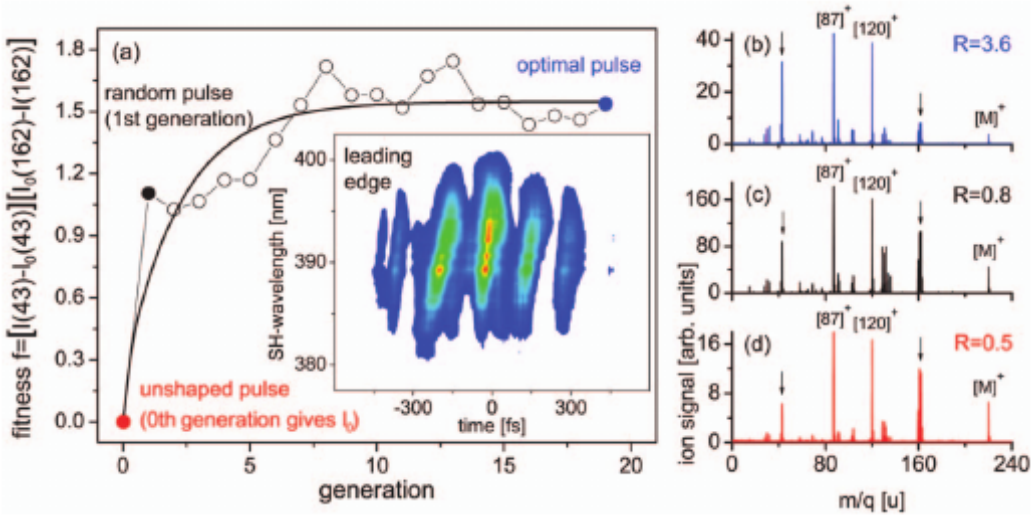


FIG. 1. (Color online) Optimal tailoring of intense femtosecond light can be used to preferentially break peptide bonds, such as the indicated N1–C3 bond in the amino acid complex Ac-Phe-NHMe.



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